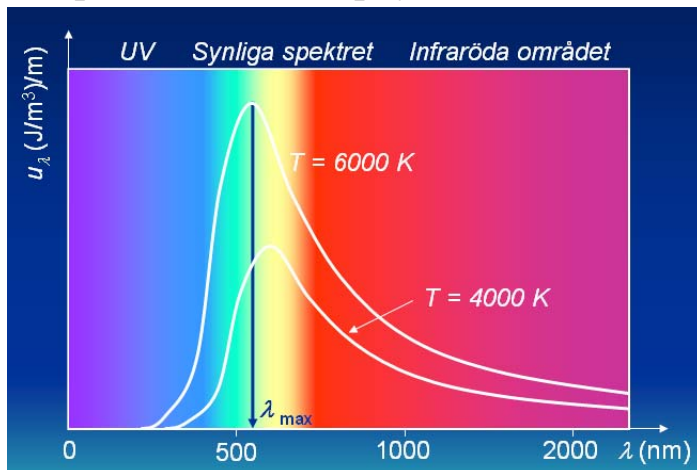


Chapter 5. Statistical physics



Black body radiation from objects with the temperatures of 6000 K (like the Sun) and at 4000 K.

5.1 Introduction

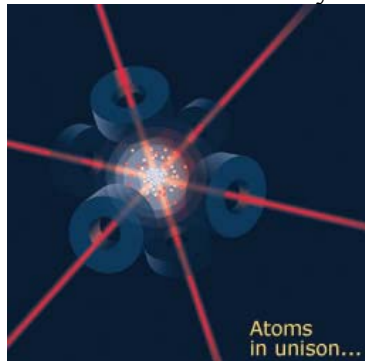
By using statistical physics one can connect macroscopic and microscopic properties of particles like molecules in a gas that can be described classically as well as electrons in solid-state physics that can be described microscopically by quantum mechanics, etc. It was of great interest to apply methods to calculate how the energy in a certain system is distributed over the constituencies, like in a gas at different temperatures.

Normally one discusses three different distribution functions:

- i) Identical particles with any spin like gas molecules.
- ii) Bose particles with 0 or integer spin obeying the exclusion principle.
- iii) Fermi particles that are identical and with spin $\frac{1}{2}$, not obeying the exclusion principle.

The Fermi distribution we will discuss in the Solid State Physics section, but here we concentrate on the Maxwell-Boltzmann's distribution function and the factors that generate the Planck law of radiation.

The phenomenon Bose-Einstein condensation has recently been awarded the Nobel prize in physics and illustrates how one works both theoretically and experimentally at very low temperatures, close to the absolute zero point of temperature. Experimentally one has achieved these extremely low temperatures with optical traps and several laser beams.



One can make an atomic beam slow down and be captured in a trap making the velocity of the atoms go towards zero. This also results in making their interaction between each other become very small, and thereby obtaining a temperature close to zero.

5.2 Maxwell-Boltzmann distribution

Suppose that we have N molecules with k different energies, $u_1, u_2, u_3, \dots, u_k$ distributed with increasing energy. We may also suppose that there are n_i particles with energy u_i . We then get the total energy:

$$U = n_1u_1 + n_2u_2 + n_3u_3 + \dots + n_ku_k$$

If we also suppose that the probability for a molecule i has the energy u_i is g_i . Maxwell and Boltzmann studied a system with molecules and came to the following conclusion regarding a continuous distribution function with discrete energies (u_1, u_2, u_3, \dots):

$$n(u)du = g e^{-\alpha} e^{-\beta u} du$$

Here we can interpret $n(u)du$ as the number of molecules with energies between u och $u+du$. We can also write the distribution function as a function of p , that is the momentum p . The energy for a particle that is not moving at a relativistic speed can be written as:

$$u = \frac{p^2}{2m}$$

Now we can rewrite the distribution function as follows:

$$n(p)dp = g e^{-\alpha} e^{-\beta p^2 / 2m} dp$$

The constants a and b can be determined if you suppose that the total number of states are N and if you use kinetic gas theory giving the total energy U , in a system of molecules that is related to the temperature T according to the following equation:

$$U = \frac{3}{2} NkT$$

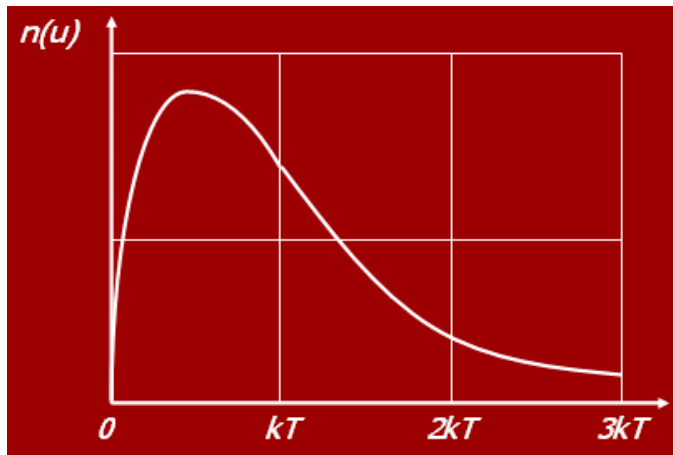
The constant $k = 1.380 \times 10^{-23}$ Joule/(molecule K) is the Boltzmann constant. By other constrains one can show that

$$\beta = \frac{1}{kT}$$

We can now rewrite the Boltzmann distribution function expressed in u , p or in the v :

$$n(u)du = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{u} e^{-u/kT} du$$

This is the number of states with energies between u and $u + du$.



Maxwell-Boltzmann distribution can also be expressed as:

$$n(p)dp = \frac{2\pi N}{(\pi mkT)^{3/2}} p^2 e^{-p^2/2mkT} dp$$

, which is the number of states with momentum between p and $p + dp$. Finally we can rearrange the expression as a function of the molecular velocity v :

$$n(v)dv = \frac{2\pi Nm^{3/2}}{(\pi kT)^{3/2}} v^2 e^{-mv^2/2kT} dv$$

With the help of the expressions above one can derive the systems total energy when we have N molecules:

$$U = \frac{3}{2} \frac{N}{\beta}$$

From this expression one can derive the mean energy per molecule:

$$\bar{u} = \frac{U}{N} = \frac{3}{2\beta}$$

But since $\beta = 1/kT$ we get the mean energy per molecule:

$$\bar{u} = \frac{3}{2} kT$$

Example

Determine the mean energy per molecule at room temperature in the unit eV /molecule.

With the Maxwell-Boltzmann distribution we get

$$\begin{aligned} \bar{u} &= \frac{3}{2} \times 1.380 \times 10^{-23} \times (273 + 20) / 1.602 \times 10^{-19} eV / molecule \approx 0.038 eV / molecule \\ &= 0.038 eV / molecule. \end{aligned}$$

We can also say that at room temperature the mean energy per molecule of a gas is around 1/25 eV, that we can compare with the electronic transitions of for instance atomic hydrogen that are of the order of 1-10 eV.

We can calculate the most probable velocity of the molecules (v_p), their mean velocity ($\bar{v} = v_{medel}$) and the so-called RMS-velocity (v_{RMS}):

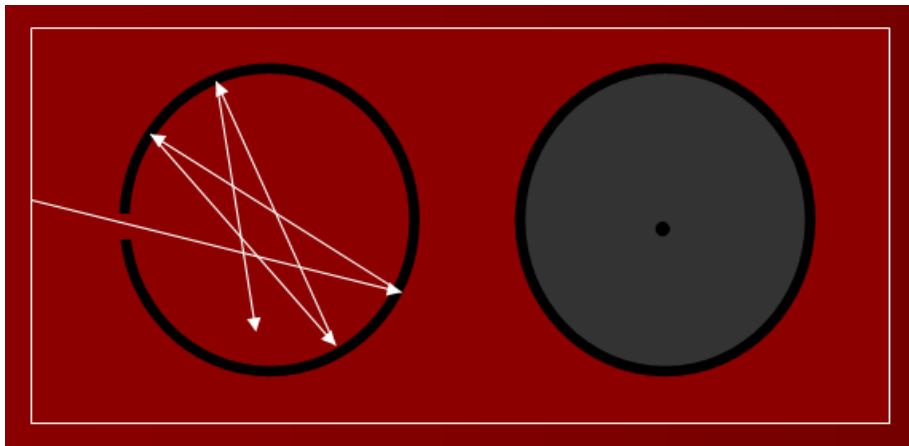
$$v_p = \sqrt{2kT / m}$$

$$\bar{v} = \sqrt{8kT / \pi m}$$

$$v_{RMS} = \sqrt{3kT / m}$$

5.3 Planck's radiation law

One often describes Planck's work with models of radiation. Let us imagine a sphere, inside painted in black and with a small hole. When you make light hit the sphere and the small hole, the light is reflected many times inside the sphere and loses intensity. The cavity absorbs and emits radiation all the time.

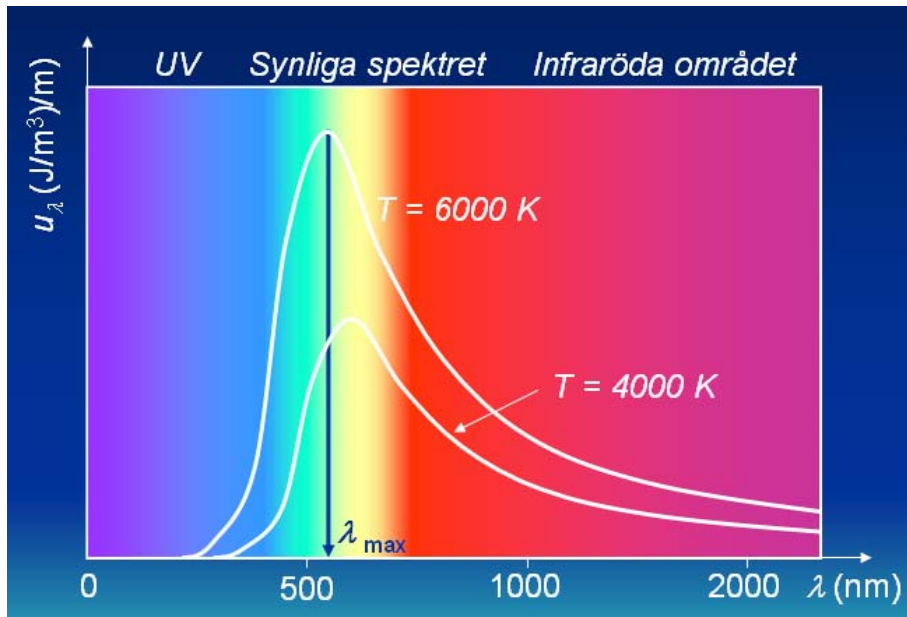


Soon we will find that the radiation intensity depends on the temperature of the sphere. We name it blackbody radiation. Planck examined the conditions of blackbody radiation and found expressions that were quite similar to the Maxwell-Boltzmann distribution functions.

He examined how the spectral energy density $u(f)df$ depended on the radiation frequency f and the temperature, T and derived the following expression:

$$u(f)df = \frac{8\pi h}{c^3} \frac{f^3 df}{e^{hf/kT} - 1}$$

This equation is called the Planck radiation law and fits with experiments.



Planck curves with energy as a function of wavelength λ .

With the equation $c = f\lambda$ we can transform the expression for the radiation law to an expression for $u = u(\lambda)$:

$$u(\lambda)d\lambda = \frac{8\pi hc \lambda^{-5} d\lambda}{e^{hc/\lambda kT} - 1}$$

If you take the derivative of this expression you will get the maximum of the function:

$$\frac{du(\lambda)}{d\lambda} = 0$$

The wavelength when the maximum occurs we can call λ_{max} . After taking the derivative we obtain:

$$\lambda_{max} = \frac{hc}{4.965kT} \text{ or with inserting of the values of the constants:}$$

$$\lambda_{max} = 2.898 \times 10^{-3} \frac{1}{T} \text{ m is the wavelength in m if the temperature is given in Kelvin.}$$

This formula is called the *Wien's displacement law*, which shows how the wavelength maximum is displaced with temperature T .

If we integrate the curve over all frequencies at a certain temperature T we obtain the Stefan-Boltzmann law that gives the total emitted energy (e) per second and over area unit:

$$e = \sigma T^4$$

$$\sigma = 5.67 \times 10^{-8} \text{ W/(m}^2 \text{ K}^4)$$

Example

If you double the temperature, how much more energy is radiated?

According to the Stefan-Boltzmann law the energy is proportional against T^4 . If $T' = 2T$ we obtain the total radiated energy becomes 2^4 times greater, that is 16 times greater.

Example

If you study the solar spectrum from the Earth, you find that the intensity maximum is found around 500 nm. Calculate the Sun's surface temperature if you regard the Sun as a blackbody radiator.

Wien's law gives: $T = (2.898 \times 10^{-3} / 500 \times 10^{-9}) \text{ K} = 5800 \text{ K}$

Chapter 6**6.1 The Schrödinger equation**

In 1926, Schrödinger presented those equations that came to be the foundations of modern physics and the development of quantum physics and quantum mechanics. Earlier unsolved problems concerning issues in chemistry, biochemistry, the processes of life, the foundations of Nature and its development were solved. After Einstein's presentation of the theory of special relativity and Bohr's successful description of the energy levels of the hydrogen, Erwin Schrödinger tried to formulate a theory that could explain the build up of the atom. He derived the following equation, the so called time-independent Schrödinger equation:

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - E_{pot})\Psi = 0$$

In the same way as in the wave dynamics of electromagnetism, Schrödinger introduced a wave function Ψ , as a function of the space coordinates, here for a matter wave associated with the electrons movement around the nucleus, that De Broglie had presented. With this equation, that includes the electron mass, Planck's constant, the electron wave function and the energy of the atom, the quantised energy levels of the atom can be evaluated.

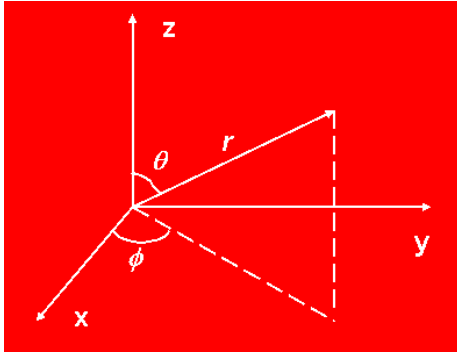
The Schrödinger equation can be generalised to three space coordinates and then becomes:

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{8\pi^2m}{h^2}(E - E_{pot})\Psi = 0$$

The potential energy E_{pot} for the hydrogen atom is the electrons potential energy at the distance r from the proton:

$$E_{pot} = -\frac{e^2}{4\pi\epsilon_0 r}$$

In order to be able to solve the Schrödinger equation, a second degree differential equation in the variables x, y, z , one finds it easiest to turn to polar coordinates:



$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \arccos \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\phi = \arctan \frac{y}{x}$$

After this exchange of variables, the Schrödinger equation can be written:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m}{h^2} (E - E_{pot})$$

This equation seems at first sight to be more complicated than the ordinary Schrödinger equation. However, we will try to divide it into three parts that depends on the variables r , θ and ϕ and then try to separate the equations and then solve them separately.

With $E_{pot} = -\frac{e^2}{4\pi\epsilon_0 r}$ and by multiplication with $r^2 \sin^2 \theta$ we obtain

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{8\pi^2 m r^2 \sin^2 \theta}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi = 0$$

If we then divide the Schrödinger equation into three products depending on r , θ and ϕ and assume that we can write the wave function according to:

$$\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Here $R(r)$ describes how the wave function Ψ varies with radius r , θ and ϕ .

We take the derivative with respect to r , θ and ϕ and find that:

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{\partial R}{\partial r}$$

$$\frac{\partial \psi}{\partial \theta} = R \Phi \frac{\partial \Theta}{\partial \theta}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = R \Theta \frac{\partial^2 \Phi}{\partial \phi^2}$$

These expressions we now put into the Schrödinger equation:

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{8\pi^2 m r^2 \sin^2 \theta}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = 0$$

Now, we move terms containing ϕ to the right side:

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{\sin \theta}{\Theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) + \frac{8\pi^2 m r^2 \sin^2 \theta}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = -\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2}$$

This equation can only be correct if both sides of the equation are equal to the same constant since they are functions of different variables. Let us call the constant m^2 (it will show later why we choose this expression for the constant). This gives the following equation:

$$-\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = m^2 \quad \text{or} \quad \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} + m^2 = 0$$

The left part of the Schrödinger equation can be written:

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{8\pi^2 m r^2}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = \frac{m^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right)$$

We have now just one variable on the left side and one variable on the right side. The various parts must be equal to the same constant. Let us call it $l(l+1)$ (It will also show why we denote it in this way).

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{8\pi^2 m r^2}{h^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) = l(l+1)$$

$$\frac{m^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) = l(l+1)$$

Thus, we have got three differential equations of the second order. The first one is relatively simple to solve. We can compare with the simple differential equation:

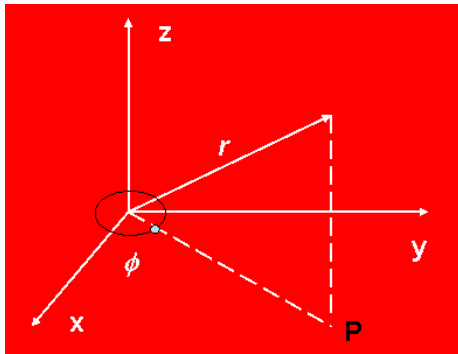
$$y'' + k^2 y = 0$$

that has the solution $y = Ae^{ikx} = C \cos kx + D \sin kx$

In our case we get the solution to one part of the Schrödinger equation:

$$\Phi(\phi) = Ae^{im\phi}$$

If we let the point \mathbf{P} rotate 360° in the xy -plane we return to the same point \mathbf{P} . We can also say that the function $\Phi(\phi)$ shall get the same value after this rotation:



$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

This leads to $Ae^{im\phi} = Ae^{im(\phi+2\pi)}$, which can only be true if m is equal to 0 or an integer, i.e.

$$m = 0, \pm 1, \pm 2, \pm 3, \dots$$

This derivation has thus given rise to possible values for the so-called **MAGNETIC QUANTUM NUMBER m** . We now realize why we introduced the constant m^2 earlier.

The solution to the equation that contains the function $\Theta(\theta)$ is more complicated to solve, but can be expressed in so-called Legendre functions. They can exist only if l in the equations above is an integer, where:

$$m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm l$$

This constant l is called the **ORBITAL QUANTUM NUMBER**.

The solution to the last part of the Schrödinger equation with respect to the radial function $R(r)$ is also rather complicated. The solutions are polynomials that are called Laguerre functions. This equation has a solution only if E is positive or if E assumes certain negative values:

$$E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2} \right)$$

This expression is the same as Bohr got for the hydrogen atom. Furthermore, n has to be an integer, where

$$l = 0, 1, 2, \dots, n-1$$

The number n is called the **PRINCIPAL QUANTUM NUMBER** and can assume the following values:

$$n = 1, 2, 3, \dots$$

So far, we have got the following quantum numbers when solving the Schrödinger equation for the hydrogen atom:

$$n = 1, 2, 3, \dots$$

The Principal Quantum number

$$l = 0, 1, 2, \dots, n-1$$

$$m = -l, -(l-1), \dots, -3, -2, -1, 0, 1, 2, 3, \dots, (l-1), l$$

The Orbital Quantum number

The Magnetic Quantum number

Thus, we can divide the wave function into three functions, where $\Psi(r, \Theta, \Phi) = R_{nl} \Theta_{lm} \Phi_m$.

Contents Chapter 5-6

- 5.1 Introduction
- 5.2 Maxwell-Boltzmann distribution
- 5.3 Planck's radiation law
- 6.1 Schrödinger equation

Learning goals

- Be able to discuss the different distribution functions and within what fields they are used
- Be able to discuss the Maxwell-Boltzmann distribution and its use within molecular physics
- Calculate the molecular velocities within a gas
- Be able to discuss the various velocity measures as mean velocity, RMS-velocity etc
- Calculate the energies of molecules as a function of temperature
- Determine temperatures with the Wien law
- Calculate the energies with the Stefan-Boltzmann law
- Generally try to follow the solution of the Schrödinger equation with the derivation of the quantum numbers
- Be able to solve the differential equation leading to the magnetic quantum number
- Be able to determine possible orbital quantum numbers and magnetic quantum numbers for a given principal quantum number

Advices for reading

- Think of the fact that one with statistical physics can connect macroscopic and microscopic phenomena
- Try to follow the derivation of the Boltzmann distribution and how to use it to determine molecular velocities in a gas
- Think of that the Planck radiation law gives us a tool for determining the temperature of stars at great distances
- Try to understand how the Schrödinger equation gives us solutions of energy levels in small systems as atoms, molecules etc

Readings

- Thornton, Modern Physics, Saunders
- Krane, Modern Physics, Wiley
- Beiser, Concepts of Modern Physics, McGraw-Hill
- Serway, Moses, Moger, Modern Physics, Saunders
- Eisberg, Resnick, Quantum Physics of Atoms, Molecules, Solids and Particles, Wiley
- Blatt, Modern Physics, McGraw-Hill
- Halliday and Resnick, Fundamentals of Physics, Wiley
- Blatt, Modern Physics, McGraw-Hill
- Benson, University physics, Wiley

WEB-redings

- <http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html>
- http://nobelprize.org/nobel_prizes/physics/laureates/1918/planck-bio.html
- http://nobelprize.org/nobel_prizes/physics/laureates/1933/schrodinger-bio.html