9.1 From classical to quantum: the birth of quantum mechanics

9.1.1 The first models of atoms

In the early XIX's, the concept of "atoms" (in its physical sense) did not exist yet: for chemists they were "pure substances" identified by stoichiometry, independently of what an atom really is. For instance

- When you react hydrogen and oxygen, you always get water with a mass ratio 1:8.
- When you react hydrogen and chlorine, you always get HCl, never H_2Cl or HCl_2 (under normal conditions).
- ...

This led Dalton (1808) to suggest that matter is made of indivisible particles (atoms), and compounds are formed in fixed integer ratios. In early chemistry, one atom just meant "the smallest repeating unit that gives the observed stoichiometric ratios".

By the middle of the XIXth century, 60 atoms were already identified by this kind of methods of fixed proportions. Chemists identified empirical patterns from atoms to atoms, for instance:

- Dobereiner (1829): “triads” (e.g., Li–Na–K had similar properties, and Na's mass $\approx$ average of Li and K).
- Newlands (1865): “law of octaves” — every 8th element had similar properties.

In 1869, Mendeleïev published his first table of the elements. His method was simple: he arranged the known elements by increasing atomic weight and grouped the ones with similar chemical behavior (valence, oxide types, reactivity) into columns. He noticed periodic repetition of properties (density, melting point, reactivity) — hence “periodic law”. Interestingly, he left blank space in his table, anticipating the existence of some atoms that were unidentified yet.

In 1897, Thomson made the first experimental setup to identify experimentally electrons by studying cathodic rays (imposing an electrical current through a gas will ionize it, causing the gas to glow and electrons emitted from the cathod to follow the electric field toward the anod that has a small hole in it to let them through). By imposing an electric and a magnetic field on the ray trajectories and using classical mechanics laws, he computed the ratio of $\frac{m}{e}$. It was too small to possibly be hydrogen, and therefore Thomson suggested the existence of "subatoms", that ended up being electrons. He first suggested an atomic model of a positively charged sphere, permeable, in which these negatively charged particles could move freely.

In 1909, Rutherford used radioactive element to study the scattering of α particles on a fine foil of gold. According to Thomson model, the Helium ions should go through the gold atoms with a light deviation due to the electrons and positively charged sphere. However, they ended up observing very important scattering angles, that were impossible to explain in Thomson model. This led to the creation of an atomic model with a positively charged nucleus, and electrons around it.

Meanwhile in the end of the XIXth century, Michelson and Morley were trying to understand the fine structure spectrum: they could not explain why the emissions of atomic gases had only discrete levels of energy. Hertz and Lenard were observing experimentally the photoelectric effect by measuring a photoelectric current when light was sent on a metallic sheet. Rayleigh and Jeans were puzzled by the spectrum of blackbodies radiations... This really was a chaotic and stimulating time to do physics ! All of these unexplained electromagnetic phenomenons, and this still debated atomic model were about to introduce a very counter-intuitive approach: quantization.

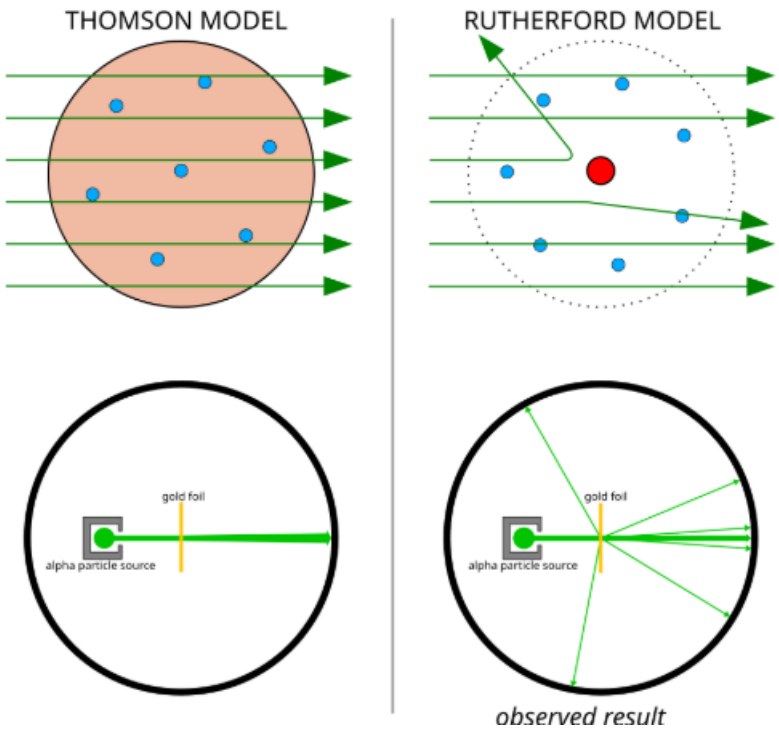

Figure 10: From wikipedia

9.1.2 Black body radiation, UV catastrophy and Planck quantization

Sources: [3], [5]

At the end of the XIXth century, physicist were particularly focused on understanding the patterns of light emitted by a blackbody. This is a theoretical object absorbing all frequencies of electromagnetic waves (hence the term "black body", suggested by Gustav R. Kirchhoff in 1862 as it would look black since it also absorbs light). When heated too a high enough temperature, it will emit a particular light pattern.

NB: While a perfect blackbody does not really exist, quartz is for instance a rather good blackbody for all wavelengths below 8 micrometers, or the inside of a cavity radiator that will trap radiations.

Back in the days, physicists have identified two laws for the blackbodies properties. **Wien's displacement law** and **Stefan's law**. Wien's displacement law allows to know what is the wavelength that a heated blackbody at temperature T will emit the most strongly.

$$\boxed{\lambda_{max} T = 2.898.10^{-3} m \cdot K} \qquad \text{WIEN'S DISPLACEMENT LAW} \tag{61}$$

NB : Wien's displacement law is used in astrophysics to know which star (assumed to behave as blackbodies) is hotter. It can also be used to explain why a blue flame is hotter than a red flame.

Meanwhile, Stefan's law provides an expression for the total power of a blackbody radiation (for all its wavelengths).

$$P(T) = \sigma A T^4 \qquad \text{STEFAN's LAW} \tag{62}$$

With A the surface of a blackbody heated at temperature T, and $\sigma = 5.670.10^{-8} W.m^{-2}.K^{-4}$. Trying to derive the expression of the energy of a radiation of frequency ν emitted by a blackbody heated at temperature T was giving the Rayleigh-Jeans spectrum (1880), using classical statistical physics arguments (see appendix). Of course, it was possible to obtain Wien's displacement law and Stefan's

law from this formula. Rayleigh-Jeans spectrum was however flawed, as it predicted a divergence in the radiation energy for short wavelength... This was called accordingly the **UV Catastrophy** and remained for 20 years one of the biggest challenges in physics.

In Physikalisch Technische Reichsanstalt (PTR), Planck was able to use some of the most precise black body measurement from that time. In 1900, he proposed a fitting formula for the amount of energy emitted by a wave of frequency ν at temperature T, now called Planck's law:

$$\boxed{u(\nu,T) = \frac{8\pi}{c^3}\frac{h\nu^3}{[e^{\frac{h\nu}{k_BT}} - 1]}} \quad \textbf{PLANCK'S LAW} \tag{63}$$

In this expression, $k_B = 1.380.10^{-23} J.K^{-1}$is the Boltzmann constant from statistical physics and $h = 6,626.10^{-34} J.s$is a new constant, soon to be called Planck constant. There has been a lot of speculation as for why and how Planck arrived at this formula, and this remain a historically debated topic. Nevertheless, to derive this expression, he assumed **energy quantization** $E_n = nh\nu$ where n is an integer and ν the frequency of the radiation. This was the first occurence of quantization appearing in physics, and the very early beginnings of quantum physics.

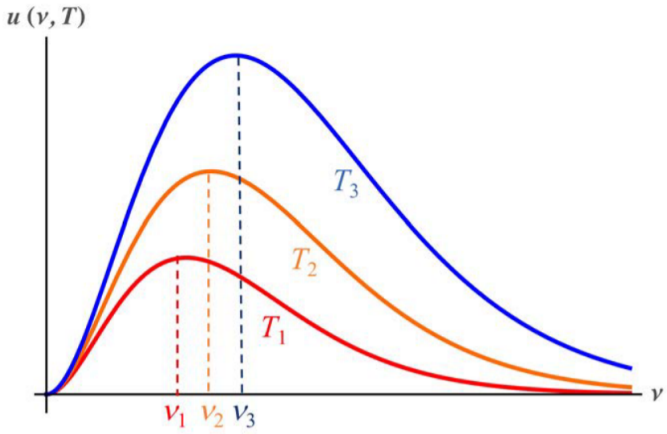

Figure 11: Display of the energy density (per meter cube) emitted by a wave of frequency ν bu a blackbody heated at temperature T.

9.1.3 First semi-classical model: the Bohr-Sommerfeld model

Guided by earlier worked from Rutherford, in 1913 the Bohr model was one of the first attempt to introduce a quantization rule through classical mechanics methods. This model considers a single electron, described as a point orbiting in a circular motion around an hydrogen nucleus.

If we write Newton second's law for the electron, we get:

$$k\frac{e^2}{r^2} = m\frac{v^2}{r} \tag{64}$$

Where $k = \frac{1}{4\pi\epsilon_0}$, a constant. To get this result, we used polar cordinates and rewrote the acceleration only along the radial coordinate.

In his model, Bohr made the assumption that the angular momentum is quantized [1] the only reason of such a choice was to match the spectroscopy results.

$$\boxed{L = mvr = n\hbar} \quad \textbf{BOHR QUANTIZATION} \tag{65}$$

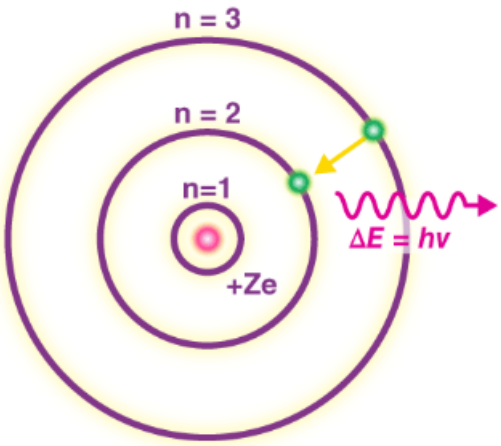

Figure 12: Sketch of the Bohr model. An electron is orbiting around a positively charge nucleus. From the angular momentum discretization, the model predicts the existence of circular orbitals. The orbital energy is increasing with the radius. For hydrogen atom (Z=1), the smallest orbital (n=1) have an associated energy of a Rydberg constant, as measured experimentally.

Combining the two equations above to eliminate the velocity, we arrive at a quantization of the allowed radios:

$$r_n = n^2 \frac{\hbar^2}{kme^2} \tag{66}$$

A numerical application leads to $r_1 = 0.0529nm$, and $r_n = nr_1$, which is the smallest radius possible between the nucleus and the electron. It is interesting to note that in this model, velocity is inversely proportional to the considered orbital, so the closest orbital has the fastest nucleus. Considering the total energy, we get

$$\begin{cases} E_n &= -\frac{1}{n^2} E_0 \\ \mathcal{R} &= \frac{k^2 me^4}{2\hbar^2} \end{cases} \tag{67}$$

The bohr model was mainly build in order to get such a quantization of the total energy. Indeed, the E_0 (also called Rydberg energy) is exactly the quantity of energy assessed to ionize an electron: $E_0 = 13.6eV$.

The Bohr model was one of the first successful result to explain spectroscopic fine structure experiments for the hydrogen atom. The energy of the several orbitals was matching the observed quantification of a gas of hydrogen.

Later in 1916, Sommerfeld made some refinements to the model by extending the assumption of circular motion to elliptic motion, assuming that the nucleus can also orbit around its center of mass and taking relativistic effect into account.

The initial hypothesis of summerfield was the following: if a system has coordinates that are periodic function of time, then the integral over a period of this coordinate is quantized:

$$\boxed{\oint p_q dq = \hbar n_q} \quad \textbf{SOMMERFELD QUANTIZATION} \tag{68}$$

Where q is the coordinate, p_q the associated momentum and n_q an integer. To see that this assumption is equivalent to elliptic motion, consider a 1D harmonic oscillator. Its total energy is

$$E = T + V = \frac{p^2}{2m} + \frac{1}{2}kx^2 \tag{69}$$

Which can be immediately rewritten as:

$$\frac{p_x^2}{2mE} + \frac{x^2}{\frac{2E}{k}} = \frac{p_x^2}{b^2} + \frac{x^2}{a^2} = 1 \tag{70}$$

Which is an ellipse equation in the (p_x, x) plane of radius b along the p_x axis and radius a along the x axis. This quantization assumption also turns out to include Planck and Bohr quantization rules. Indeed, the area of an ellipse is πab, so applying this to the momentum integral gives:

$$\oint p_x dx = \pi ab = \frac{2\pi E}{\sqrt{\frac{K}{m}}} \tag{71}$$

If we recall the quantization assumption on p_x and pose $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$, we get

$$E = nh\nu \tag{72}$$

Which is exactly Planck quantization assumption. For the Bohr model, if we consider the system of an electron orbiting around a nucleus, the angular momentum is a function of the polar coordinates r and θ, which are periodic. So according to Sommerfeld quantization assumption,

$$\begin{cases} \oint L d\theta &= n_\theta h \\ \oint p_r dr &= n_r h \end{cases} \tag{73}$$

As $L = mvr$ is independant of θ, we get $L = n_\theta \hbar$ from the first equation. In order to compute the momentum equation, we need to express it. This can be done by writing the total energy of the electron (kinetic + Coulomb potential):

$$E = \frac{1}{2m}(\dot{r}^2 + r^2\dot{\theta}^2) - \frac{k}{r} = \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} - \frac{k}{r} \tag{74}$$

In the above expression, we used the expression of the velocity in polar coordinates ($v^2 = (\dot{r}^2 + r^2\dot{\theta}^2)$, along with $L = mr^2\dot{\theta}$. The above equation provide an explicit expression for p_r:

$$p_r = \sqrt{2m(E - \frac{k}{r}) - \frac{L^2}{r^2}} \tag{75}$$

In this expression we took the absolute value, as the sign of the momentum corresponds to inward or outward radial motion. The integral over momentum can then be performed using Kepler's parametrization (posing $r(\eta) = a(1 - ecos(\eta))$ with a the bigger radius of the ellipse and e the excentricity). This led to:

$$\oint p_r dr = 2\pi \left(\frac{mk}{\sqrt{-2mE}} - L \right) \tag{76}$$

If we now use the quantization rules from eq. 73, we get:

$$hn_r = 2\pi \left(\frac{mk}{\sqrt{-2mE}} - n_\theta \hbar \right) \Leftrightarrow E = -\frac{2\pi^2 mk^2}{(n_r + n_\theta)^2 h^2} \tag{77}$$

We can introduce the quantum principal number $n = n_r + n_\theta$ that fixes the total energy. The numbers n_θ and n_r corresponds to the quantization of the angular and radial momentum. This anticipates the appearance of orbital angular momentum quantum number in modern quantum mechanics. Indeed, we can introduce the quantum orbital number $l = n_\theta$: several orbitals (values

of n_θ) can exist for a given energy (value of n) because there are values of n_r so that $n_r + n_\theta = n$. we get that for a given value of n, n_θ and n_r can only takes values between 0 and n: this define the quantum second number. These concepts will be developed later.

Finally, note there have been relativistic refinement to this model, allowing to match the fine structure spectrum and assuming the nucleus has a precession motion around the ellipse center.

The Bohr model have been first experimentally confirmed by Franck and Hertz in 1914 by sending electrons from a cathode to an anode through a gas of mercury atoms. Electrons will collide with mercury atoms either elastically (no energy transfer, so the energy should not be altered) or inelastically: according to Bohr model, the electrons should loose energy as multiples of $h\nu$. This has been clearly observed using the voltage/current curves, confirming the energy quantization.

9.1.4 The photoelectric effect and its confirmation: the Compton effect

Experimentally reported by Hertz in 1887 by sending monochromatic high frequency light on a metallic anode, the photoelectric effect consists in the emission of photo-electrons toward the cathod, as if they were tear away from the anode. Without light, there's no current, as the circuit is open. More precisely, a typical photoelectric effect apparatus consists of:

1. A metal surface (the photocathode) placed inside a vacuum tube.
2. A light source (often monochromatic) shining on the metal surface.
3. An anode (a positively charged plate) that collects emitted electrons.
4. A variable voltage source connected between the cathode and anode.
5. A current detector (ammeter) to measure the flow of photoelectrons.

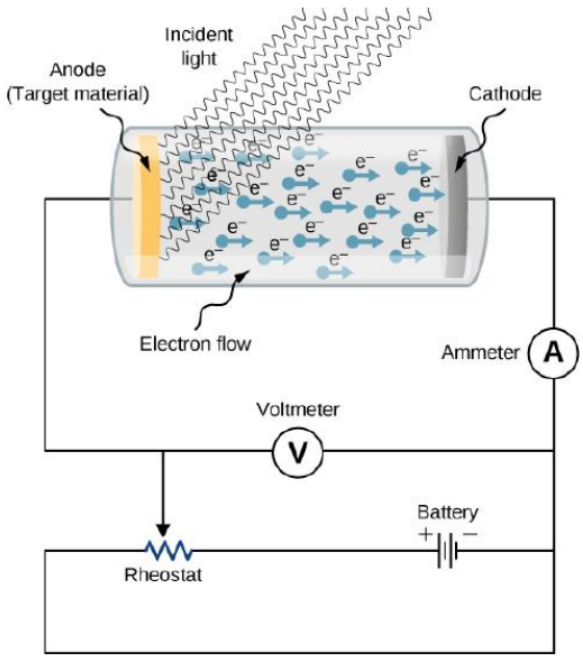

Figure 13: Sketch of the photoelectric effect. Light is sent on a metallic anode, that emits electrons through the air separating it from the cathode, if a big enough potential difference is imposed. From libretexts physics

When light shines on the metal, electrons are ejected from its surface. The electrons travel toward the anode, producing a measurable current. We can then apply a negative potential, the electrons will slow down and completely stop at the stopping voltage V_s, dropping the induced photocurrent

to zero. Hence, we can use this voltage to directly measures the maximum kinetic energy of the emitted electrons:

$$eV_s = \frac{1}{2}mv^2_{emitted} \tag{78}$$

Three phenomenons particularly stand out in the photoelectric effect, and couldn't be correctly explained by classical physics:

- There exists a threshold frequency f_0 below no electrons are emitted, no matter the amplitude of the light. The kinetic energy of the emitted electrons depends only on the light frequency, not on its intensity. This is contradicting classical electromagnetism.
- The photoelectric current (number of emitted electrons) increases with light intensity, but not their kinetic energy. Classically, a stronger light amplitude should mean a higher kinetic energy.
- The emission is immediate — no measurable delay even for very low intensities. Classically, there should be a time delay before emission at low intensities, as electrons accumulate energy gradually from the wave.

All of these predictions failed. So, inspired by Planck energy quantization, Einstein proposed in 1905 that light is made of quanta (photons) of energy:

$$E = hf \tag{79}$$

where h is Planck's constant and f the frequency. Einstein assumed that: - each photon would interact only with a single electron. - The electron needs a minimum energy ϕ to escape from the metal.

In this model, under these hypothesis the energy balance is given by:

$$hf = \phi + \frac{1}{2}mv^2_{max} \tag{80}$$

If $f < f_0 = \frac{\phi}{h}$, no electron is emitted (insufficient energy per photon). Increasing intensity just means more photons, not more energy per photon.

Although Eistein model was good to explain the photoelectric effect, the scientific community remained skeptical about his assumption of light quantization, for almost 15 years !

In the early 1920's, an experiment by Arthur H. Compton on light scattering by electrons acted as an important milestone to convince the community that light is indeed quantized.

Compton experiments consisted in sending high energy light (X-rays) onto electrons and studying the properties of the reflected light. The most interesting feature he noted was a change of the scattered light wavelength as follow:

$$\lambda_{sc} = A\,(1 - cos(\theta)) + \lambda \tag{81}$$

With λ_{sc} the wavelength of the scattered light, θ the deviation angle of light after the collision on the electron, A a constant and λ the wavelength of incident light.

To explain this shift in the wavelength, Compton tried to use Einstein theory of light quantization. He was not trying to prove it, on the contrary. But he found no other ways of explaining the shift than using his results. Compton model is based on energy and momentum conservation. Initially, the electron is at rest with a resting energy $E_{i,electron} = mc^2$ and momentum $\overrightarrow{p}_{i,electron} = \overrightarrow{0}$. After the collision, the electrons recoiled at some angle ϕ with energy $E_{f,electron} = \gamma mc^2$ and momentum $\overrightarrow{p}_{f,electron} = \gamma mv$ (We used special relativity in this model because it was already well established

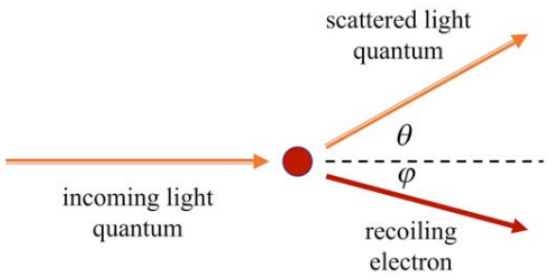

Figure 14: Sketch of Compton scattering experiment. Light is on an electron and reflected at an angle θ. The electron, initially at rest, recoil from the collision along an angle ϕ. From Ref. [5]

by the time Compton made his experiments, and the X-rays have significant energy requiring us to use this framework).

To derive the system energy and momentum conservation laws, Compton had to use Einstein light quantization theory. Hence he assumed the energy and momentum of a photon are

$$\begin{cases} E_{light} &= h\nu = \frac{hc}{\lambda} \\ p_{light} &= \frac{E_{light}}{c} = \frac{h}{\lambda} \end{cases} \tag{82}$$

With this expression, he can directly try to express the wavelength he observed between scattered and incident light using the system conservation laws:

$$\begin{cases} \frac{hc}{\lambda} + mc^2 &= \frac{hc}{\lambda_{sc}} + \gamma mc^2 & \text{Energy conservation} \\ \frac{h}{\lambda} + 0 &= \frac{h}{\lambda_{sc}}\cos(\theta) + \gamma mv\,\cos(\phi) & \text{conservation of } p_y \\ 0 + 0 &= \frac{h}{\lambda_{sc}}\sin(\theta) - \gamma mv\,\sin(\phi) & \text{conservation of } p_x \end{cases} \tag{83}$$

This led to a system of 3 equations and 3 unknown, which can be rewritten as :

$$\boxed{\lambda_{sc} = \left(\frac{h}{mc}\right)(1 - cos(\theta)) + \lambda} \qquad \textbf{COMPTON SCATTERING} \tag{84}$$

So, using Einstein theory of light quantization to replace the energy and momentum of light allowed Compton to get an expression of the proportionality constant in the wavelength difference, which perfectly matched his experiments. This prefactor $\frac{h}{mc}$ was later named **Compton's wavelength**.

Thus, Compton scattering was a fundamental experiment that validated Eistein model of photons, quantums of lights. The derivation uses both waves and particles concepts, involving wavelength as well as photons. This set the stage for the particle-wave duality and the beginning of modern quantum physics.

9.1.5 Young splits, Franck-Hertz experiment and De Broglie thermal wavelength

Motivated by the particle behavior of light, De Broglie suggested in 1924 that particles like electrons and atoms could also behave as waves, introducing the notion of particle wave duality. De broglie extended Einstein quantization relations from photons to any particles:

$$\begin{cases} E &= hf \\ \lambda_{DB} &= \frac{h}{p} \end{cases} \qquad \textbf{De Broglie wavelength} \tag{85}$$

In the above expression, λ_{DB} is a wave property that can be associated to particles, and is called the De Broglie wavelength. We can express the wave group velocity using the wavevector $\overrightarrow{k}$ with $||\overrightarrow{k}|| = \frac{2\pi}{\lambda}$ and the wave frequency $\omega = 2\pi f$, and explicit the relativistic energy $E = mc^2$ and momentum $||\overrightarrow{p}|| = m||\overrightarrow{u}||$ with $\overrightarrow{u}$ with $\overrightarrow{u}$ the velocity of the particle. We get:

$$\lambda f = \frac{\omega}{k} = \frac{E/\hbar}{p/\hbar} = \frac{mc^2}{mu} = \frac{c}{\beta} \tag{86}$$

Where $\beta = \frac{u}{c}$. For a massless particle, $u = c$ and we get the usual light dispersion relation in vacuum: $\lambda f = c$.

If one needs to compute the De Broglie wavelength, it's important to use the relativistic expression $p = m_0\gamma u = E_0\gamma\frac{\beta}{c}$, with $E_0 = mc^2$ the rest energy and $\gamma = (1-\beta^2)^{-\frac{1}{2}}$. This expression can be simplified only if $\beta \ll 1$ into the classical non-relativistic expression $p = mu$.

If instead of a single particle we consider a thermal ensemble at equilibrium temperature T, then the characteristic momentum scale is given by the Maxwell-Boltzmann distribution as $p = \sqrt{2\pi m k_B T}$, leading to the so-called thermal De Broglie wavelength

$$\boxed{\lambda_T = \frac{h}{p} = \frac{h}{\sqrt{2\pi m k_B T}}} \quad \textbf{Thermal De Broglie wavelength} \tag{87}$$

The De Broglie and thermal De Broglie wavelength allows to assess when the laws of quantum physics are important, or when they can be neglected. As a rule of thumb, quantum physics will be consequent for very small or very cold objects.

NB: the De Broglie wavelength allows to nicely explain Bohr quantization : if we assume one orbital is a string on length l (connected to the radius), then it can only vibrate in a discrete numbers on modes. This allows to express Bohr quantization directly as a function of the De Broglie wavelength: $2\pi r_n = 2n\frac{\lambda}{2}$.

The first experimental proof of the De Broglie wavelength came in 1927 with the Davisson–Germer experiment [2]. They fired a beam of electrons onto a nickel crystal and measured the intensity of electrons scattered at various angles. When the nickel surface was well ordered (after oxidation and annealing), they observed sharp intensity peaks at certain angles — exactly like X-ray diffraction patterns from crystals.

By analyzing the angles and using Bragg's law $n\lambda = 2a_0\sin(\theta)$ with a_0 the lattice spacing and θ the scattering angle of the electrons, they determined that the wavelength λ of the electrons matched perfectly the De Broglie prediction.

Many other experiment came afterward to confirm this particle-wave duality De Broglie established: we can cite here the notoriously known Young slits setup experiments. In 1801, Young did this famous experiment and observed constructive and destructive interference of light, typical of waves behavior. The same interferences have been obtained with individual photons (G.I. Taylor, 1909) and even with electrons (Claus Jönsson, 1961). Nowadays the particle-wave duality is a very well experimentally established result, and the core foundation of modern quantum mechanics.