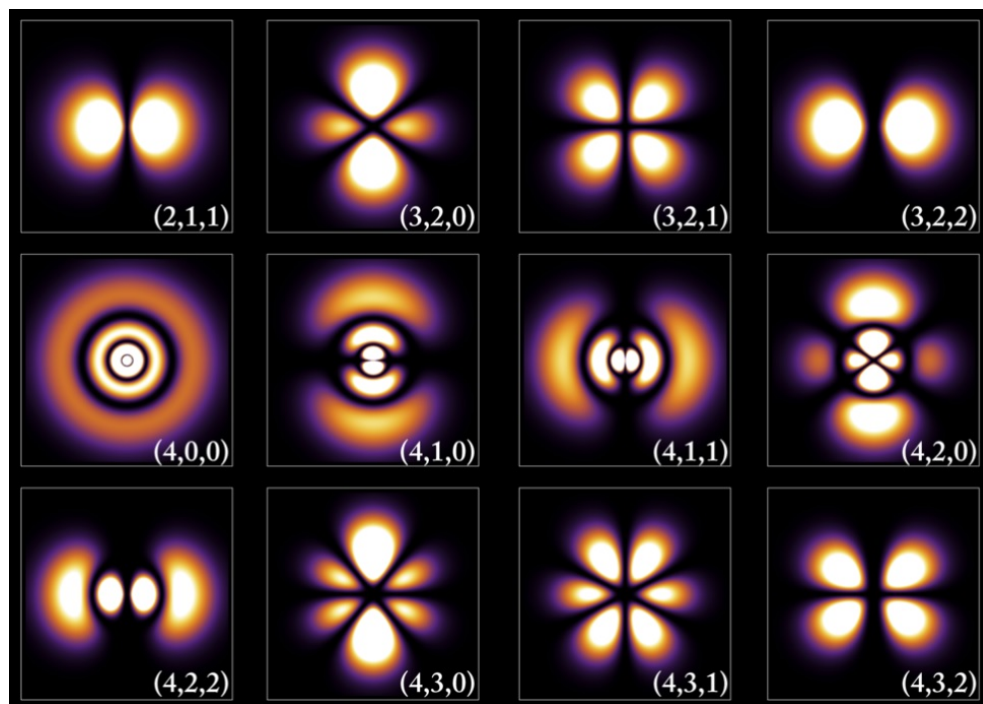


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## Bohr, Spectra and the Quantum model of the Atom

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**Cover photo credit:** Atomic orbitals of the electron in a hydrogen atom at different energy levels. Source: Wikipedia [public domain]

## Development of the nuclear model of the atom

### Background: Thomson's "plum pudding" model of the atom

After his discovery of the electron, J.J. Thomson worked on an atomic model in which he proposed that all atoms are constituted by some number of fundamental particles - the corpuscles he discovered (now known as electrons) embedded within a region of diffuse positive charge<sup>1</sup>.

Thomson refined his model between 1904 and 1909, calculating that stability could be achieved if large numbers of electrons (of the order of several thousand) rotated in concentric rings. For large numbers of electrons, Thomson could show that the emission of radiation due to their acceleration became very small and could effectively be neglected.

In the introduction to his 1904 paper, Thomson describes the model he is investigating:

The view that the atoms of the elements consist of a number of negatively electrified corpuscles enclosed in a sphere of uniform positive, electrification, suggests... ..the motion of a ring of  $n$  negatively electrified particles placed inside a uniformly electrified sphere.

Difficulties with the model were:

- the vague nature of the positive charge in which the electrons were embedded
- the gradual accumulation of evidence after 1906 that the number of electrons in atoms was small - likely of the same magnitude as the ordering number of the atom in the periodic table
- the inability of the model to quantitatively predict the spectral lines of atoms
- by 1909, its inconsistency with the results of the  $\alpha$  scattering experiments of Geiger and Marsden



Figure 1: J.J. Thomson. [Public domain]

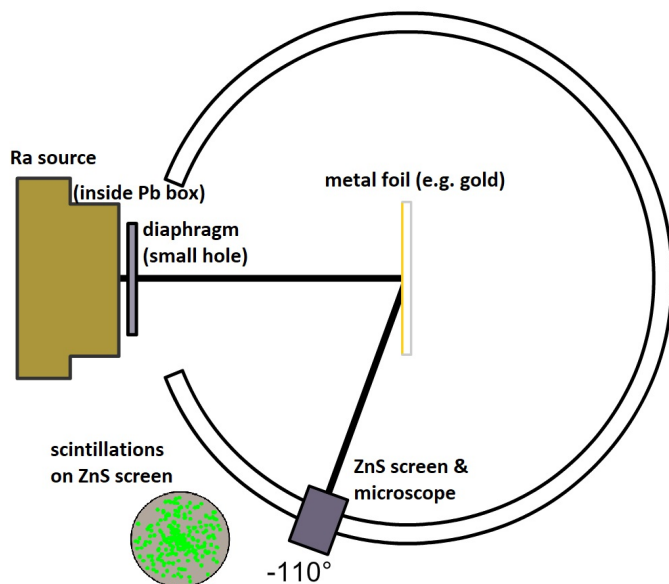
<sup>1</sup> References for this section: J.J. Thomson's 1897 and 1904 papers ([http://www.hep.princeton.edu/~mcdonald/examples/EP/thomson\\_pm\\_44\\_293\\_97.pdf](http://www.hep.princeton.edu/~mcdonald/examples/EP/thomson_pm_44_293_97.pdf) and [http://fizika.unios.hr/~ilukacevic/dokumenti/materijali\\_za\\_studente/qm1/Thomson\\_1904.pdf](http://fizika.unios.hr/~ilukacevic/dokumenti/materijali_za_studente/qm1/Thomson_1904.pdf)), "Quantum Generations" by Helge Kragh, pg. 44, and "Inward Bound" by Abraham Pais, pg. 185

### The Geiger-Marsden experiment

Working at the University of Manchester under the guidance of Ernest Rutherford just prior to 1909, postdoctoral fellow Hans Geiger and undergraduate student Ernest Marsden conducted experiments to detect the scattering of  $\alpha$  particles incident upon thin metal films<sup>2</sup>.

Ernest Marsden described the genesis of the experiment as follows:

One day Rutherford came into the room where we were counting...  $\alpha$ -particles... turned to me and said "See if you can get some effect of  $\alpha$ -particles directly reflected from a metal surface". I do not think he expected any such result, but it was one of those "hunches" that perhaps some effect might be observed... To my surprise I was able to observe the effect looked for... I well remember reporting the result to Rutherford a week after, when I met him on the steps leading to his private room"



In 1909 Geiger and Marsden reported their initial results that a small fraction ( $1/8000$  in the case of platinum)  $\alpha$  particles incident on thin metal experiences large angle  $\alpha$  scattering. In a more complete paper in 1913 they reported results which showed agreement with detailed predictions of Rutherford's 1911 model of the atom.

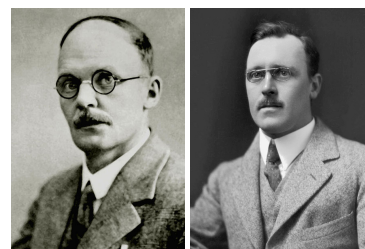


Figure 2: Hans Geiger (left) and Ernest Marsden (right). [Public domain]

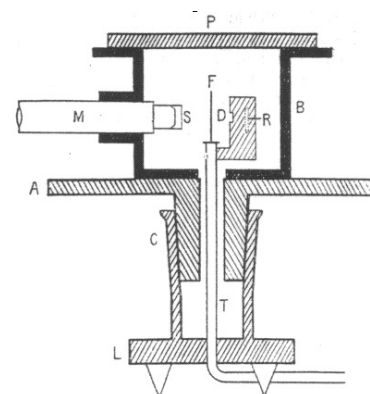


Figure 3: The diagram of the experimental setup from Geiger and Marsden's 1913 paper. M-microscope, F-metal film, S-ZnS screen, R-radon source (surrounded by Pb box to contain  $\beta$  emissions), D-diaphragm to allow narrow  $\alpha$ -particle beam, P-glass plate to seal chamber, T-tube used to evacuate chamber, A-graduated circular platform on which the microscope and screen can be rotated.

<sup>2</sup> References for this section: Geiger and Marsden's 1909 and 1913 papers (<https://www.chemteam.info/Chem-History/GeigerMarsden-1913/GeigerMarsden-1913.html>, "Quantum Generations" by Helge Kragh, pg. 51, and "Inward Bound" by Abraham Pais, pg. 189

Figure 4: Diagram of Geiger and Marsden's 1913 experiment. Image credit: Applet created by the King's center for visualisation in science: [http://www.kcvs.ca/site/projects/physics\\_files/rutherford/historical\\_scattering2.swf](http://www.kcvs.ca/site/projects/physics_files/rutherford/historical_scattering2.swf). Labeled according to the diagram in Geiger and Marsden's 1913 paper <https://www.chemteam.info/Chem-History/GeigerMarsden-1913/GeigerMarsden-1913.html>

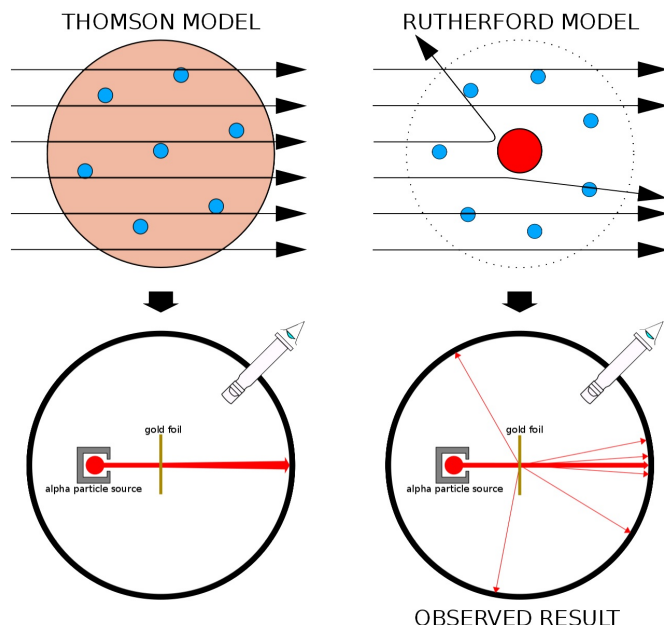


Figure 5: Predictions of Thomson and Rutherford models of the atom for  $\alpha$ -particle scattering through thin metal foils. Image credit: By Kurzon - Own work, CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=32215297>

### Rutherford's atomic model

Later in life, Rutherford expressed his surprise at Geiger and Marsden's initial results showing large angle deflections of  $\alpha$  particles as follows:

"It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"

Based on their results, Rutherford developed a model of the atom which he published in 1911.<sup>3</sup> In the introduction to the paper he describes his model as follows:

Consider an atom which contains a charge  $\pm Ne$  at its centre surrounded by a sphere of electrification containing a charge  $\mp Ne$  supposed uniformly distributed throughout a sphere of radius  $R$ .  $e$  is the fundamental unit of charge... We shall suppose that for distances less than  $10^{-12}$  cm. the central charge and also the charge on the  $\alpha$  particle may be supposed to be concentrated at a point. It will be shown that the main deductions from the theory are independent of whether the central charge is supposed to be positive or negative. For convenience, the sign will be assumed to be positive. The question of the stability of the atom proposed need not be considered at this stage, for this will obviously depend upon the minute structure of the atom, and on the motion of the constituent charged parts.

While Rutherford does not propose his own model for the distribution of outer charges (i.e. the electrons), in the conclusion to his paper, Rutherford makes a brief reference to an earlier proposed "planetary" model of the atom by the Japanese physicist Nagaoka:

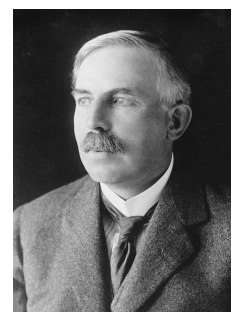


Figure 6: Ernest Rutherford. [Public domain]

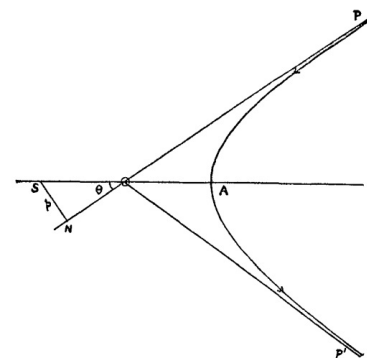


Figure 7: Scattering of an  $\alpha$  particle in a hyperbolic trajectory in Rutherford's 1911 paper.

<sup>3</sup> References for this section: Rutherford's 1911 paper: [http://www.ymambrini.com/My\\_World/MMJC4Nov13\\_files/rutherford\\_PhilMag\\_21\\_669\\_1911.pdf](http://www.ymambrini.com/My_World/MMJC4Nov13_files/rutherford_PhilMag_21_669_1911.pdf), Rutherford's 1914 paper: <https://www.chemteam.info/Chem-History/Rutherford-1914.html>, "Quantum Generations" by Helge Kragh, pg. 51, and "Inward Bound" by Abraham Pais, pg. 189

It is of interest to note that Nagaoka has mathematically considered the properties of a "Saturnian" atom which he supposed to consist of a central attracting mass surrounded by rings of rotating electrons. He showed that such a system was stable if the attractive force was large. From the point of view considered in this paper, the chance of large deflexion would practically be unaltered, whether the atom is considered to be a disk or a sphere.

By 1914, Rutherford had additional evidence from the more detailed experiments of Geiger and Marsden to allow him to refine his theory further. In his 1914 paper he describes his model as follows:

In my previous paper I pointed out the importance of the study of the passage of the high speed  $\alpha$  and  $\beta$  particles through matter as a means of throwing light on the internal structure of the atom. Attention was drawn to the remarkable fact, first observed by Geiger and Marsden, that a small fraction of the swift  $\alpha$  particles from radioactive substances were able to be deflected through an angle of more than  $90^\circ$  as the results of an encounter with a single atom. It was shown that the type of atom devised by Lord Kelvin and worked out in great detail by Sir J. J. Thomson was unable to produce such large deflexions unless the diameter of the positive sphere was exceedingly small. In order to account for this large angle scattering of  $\alpha$  particles, **I supposed that the atom consisted of a positively charged nucleus of small dimensions in which practically all the mass of the atom was concentrated. The nucleus was supposed to be surrounded by a distribution of electrons to make the atom electrically neutral, and extending to distances from the nucleus comparable with the ordinary accepted radius of the atom.** Some of the swift  $\alpha$  particles passes through the atoms in their path and entered the intense electric field in the neighbourhood of the nucleus and were deflected from their rectilinear path.

Finally, Rutherford acknowledges the issues with the stability of a 'nuclear' atomic model, and the solution that Bohr proposed in 1913:

Bohr has drawn attention to the difficulties of constructing atoms on the "nucleus" theory, and has shown that the stable positions of the external electrons cannot be deducted from the classical mechanics. By the introduction of a conception connected with Planck's quantum, he has shown that on a certain assumptions it is possible to construct simple atoms and molecules out of positive and negative nuclei, e. g. the hydrogen atom and molecule and the helium atom, which behave in many respects like the actual atoms or molecules. While there may be much difference of opinion as to the validity and of the underlying physical meaning of the assumptions made by Bohr, there can be no doubt that the theories of Bohr are of great interest and importance to all physicists as the first definite attempt to construct simple atoms and molecules and to explain their spectra.

### *An aside: The quantum model of light*

In 1900 Max Planck demonstrated that in order to understand the spectrum of light emitted by hot objects ("blackbodies") it was necessary to assume that light was emitted and absorbed in packets of energy, where the size of the packet was proportional to the frequency of the radiation.

Electromagnetic radiation is emitted and absorbed by matter in "quanta" with energy

$$E = hf$$

where  $h = 6.626 \times 10^{-34} \text{Js}$  is now known as Planck's constant.

This assumption was without precedence at the time, and initially Planck believed it might be just a mathematical "trick" that could be eliminated from the derivation once physicists understood the physics of blackbodies more thoroughly.

*Over the next 10 years it became clear that the idea of quantisation was not just essential to understanding blackbody radiation, but was of fundamental significance in physics, laying the foundations for the field of quantum mechanics and our understanding of the atom.*

#### *Overview - What is Blackbody radiation?*

How much radiation is emitted and at what wavelengths depends primarily on the temperature of the object, but also how efficiency the object absorbs and emits EM radiation at different wavelengths. Objects that absorb radiation poorly at a certain wavelength also emit poorly at that wavelength.

It is usual to consider an ideal material (a 'black body'), that absorbs perfectly at all wavelengths:

A **black body** is an idealised object that absorbs all radiation incident upon it.

Black bodies are also "perfect emitters" of radiation, in the sense that they emit the most thermal radiation that it is possible for an object of that temperature to emit at each wavelength. Our sun and other stars are almost perfect black bodies and many terrestrial materials can be treated approximately as black bodies.

The spectrum of wavelengths emitted by such an idealised object is called a "black body spectrum". It depends *only* on the temperature of the object and is shown in figure 10.

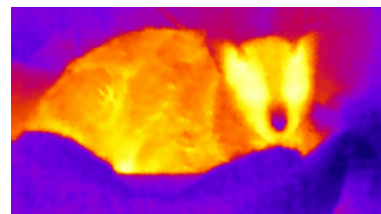


Figure 8: An image of my cat taken with an infrared camera.

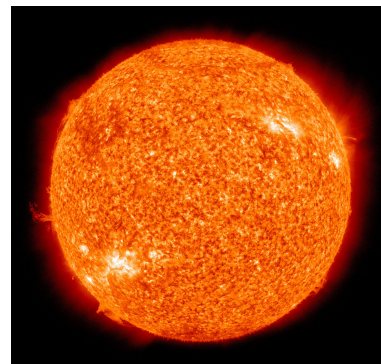


Figure 9: The Sun is a black body to an excellent approximation. By NASA/SDO (AIA)[Public Domain], <https://commons.wikimedia.org/w/index.php?curid=11348381>.

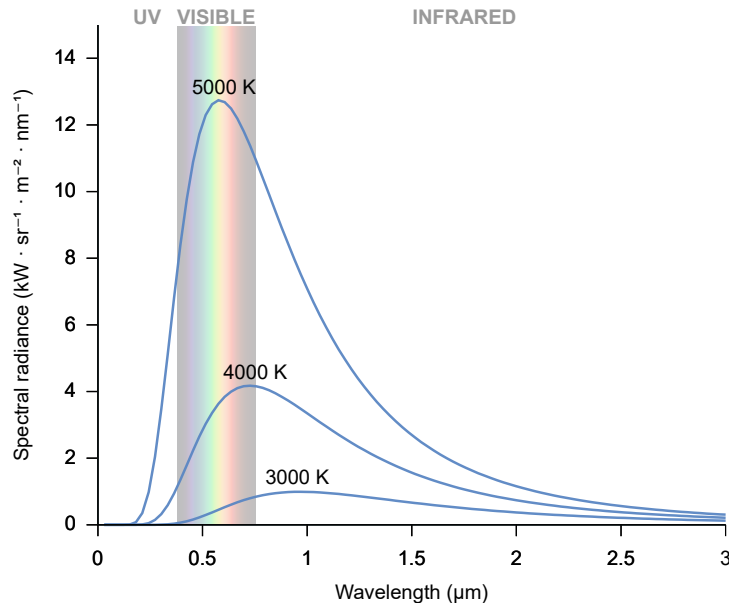


Figure 10: The spectrum of radiation emitted by black bodies of three different temperatures. Figure attribution: Based on work by Darth Kule [Public domain].

### Wein's law

The spectrum of radiation emitted by a black body depends on temperature in two ways. One of these is Wein's law, describing the fact that the wavelength at which the body emits the most radiation (the 'peak' wavelength) is inversely proportional to temperature<sup>4</sup>.

**Wein's law:**

$$\lambda_{\max} = \frac{b}{T} \quad (1)$$

where  $b = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}$  is Wein's displacement constant.

<sup>4</sup> Observe in figure 10 that the **peak wavelength** moves to lower wavelengths with increasing temperature.

### The Stephan-Boltzmann law

The other way in which temperature affects the black body spectrum is via the power emitted by the object, where the power is proportional to the area under the black body spectrum<sup>5</sup>.

**The Stephan-Boltzmann law:**

$$P = A\sigma\epsilon T^4 \quad (2)$$

where  $P$  is the power emitted,  $A$  the surface area,  $\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$ ,  $\epsilon$  is the emissivity ( $\epsilon = 1$  for a black body, and  $0 < \epsilon < 1$  for objects that are not perfect black bodies) and  $T$  is the temperature of the object.

<sup>5</sup> Observe in figure 10 that the **area under the curve** (which is proportional to the emitted power) increases very substantially as temperature increases due to the dependence on  $T^4$ .



## Bohr's Model of the atom

### Atomic spectra

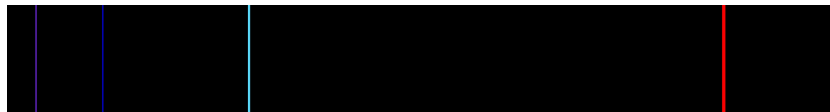


Figure 11: Visible emission spectra of hydrogen (The 'balmer series').

Newton was the first to observe that white light is composed of a continuous spectrum of colours. In 1853, Angstrom observed that the spectrum produced by an electrical discharge through hydrogen gas consisted of individual lines. In the visible region of the hydrogen spectra there are four lines, one red, one blue-green and two violet, as shown in figure 11.

Angstrom, and later Plücker, examined the spectra of many gases, and noted that they were unique to the gas that emitted them, providing a way of detecting the presence of that particular element. This work was later extended to many elements, including metals, by Kirchhoff and Bunsen.

### Balmer's formula

In 1885 Johann Balmer, a Swiss mathematics teacher, was the first to produce a mathematical formula which described the visible spectral lines of hydrogen (which now bear his name).

In 1888 Johannes Rydberg proposed a more general form of Balmer's equation. In modern notation his formula can be written as:

$$\frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (3)$$

where  $\lambda$  is the wavelength of the spectral line,  $R$  is a constant now known as the Rydberg-Ritz constant,  $R = 1.097 \times 10^7 \text{ m}^{-1}$  and where  $n_f$  and  $n_i$  are integers, with  $n_i > n_f$ .

For the visible hydrogen spectra,  $n_f = 2$ , however the formula predicts the existence of other spectral lines for hydrogen outside the visible range where  $n_f$  (in fact, it predicts an infinite number of lines!). Subsequent to Rydberg publishing his formula, the spectral lines for hydrogen in the UV (corresponding to  $n_f = 1$ ) and the infrared (corresponding to  $n_f = 3$ ) were discovered experimentally.



Figure 12: Johann Balmer. Image credit: Wikipedia [public domain].



Figure 13: Johannes Rydberg. Image credit: Wikipedia [public domain].

### Introduction to Bohr's model

Bohr's model of the hydrogen atom was a great advance as it could predict the spectral lines that are observed for hydrogen, and it addressed the issue of the instability of the electron configuration.<sup>6</sup>

Bohr began the first of his three papers of 1913 (which later become known as the 'great trilogy') by carefully pointing out the difficulties in the previous models by Thomson and Rutherford.<sup>7</sup>

In order to explain the results of experiments on scattering of  $\alpha$  rays by matter Prof. Rutherford has given a theory of the structure of atoms. According to this theory, the atom consists of a positively charged nucleus surrounded by a system of electrons kept together by attractive forces from the nucleus; the total negative charge of the electrons is equal to the positive charge of the nucleus. Further, the nucleus is assumed to be the seat of the essential part of the mass of the atom, and to have linear dimensions exceedingly small compared with the linear dimensions of the whole atom. The number of electrons in an atom is deduced to be approximately equal to half the atomic weight. Great interest is to be attributed to this atom-model; for, as Rutherford has shown, the assumption of the existence of nuclei, as those in question, seems to be necessary in order to account for the results of the experiments on large angle scattering of the  $\alpha$  rays.

In an attempt to explain some of the properties of matter on the basis of this atom-model we meet, however, with difficulties of a serious nature arising from the apparent instability of the system of electrons: difficulties purposely avoided in atom-models previously considered, for instance, in the one proposed by Sir. J.J. Thomson. According to the theory of the latter the atom consists of a sphere of uniform positive electrification, inside which the electrons move in circular orbits.

The principal difference between the atom-models proposed by Thomson and Rutherford consists in the circumstance that the forces acting on the electrons in the atom-model of Thomson allow of certain configurations and motion of the electrons for which the system is in a stable equilibrium; such configurations, however, apparently do not exist for the second atom-model.

Bohr then outlines how quantum theory forms the foundation for his new model of the atom:

Now the essential point in Planck's theory of radiation is that the energy radiation from an atomic system does not take place in the continuous way assumed in the ordinary electrodynamics, but that it, on the contrary, takes place in distinctly separated emissions, the amount of energy radiated out from an atomic vibrator of frequency  $f$  in a single emission being equal to  $nhf$ , where  $n$  is an entire number, and  $h$  is a universal constant.

<sup>6</sup> See the Phet on 'models of the hydrogen atom' for a nice visualisation: <https://phet.colorado.edu/en/simulation/hydrogen-atom>

<sup>7</sup> References for this section: Bohr, N. (1913), "On the constitution of Atoms and Molecules", Part 1, *Philosophical Magazine*, 26, 1-24. <http://web.ihep.su/dbserve/compas/src/bohr13/eng.pdf>, Pais, A. (1982). *Subtle is the Lord: The science and the life of Albert Einstein*. (Oxford: Oxford University Press), Kragh, H. (1999). *Quantum generations: A history of physics in the twentieth century*. (Princeton, New Jersey: Princeton University Press).

*Bohr's assumptions*

In his papers Bohr introduces a number of postulates (note that in other texts some may be combined - Bohr did not write them in exactly these words):

1. The electron moves in a circular orbit around the nucleus, with the required centripetal force provided by the electrostatic attraction between the electron and the nucleus.
2. Although the electron is continually accelerating, it does not lose energy by emitting electromagnetic radiation.
3. The electron cannot orbit at any radius, only fixed values, where  $mvr = n\hbar$  where  $mvr$  is the angular momentum of the electron,  $n$  is an integer and  $\hbar = \frac{h}{2\pi}$
4. The electron emits or absorbs electromagnetic radiation as it discontinuously moves between these fixed orbits, where the energy of the photon emitted or absorbed is equal to the energy difference between the orbits (so that  $hf = E_i - E_f$ ).

Note that the postulates use a mixture of classical mechanics (postulate 1) and quantisation (postulate 3). The second postulate is proposing that classical mechanics - the predictions of Maxwell's equations - cannot be applied (without modification) to a physical system as small as an atom. This is a distinct break from previous efforts by Thomson and others to describe the behaviour of electrons in atoms using classical physics. The final postulate addresses the mechanism for the production of spectra by atoms, and also utilises Planck's quantisation theory.

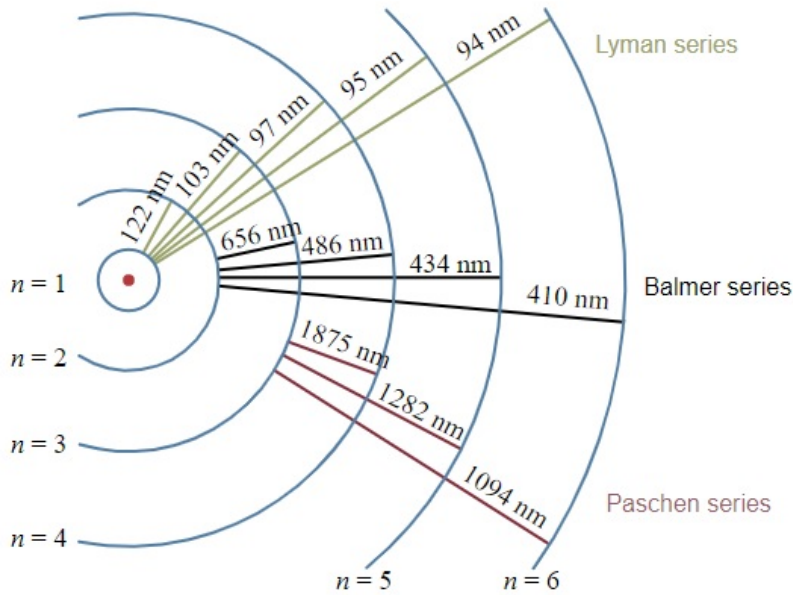


Figure 14: Transitions of electrons in the Bohr model responsible for the Balmer series (as well as the Lyman UV and Paschen infrared series).

Image credit: [https://commons.wikimedia.org/wiki/File:Hydrogen\\_transitions.svg](https://commons.wikimedia.org/wiki/File:Hydrogen_transitions.svg)

A hydrogen szinkepei.jpg:  
User:Szdoriderivative work:  
OrangeDog (talk contribs) [CC BY 2.5  
(<https://creativecommons.org/licenses/by/2.5/>)]

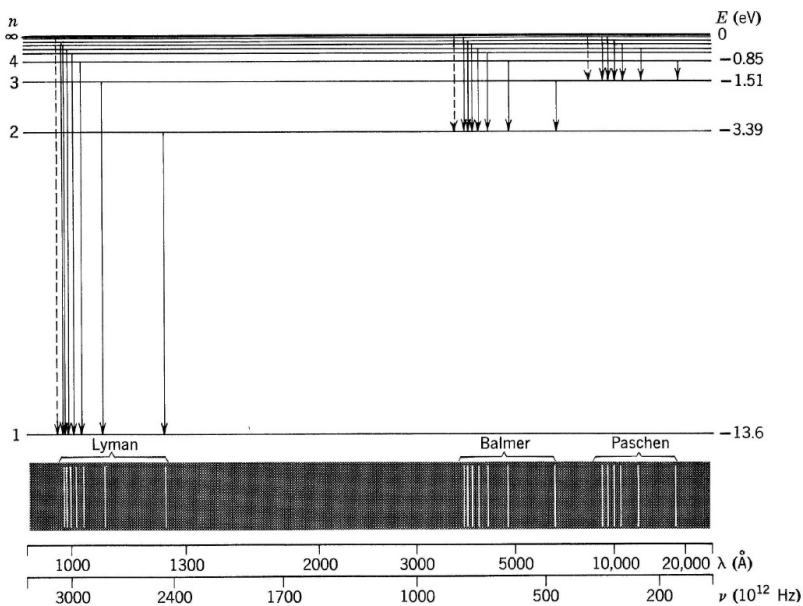


Figure 15: The energy level diagram for hydrogen. Note that the Balmer series finishes on the  $n = 2$  energy level.

Image credit: Figure 4-12 from  
Eisberg, R. Resnick, R. (1974) Quantum  
Physics of Atoms, Solids, nuclei and  
particles. (John Wiley Sons, New York).

### Limitations of Bohr's model

The Bohr model was the first important step in the application of quantisation to the atom, but it had obvious limitations. These included:

- The relative intensity (brightness) of different spectral lines. These occur due to the different probabilities of different transitions (The Bohr model cannot account for this)
- The spectra of larger atoms are not described by the Bohr model, which is limited to one electron systems (it is reasonably accurate for singly ionised Helium, another one electron system)

### De Broglie's matter waves

Louis de Broglie (later Prince Louis de Broglie!) proposed the existence of matter waves in his doctoral (PhD) thesis in 1924. His hypothesis was one that suggested a deep symmetry in nature - just as light is found to exhibit both wave-like and particle-like behaviour, so too matter is subject to waveparticle duality. Initially the idea was met with skepticism due to the lack of experimental evidence, but Einstein provided support for the idea<sup>8</sup>. We can begin by considering the derivation for the momentum of a photon, which is a massless particle. From special relativity we have the expression for relativistic energy:

$$E^2 = (pc)^2 + (mc^2)^2$$

For particles with zero rest mass, such as the photon, this becomes

$$E = pc$$

Putting this together with the expression for the energy of a photon obtained from quantum theory we have:

$$pc = hf = \frac{hc}{\lambda}$$

so finally

$$\lambda = \frac{h}{p}$$

De Broglie's insight was that this link between the energy and frequency, and between the momentum and wavelength holds for particles with mass as well as for light.



Figure 16: Louis de Broglie. Credit: Wikipedia [public domain].

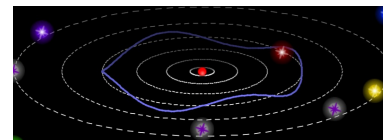


Figure 17: Visualisation of the De Broglie standing wave for  $n = 4$  in Bohr's model of the atom

<sup>8</sup> Eisberg, R. Resnick, R. (1974) Quantum Physics of Atoms, Solids, nuclei and particles. (John Wiley Sons, New York).

**De Broglie's hypothesis:**

Matter has both wave and particle properties.

The wavelength  $\lambda$  associated with a particle with momentum  $p$  is

$$\lambda = \frac{h}{p}$$

In the context of the hydrogen atom, he suggested that if the electron was behaving as a wave as it orbited the nucleus, then it would need to orbit at radii where it constructively interfered with itself. That is, where the circumference of the orbit was an integer number of wavelengths:

$$n\lambda = 2\pi r$$

If we substitute in De Broglie's proposal that the wavelength of the electron is  $\lambda = h/p$  we obtain Bohr's quantisation condition:

$$mvr = h \frac{h}{2\pi}$$

This provides some level of physical explanation for the quantisation of angular momentum that occurs in Bohr's theory.

### *Schrödinger's contribution to the current model of the atom*

De Broglie was responsible for the idea that particles could behave as waves, but did not develop a detailed mathematical theory that could be applied to quantum systems such as the hydrogen atom.

Inspired by De Broglie's work, Erwin Schrödinger developed and published his wave mechanics between 1925-1926.<sup>9</sup>

Schrödinger's theory specifies the laws of wave motion that the particles of any microscopic system obey. It is an *internally consistent* theory, which does not involve the "cobbling together" of classical and quantum ideas that was present in Bohr's model of the atom.

In Schrödinger's theory:

- Particles are described by a "wave function". This wavefunction does not have physical significance in the same sense as the wave equation which describes the amplitude of a water or sound wave in classical physics. Rather, the square of Schrödinger's wavefunction (more precisely, the product of the wavefunction and its complex conjugate) can be understood as the *probability* that a particle is found at a particular position and time (Born's postulate).
- Schrödinger's equation itself is a statement that the total energy of a particle is equal to the sum of its kinetic and potential energies.



Figure 18: Erwin Schrödinger. [Public domain]

<sup>9</sup> References for this section: Gamow, G. (1966). *Thirty years which shook physics: The story of Quantum Theory*. (New York: Dover publications), Kragh, H. (1999). *Quantum generations: A history of physics in the twentieth century*. (Princeton, New Jersey: Princeton University Press). Eisberg, R. Resnick, R. (1974) *Quantum Physics of Atoms, Solids, nuclei and particles*. (John Wiley Sons, New York). Pais, A. (1982). *Subtle is the Lord: The science and the life of Albert Einstein*. (Oxford: Oxford University Press)

- Relationships between the total energy of the particle and the frequency of the wavefunction ( $E = hf$ , Planck's quantisation condition) and between the kinetic energy of the particle ( $KE = \frac{p^2}{2m}$ ) and the wavelength ( $p = \frac{h}{\lambda}$ , De Broglie's postulate) arise naturally, and do not have to be asserted or assumed in an ad-hoc manner.

Schrodinger's theory can be applied to the hydrogen atom by using a potential energy function that is inversely proportional to the distance from the nucleus. The solutions (eigenfunctions) for the wavefunction of bound electrons in the hydrogen atom can be expressed in terms of three *quantum numbers*. The fact that three numbers are required arises directly from the fact that the solutions correspond to three-dimensional "standing waves" for electrons.

These quantum numbers are known as the

- *principal* quantum number, which can take the values  $n = 1, 2, 3, \dots$  and refers to the shell (in the sense of Bohr's model) that the electron occupies
- *orbital* or *azimuthal* quantum number, which can take the values  $l = 0, 1, 2, \dots, n - 1$ , and represents the magnitude of the orbital angular momentum, and refers to the subshell that the electron occupies (e.g. 's', 'p', 'd' or 'f').
- *magnetic* quantum number, which can take the values  $m = -l, \dots, l$ , and represents the z-component (i.e. the projection) of angular momentum, and refers to the orientation of the subshell (i.e. whether a 'p' subshell is orientated along the x-, y-, or z-axis).

See the image on the front cover for illustrations of the probability density functions associated with different combinations of these quantum numbers.

*Extension: Schrödinger's equation (just for fun for anyone who finds it fun - you definitely don't need to know this!)*

Here our aim here is to demonstrate that Schrödinger's equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} + V(x, t) \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

is plausibly an expression for the total energy of a particle, where the first term represents the kinetic energy and the rightmost term represents its total energy, and that the solutions to this equation meet Planck's condition that the total energy of a particle is  $E = hf$  and De Broglie's condition that the momentum of the particle is  $= \frac{h}{\lambda}$ .

The energy of a (non-relativistic) particle is:

$$E = \frac{p^2}{2m} + V$$

If a particle has no net force acting on it then this total energy remains constant over time (and is independent of position). If a particle is to obey Einstein/Planck's condition that the total energy of a particle is  $E = hf$  and De Broglie's criteria that the momentum of the particle is  $p = \frac{h}{\lambda}$ , then the expression for the total energy of a (non-relativistic) particle could also be written as:

$$\frac{h^2}{2m\lambda^2} + V = hf$$

By taking the partial derivatives with respect to position and time, show that the following wave-function is a solution of Schrödinger's equation for  $V(x, t) = V_0$  (i.e. no force acting), and that it satisfies the (non-relativistic) equation for the energy of a particle given above:

$$\Psi(x, t) = \cos\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T}\right) + i \sin\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T}\right)$$