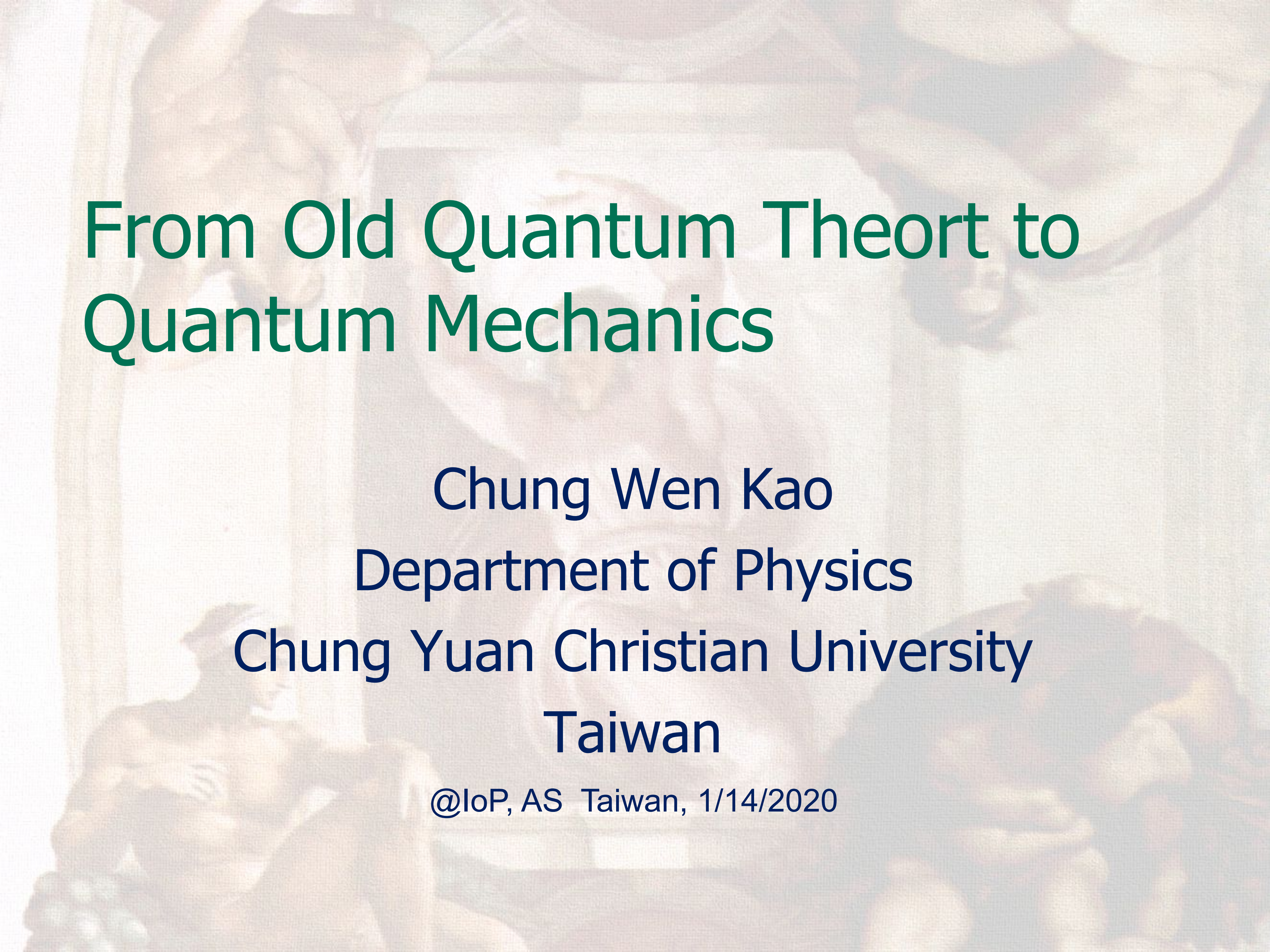

From Old Quantum Theort to Quantum Mechanics

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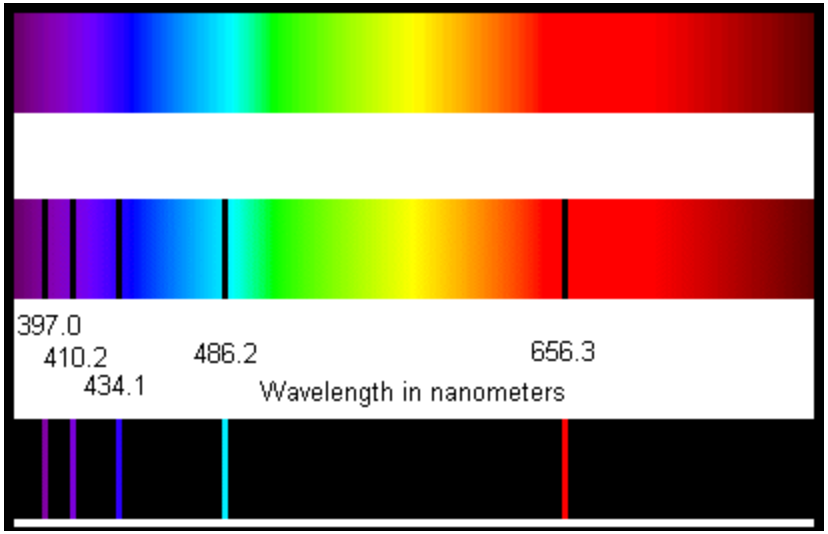
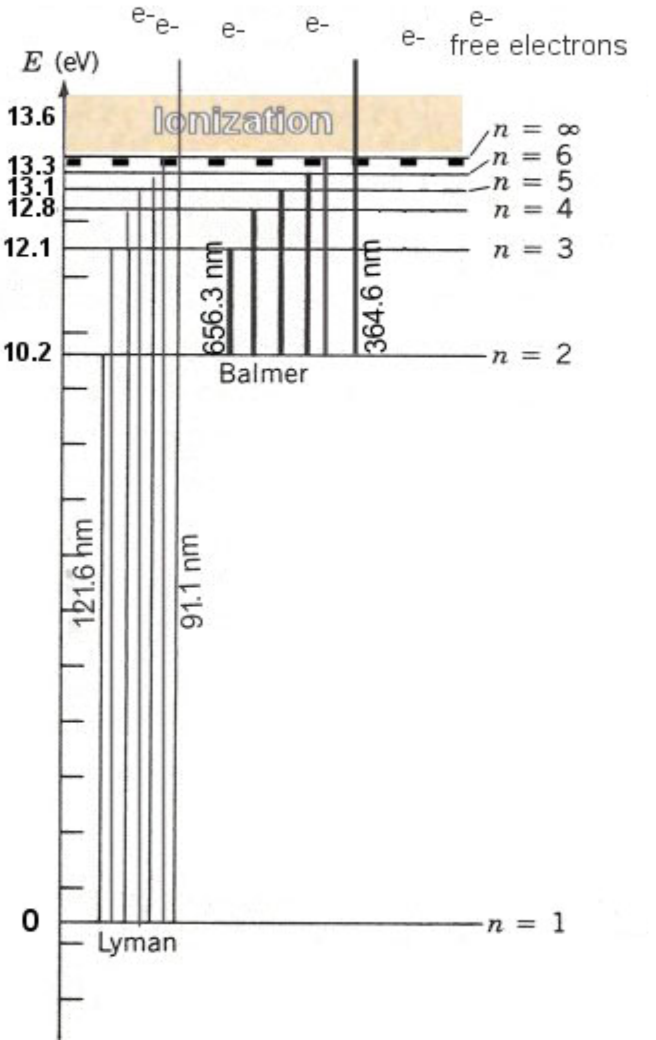
Old Quantum Theory

- The old quantum theory is a collection of results from the years 1900–1925 which predate modern quantum mechanics.
- The theory was never complete or self-consistent, but was rather a set of heuristic corrections to classical mechanics. The theory is now understood as the semi-classical approximation to modern quantum mechanics.
- How scientists created Quantum Mechanics from old qunatum theory is the most exciting story in human history.

Mysterious spectral lines of hydrogen





Transition of *n*	3→2	4→2	5→2	6→2	7→2	8→2	9→2	→2
Name	H-α	H-β	H-γ	H-δ	H-ε	H-ζ	H-η	
Wavelength (nm)	656.3	486.1	434.1	410.2	397.0	388.9	383.5	364.6
Color	Red	Blue-green	Violet	Violet	(Ultraviolet)	(Ultraviolet)	(Ultraviolet)	(Ultraviolet)

Decode the mystery of hydrogen spectrum

Johann Jakob Balmer
(B.1825 – D.1898) was a Swiss mathematical physicist. Johann then spent his entire life in Basel, where he taught at a school for girls. He also lectured at the University of Basel. Using Ångström's measurements of the hydrogen lines, he arrived at a formula for computing the wavelength as follows:

$$\lambda = \frac{hm^2}{m^2 - n^2}$$ (1885)

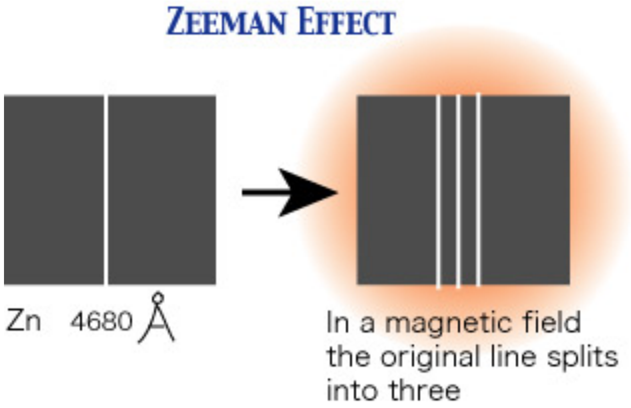
Balmer's formula was later found to be a special case of the Rydberg formula, devised by Johannes Rydberg.

$$\frac{1}{\lambda} = \frac{4}{h}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$ (1888)

$$R_\infty = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} = 1.097\,373\,156\,852\,5\,(73) \times 10^7\ \mathrm{m}^{-1},$$

Johannes Robert Rydberg,
(B1854 –D. 1919) Swiss Physicist

Zeeman effect (1897)



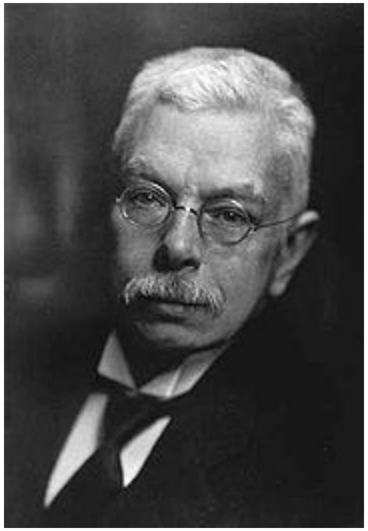
A line in the emission spectrum of an element, splits into three different lines (one on both sides of the original line) if placed in a magnetic field, and the displacement is proportional to the strength of the magnetic field.

Zeeman effect in the classical Picture.

$$\mu = \frac{1}{2m}\oint \boldsymbol{r}\times\boldsymbol{p}\,\mathrm{d}q = \frac{1}{2m}\oint \boldsymbol{L}\,\mathrm{d}q = \frac{1}{2m}\boldsymbol{L}(-e)$$

$$\Delta E = -\vec{\mu}\cdot\vec{B}$$

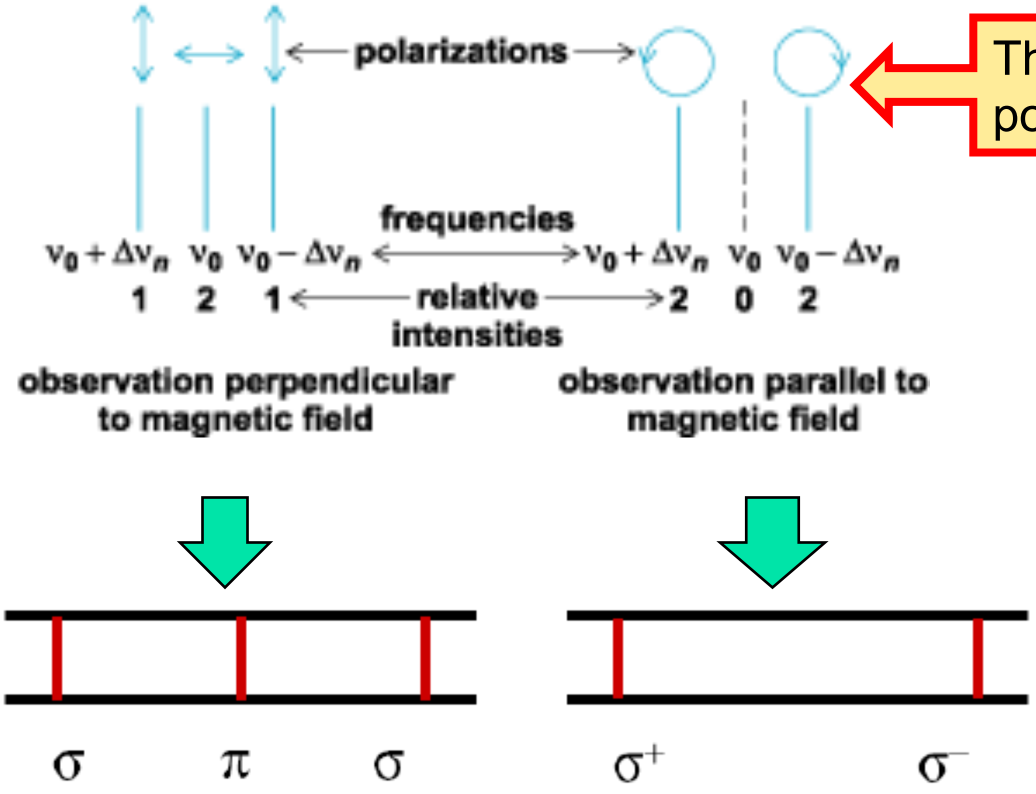
Pietr Zeeman



Pieter Zeeman
(B.1865 – D. 1943)
was a Dutch physicist who shared the 1902 Nobel Prize in Physics with Hendrik Lorentz for his discovery of the Zeeman effect.

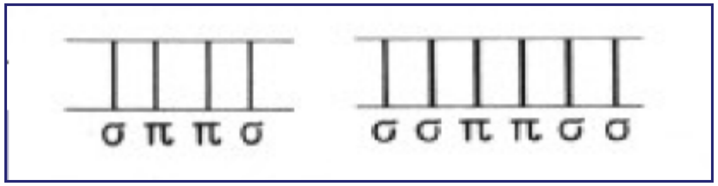
In 1883, the Aurora borealis happened to be visible in the Netherlands. As a student of the high school, he made a drawing and description of the phenomenon and submitted that to Nature, where it was published. The editor praised *"the careful observations of Professor Zeeman from his observatory in Zonnemaire"*, which should have been pleasing to the high school student.

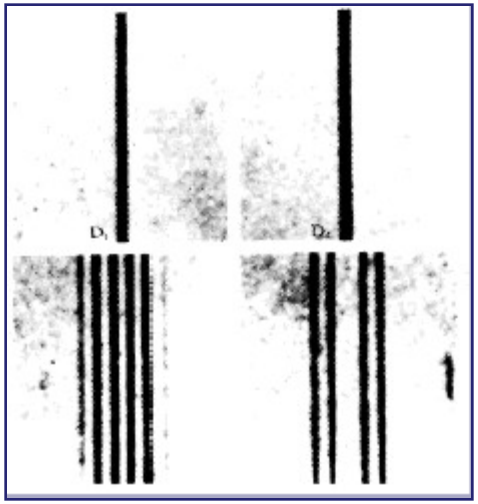
More on Zeeman effect



The splitted spectral lines are polarized.

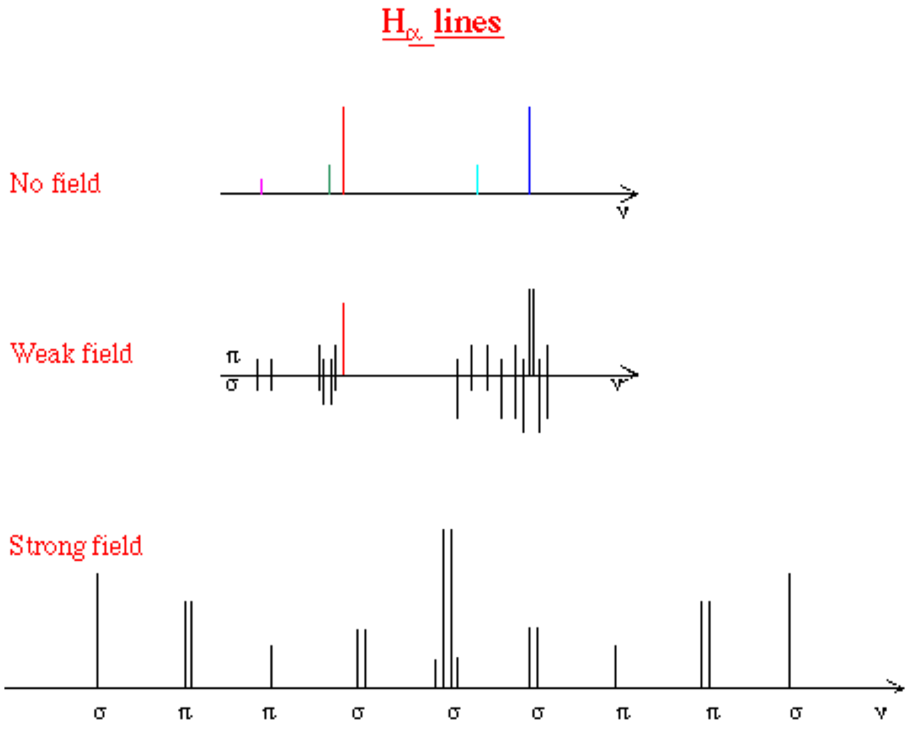
Anomalous Zeeman effect(1897)





However, there is an **anomalous Zeeman effect** which shows up particularly for atoms with odd atomic number (hydrogen, for example). In such cases, it is found that the number of Zeeman sub-levels is actually **even** rather than **odd**. This phenomenon cannot be explained by classical physics. It has remained a puzzle for long time.

Stark effect (1913)



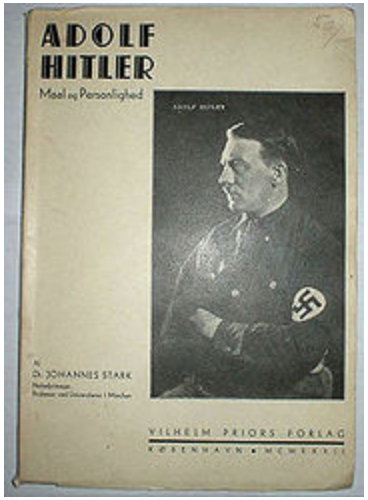
The **Stark effect** is the shifting and splitting of spectral lines of atoms and molecules due to the presence of an external static electric field. The amount of splitting and or shifting is called the Stark splitting or Stark shift. In general one distinguishes first- and second-order Stark effects. The first-order effect is linear in the applied electric field, while the second-order effect is quadratic in the field.

Who is Stark ?

Johannes Stark
(B. 1874 – D.1957)
was a German physicist, and Physics Nobel Prize laureate who was closely involved with the *Deutsche Physik* movement under the Nazi regime. Stark's scientific works cover three large fields: the electric currents in gases, spectroscopic analysis, and chemical valency. His spectroscopic work deals with the connection between the alteration in the structure and in the spectrum of chemical atoms. In 1919 Stark was awarded the Nobel Prize for Physics for his "discovery of the Doppler effect in canal rays and the splitting of spectral lines in electric fields". The prize enabled him to set up his own private laboratory.

During the Nazi regime, Stark attempted to become the Führer of German physics through the *Deutsche Physik.* In 1947, following the defeat of Germany in World War II, Stark was classified as a "Major Offender" and received a sentence of four years imprisonment by a denazification court.

Führer of German physics



The cover of a 1932 Danish translation of Stark's "Adolf Hitler: Aims and Personality

During the Nazi regime, Stark attempted to become the Führer of German physics through the *Deutsche Physik.* movement (along with Philipp Lenard) against the "Jewish physics" of Albert Einstein and Werner Heisenberg (who wasn't Jewish). After Werner Heisenberg defended Albert Einstein's theory of relativity Stark wrote an angry article in the SS newspaper *Das Schwarze Korps*, calling Heisenberg a "White Jew".

On August 21, 1934 Stark wrote to physicist and fellow Nobel laureate Max von Laue to toe the party line or else. The letter was signed off with a "Heil Hitler."

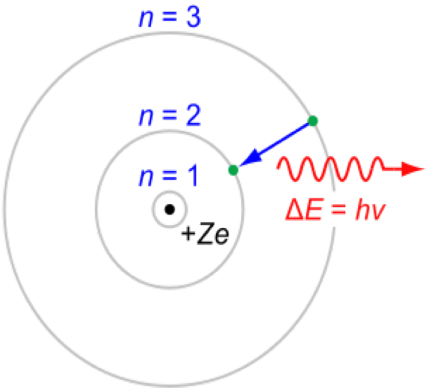
In 1947, following the defeat of Germany in World War II, Stark was classified as a "Major Offender" and received a sentence of four years imprisonment by a denazification court.

Old Quantum Theory

- The spectrum of the elements reveals the inner structure of the atom, but its properties are unable to be explained by electrodynamics and cause confusion.
- With the discovery of the electron and the development of the atom model, the conflict between the spectrum and classical physics becomes more and more obvious.
- Then comes the most strange physics theory...

Bohr Model (1913,Manchester)

$$\frac{m_e v^2}{r} = \frac{k_e e^2}{r^2} \qquad E = \frac{1}{2} m_e v^2 - \frac{k_e e^2}{r} = -\frac{k_e e^2}{2r}$$



Quantization Condition:

$$L = n\frac{h}{2\pi} = n\hbar \quad \Longrightarrow \quad m_e v r = n\hbar \quad \Longrightarrow \quad r_n = \frac{n^2\hbar^2}{k_e e^2 m_e}$$

Quantization of energy

$$E = -\frac{k_e e^2}{2r_n} = -\frac{(k_e e^2)^2 m_e}{2\hbar^2 n^2} = \frac{-13.6\text{eV}}{n^2} \qquad E_n = -\frac{Z^2 R_E}{n^2}$$

Quantum Jump !

$$E = E_i - E_f = R_E\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \qquad E = \frac{hc}{\lambda}, \quad \Longrightarrow \quad \boxed{\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).}$$

Bohr and photon

- Odd enough, Bohr didn't believe the so-called photon advocated by Einstein in 1905.
- Actually by 1913 few people believed in the concept of photon, even Planck didn't believe it.
- Planck and most of scientists believed the quantum condition is the property of the oscillator, not the electromagntic field.
- Bohr believed the electron somwhow behaves as an oscillator satisfying the quantum condition.

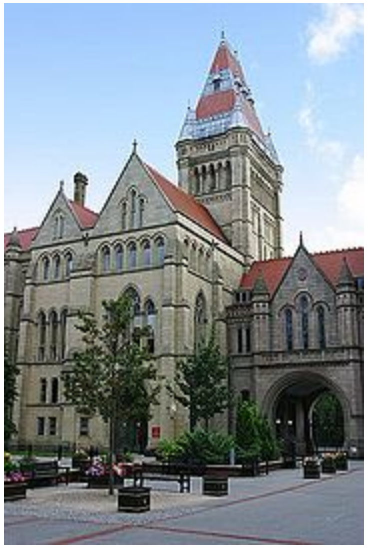
Niels Bohr

Copenhagen
c. 1895

Niels Henrik David Bohr
(B. 1885 – D.1962)
was a Danish physicist who made fundamental contributions to understanding atomic structure and quantum mechanics, for which he received the Nobel Prize in Physics in 1922. Bohr mentored and collaborated with many of the top physicists of the century at his institute in Copenhagen. He was part of a team of physicists working on the Manhattan Project. Bohr married Margrethe Nørlund in 1912, and one of their sons, Aage Niels Bohr, grew up to be an important physicist who in 1975 also received the Nobel prize. Bohr has been described as one of the most influential physicists of the 20th century.

Aage N. Bohr
The Nobel Prize in Physics 1975

Niels Bohr at Manchester



In the spring of 1912 he was at work in Rutherford's laboratory in Manchester, where just in those years such an intensive scientific life and activity prevailed as a consequence of that investigator's fundamental inquiries into the radioactive phenomena. Having there carried out a theoretical piece of work on the absorption of alpha rays which was published in the *Philosophical Magazine*, 1913, he passed on to a study of the structure of atoms on the basis of Rutherford's discovery of the atomic nucleus. By introducing conceptions borrowed from the Quantum Theory as established by Planck, which had gradually come to occupy a prominent position in the science of theoretical physics, he succeeded in working out and presenting a picture of atomic structure.

Niels Bohr Institute

The **Niels Bohr Institute** is a research institute at the University of Copenhagen.
The Institute was founded in 1921 by the Danish theoretical physicist Niels Bohr, who had on the staff of the University of Copenhagen 1914 onwards and who had been lobbying for the creation since he was appointed professor in 1916. Some of its original funding came from the Carlsberg brewery.
During the 1920s, and 1930s, the Institute was the center of the developing disciplines of atomic physics and quantum physics. Physicists from across Europe (and sometimes further abroad) often visited the Institute to confer with Bohr on new theories and discoveries. The Copenhagen interpretation of quantum mechanics is named after work done at the Institute during this time.

Bohr in WWII

Werner Heisenberg with Niels and Margrethe Bohr, and family - 1923

When the Germans occupied Denmark in 1940, life for the Bohrs became difficult. Although Niels was baptized a Christian, his mother was Jewish, marking him in the eyes of the Nazis. Because of this Jewish heritage, and because she did not want her family to appear to be collaborators to the Danes, Margrethe was concerned when Werner Heisenberg came to Copenhagen in 1941 to talk with her husband. In 1943, when the Gestapo rounded up Danish Jews and had orders to arrest Niels, the family divided up and escaped by separate fishing boats to Sweden, where they were reunited. Bohr continued on to England, and then with his son Aage later traveled to America. Margrethe remained in Sweden for the duration of the war with the rest of the family.

Quotations of Bohr

If quantum mechanics hasn't profoundly shocked you, you haven't understood it yet.

Never express yourself more clearly than you are able to think.

No, no, you're not thinking; you're just being logical.

We are all agreed that your theory is crazy. The question which divides us is whether it is crazy enough to have a chance of being correct. My own feeling is that it is not crazy enough.

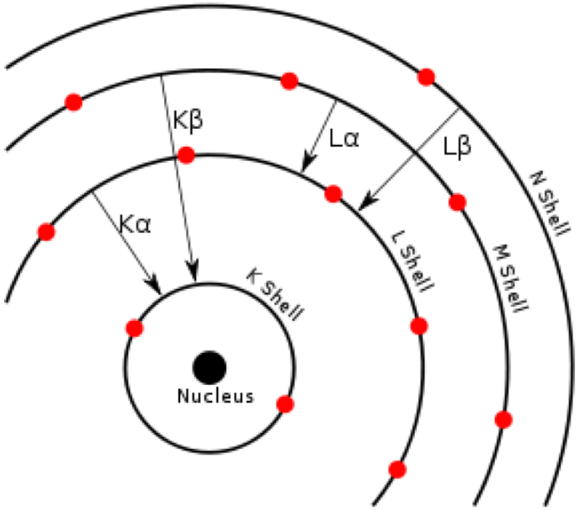
The opposite of a fact is falsehood, but the opposite of one profound truth may very well be another profound truth.

Every sentence I utter must be understood not as an affirmation, but as a question.

How wonderful that we have met with a paradox. Now we have some hope of making progress.

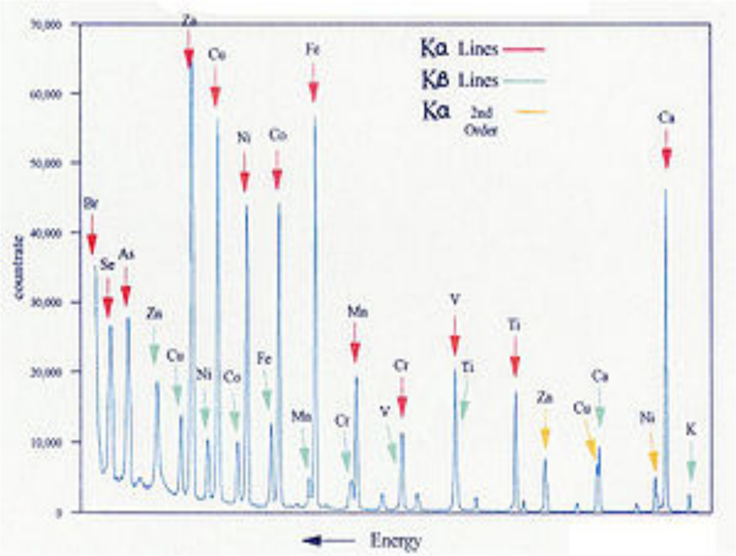
Characteristic radiation

Each element has electronic orbitals of characteristic energy. Following removal of an inner electron by an energetic photon provided by a primary radiation source, an electron from an outer shell drops into its place. There are a limited number of ways in which this can happen, as shown in the figure . The main transitions are given names: an L→K transition is traditionally called Kα, an M→K transition is called Kβ, an M→L transition is called Lα, and so on.



Each of these transitions yields a fluorescent photon with a characteristic energy equal to the difference in energy of the initial and final orbital. The wavelength of this fluorescent radiation can be calculated from Planck's Law: $\lambda = h \cdot c / E$

Moseley’s Law



Using x-ray diffraction techniques in 1913-1914, Moseley found that the most intense short-wavelength line in the x-ray spectrum of a particular element was indeed related to the element's periodic table atomic number, *Z*. This line was known as the K-alpha line. Following Bohr's lead, Moseley found that this relationship could be expressed by a simple formula, later called *Moseley's Law*.

$$f(K_\alpha) = (3.29 \times 10^{15}) \cdot 3/4 \cdot (Z-1)^2$$

$$f(L_\alpha) = (3.29 \times 10^{15}) \cdot 5/36 \cdot (Z-7.4)^2$$

Mosley’s law

In 1914 it was realized that Moseley's formula could be adapted from Bohr's, if two assumptions were made. The first was that the electron responsible for the brightest spectral line (K-alpha) which Moseley was investigating from each element, results from a transition by a single electron between the K and L shells of the atom (i.e., from the nearest to the nucleus and the one next farthest out), with energy quantum numbers corresponding to 1 and 2. Finally, the *Z* in Bohr's formula, though still squared, required diminishment by 1 to calculate K-alpha

$$E = h\nu = E_i - E_f = \frac{m_e q_e^4 (Z-1)^2}{8h^2\epsilon_0^2}\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

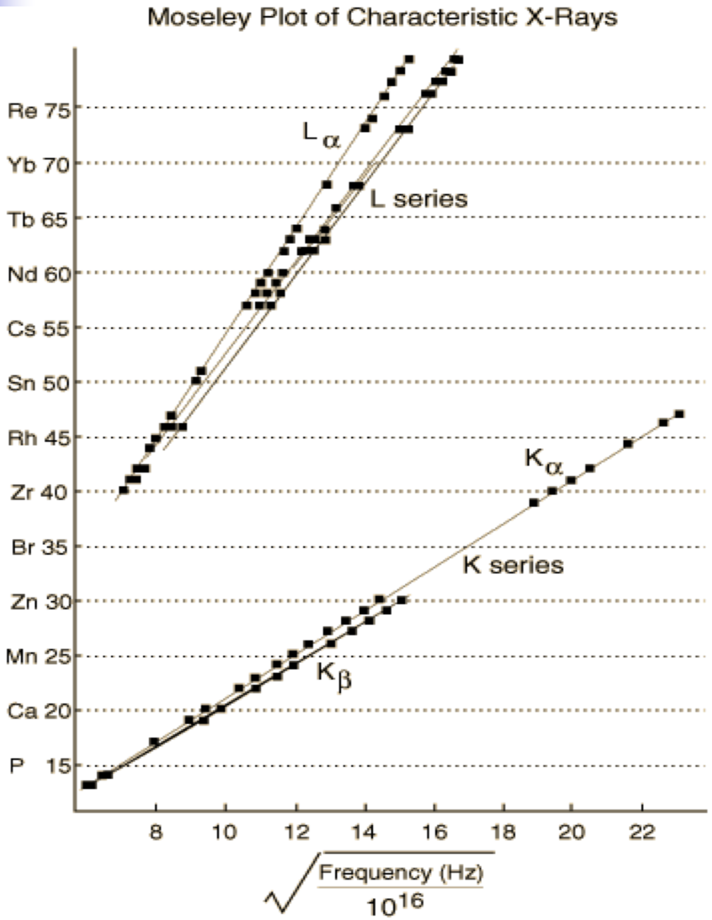
$$f = \nu = \frac{m_e q_e^4}{8h^3\epsilon_0^2}\left(\frac{3}{4}\right)(Z-1)^2 = (2.48 * 10^{15}\ \mathrm{Hz})(Z-1)^2$$

the necessity of reduction of *Z* by a number close to 1 for these K-alpha lines in heavier elements (aluminum and above) was derived completely empirically by Moseley.

1 and 7.4

The parameterization that Moseley discovered, and that he 'incorrectly' interpreted in terms of the Bohr theory of hydrogen, is actually, predominantly a consequence of the difference of the value of the electron-electron repulsion in the initial and final states of the atom that undergoes the x-ray transition.) As regards Moseley's L-alpha transitions, the modern view associates electron shells with principle quantum numbers n, with each shell containing $2n^2$ electrons, giving the $n=1$ "shell" of atoms 2 electrons, and the $n=2$ shell 8 electrons. The empirical value of 7.4 for Moseley's K_2 is thus associated with $n = 2$ to 3, then called L-alpha transitions (not to be confused with Lyman-alpha transitions), and occurring from the "M to L" shells in Bohr's later notation. This value of 7.4 is now known to represent an electron screening effect for a fraction (specifically 0.74) of the total of 10 electrons contained in what we now know to be the $n = 1$ and 2 (or K and L) "shells."

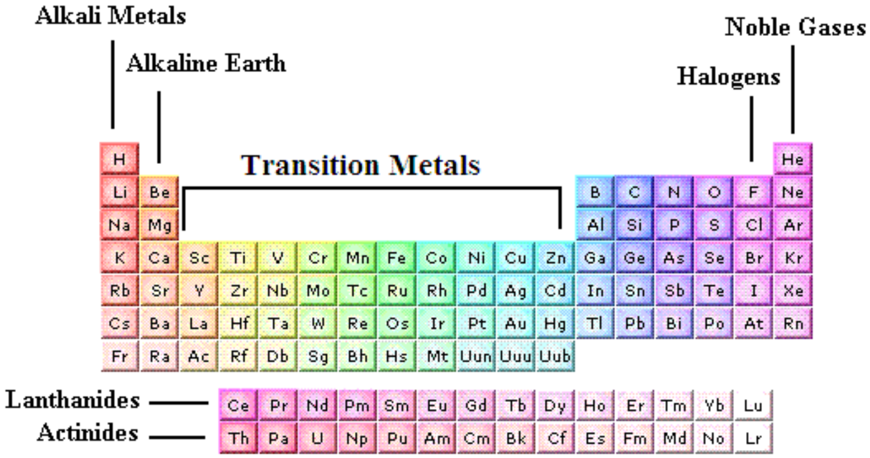
Mosley’s Law (1913)



Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

Moseley measured and plotted the x-ray frequencies for about 40 of the elements of the periodic table. He showed that the K-alpha x-rays followed a straight line when the atomic number Z versus the square root of frequency was plotted.

Z and A



At the time when Mosley was working, most physicists regarded the atomic weight A as the key to ordering the periodic table, rather than the atomic number Z. For example, nickel, with atomic weight 58.7 was placed ahead of cobalt, atomic weight 58.9, in the periodic table.

Moseley's work showed that cobalt had an atomic number of 27 and nickel 28. Potassium ($Z=19$, $A=39.10$) and Argon ($Z=18$, $A=39.95$) were also reversed when listed by atomic weight order. Moseley predicted the existence of an element at $Z=72$ (Hafnium) which was subsequently discovered in Bohr's laboratory in Copenhagen.

Who is Mosley?

Henry Gwyn-Jeffreys Moseley (B.1887 –D.1915) was an English physicist. Moseley's outstanding contribution to the science of physics was the justification from physical laws of the previous empirical and chemical concept of the atomic number. This stemmed from his development of Moseley's law in X-ray spectra. This law justified many concepts in chemistry by sorting the chemical elements of the Periodic Table of the Elements in a quite logical order based on physics.

Gap discovered by Mosley

Moseley showed that there were gaps in the atomic number sequence at numbers 43, 61, 72, and 75. These spaces are now known, respectively, to be the places of the radioactive synthetic elements technetium and promethium, and also the last two quite rare naturally-occurring stable elements hafnium (discovered 1923) and rhenium (discovered 1925). Nothing about these four elements was known of in Moseley's lifetime, not even their very existence. Based on the intuition of a very experienced chemist, Dimitri Mendeleev had predicted the existence of a missing element in the Periodic Table, which was later found to be filled by technetium, and Bohuslav Brauner had predicted the existence of another missing element in this Table, which was later found to be filled by promethium. Henry Moseley's experiments confirmed these predictions, by showing exactly what the missing atomic numbers were, 43 and 61. In addition, Moseley predicted the two more undiscovered elements, those with the atomic numbers 72 and 75, and he gave very strong evidence that there were no other gaps in the Periodic Table between the elements aluminium (atomic number 13) and gold (atomic number 79).

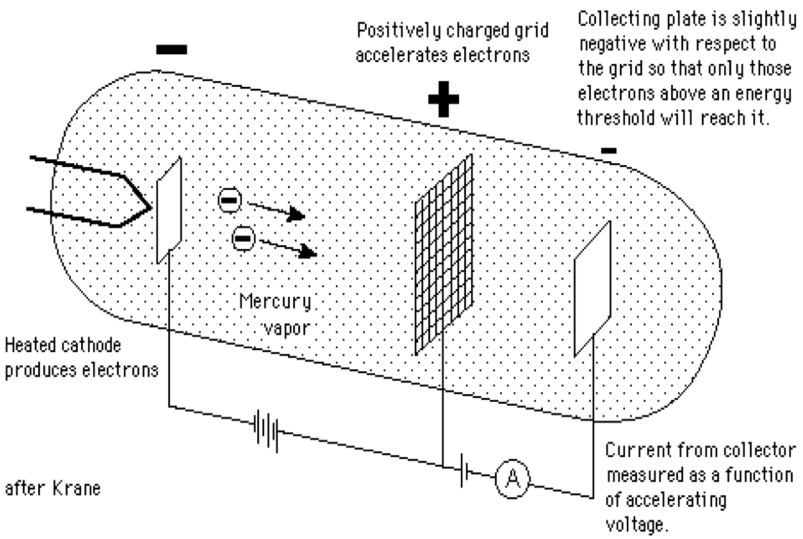
Resolve “missing elements”

This possibility of more undiscovered ("missing") elements had been a standing problem among the chemists of the world, particularly given the existence of the large family of the lanthanide series of rare earth elements. Moseley was able to demonstrate that these lanthanide elements, i.e. lanthanum through lutetium, must have exactly 15 members - no more and no less. The number of elements in the lanthanides had been a question that was very far from being settled by the chemists of the early 20th Century. They could not yet produce pure samples of all the rare-earth elements, even in the form of their salts, and in some cases they were unable to distinguish between mixtures of two very similar (adjacent) rare-earth elements from the nearby pure metals in the Periodic Table. For example, there was a so-called "element" that was even given the chemical name of "didymium". "Didymium" was found some years later to be simply a mixture of two genuine rare-earth elements, and these were given the names neodymium and praseodymium, meaning "new twin" and "green twin". Also, the method of separating the rare-earth elements by the method of ion exchange had not been invented yet in Moseley's time.

Tragic loss in Gallipoli

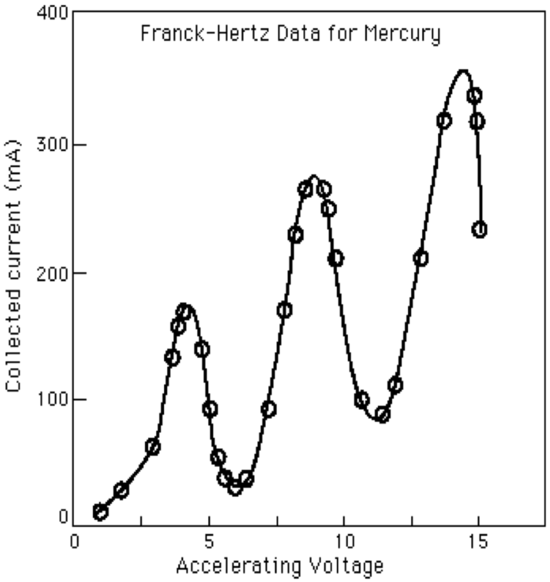
When World War I broke out in Europe, Moseley left behind his research work at the University of Oxford to volunteer for the Royal Engineers of the British Army. Moseley was assigned to the force of British Empire soldiers that invaded Gallipoli, Turkey, in April 1915. In a tragic loss to science, Moseley was shot and killed during the Battle of Gallipoli on August 10, 1915, at the age of just 27. Some prominent authors, such as the chemist Isaac Asimov, have speculated that Moseley would have been deserving of the Nobel Prize in Physics in 1916—a Nobel Prize that in this case was awarded to nobody—if he had not died in the service of the British Army. Because of Moseley's death in World War I, the British government instituted a policy of no longer allowing its prominent and promising scientists to enlist for combat duty in the armed forces of the Crown

Frank-Hertz experiment (1914)



In 1914, James Franck and Gustav Hertz performed an experiment which demonstrated the existence of excited states in mercury atoms, helping to confirm the quantum theory which predicted that electrons occupied only discrete, quantized energy states. Electrons were accelerated by a voltage toward a positively charged grid in a glass envelope filled with mercury vapor. Past the grid was a collection plate held at a small negative voltage with respect to the grid. The values of accelerating voltage where the current dropped gave a measure of the energy necessary to force an electron to an excited state.

Frank-Hartz experiment (1914)



Electrons are accelerated in the Franck-Hertz apparatus and the collected current rises with accelerated voltage. As the Franck-Hertz data shows, when the accelerating voltage reaches 4.9 volts, the current sharply drops, indicating the sharp onset of a new phenomenon which takes enough energy away from the electrons that they cannot reach the collector. This drop is attributed to inelastic collisions between the accelerated electrons and atomic electrons in the mercury atoms. The sudden onset suggests that the mercury electrons cannot accept energy until it reaches the threshold for elevating them to an excited state. This 4.9 volt excited state corresponds to a strong line in the ultraviolet emission spectrum of mercury at 254 nm (a 4.9eV photon). Drops in the collected current occur at multiples of 4.9 volts since an accelerated electron which has 4.9 eV of energy removed in a collision can be re-accelerated to produce other such collisions at multiples of 4.9 volts. This experiment was strong confirmation of the idea of quantized atomic energy levels.

James Franck

James Franck
(B. 1882 – D. 1964) was a German physicist and Nobel laureate . In 1920, Franck became ordinarius professor of experimental physics and Director of the Second Institute for Experimental Physics at the University of Göttingen. While there he worked on quantum physics with Max Born, who was Director of the Institute of Theoretical Physics. In 1925, Franck received the Nobel Prize in Physics, mostly for his work in 1912-1914, which included the Franck-Hertz experiment, an important confirmation of the Bohr model of the atom.

A man of courage

Mention should be made of Professor Franck's courage in following what was morally right. He was one of the first who openly demonstrated against the issue of racial laws in Germany, and he resigned from the University of Göttingen in 1933 as a personal protest against the Nazi regime under Adolf Hitler. Later, in his second homeland, his moral courage was again evident when in 1945 (two months before Hiroshima) he joined with a group of atomic scientists in preparing the so-called "Franck Report" to the War Department, urging an open demonstration of the atomic bomb in some uninhabited locality as an alternative to the military decision to use the weapon without warning in the war against Japan. This report, although failing to attain its main objective, still stands as a monument to the rejection by scientists of the use of science in works of destruction.

Frank’s Medal

George Charles de Hevesy,
(B 1885 – D1966)
was a Hungarian radiochemist and Nobel laureate, recognized in 1943 for his key role in the development of radioactive tracers to study chemical processes such as in the metabolism of animals.

When Nazi Germany invaded Denmark in World War II, the Hungarian chemist George de Hevesy dissolved the gold Nobel Prizes of Max von Laue and James Franck in aqua regia to prevent the Nazis from stealing them. He placed the resulting solution on a shelf in his laboratory at the Niels Bohr Institute. After the war, he returned to find the solution undisturbed and precipitated the gold out of the acid. The Nobel Society then recast the Nobel Prizes using the original gold.

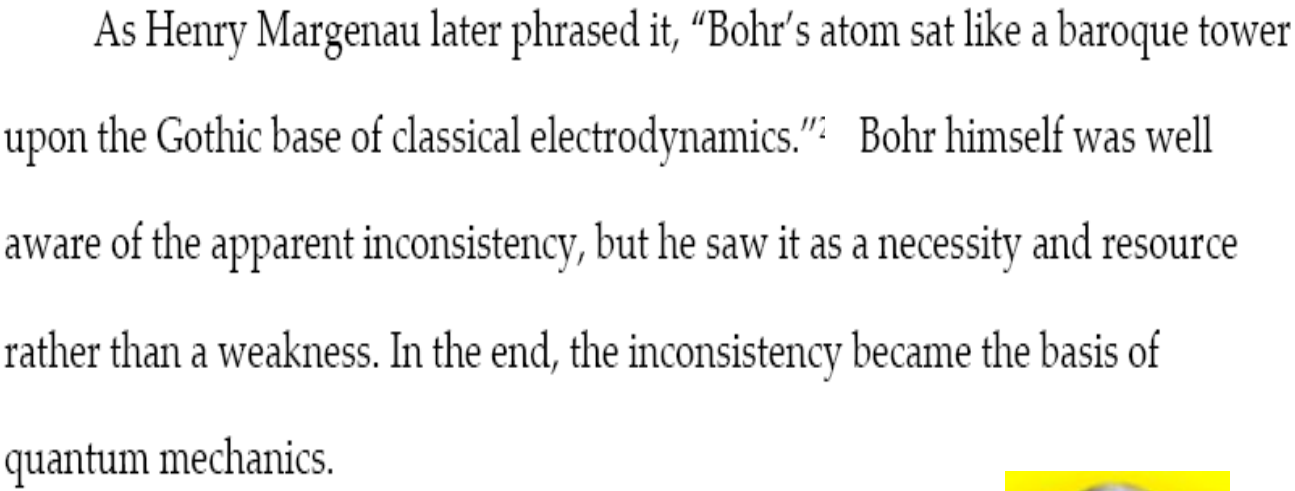
Gustav Ludwig Hertz

Gustav Ludwig Hertz (B. 1887 – D. 1975) was a German experimental physicist and Nobel Prize winner, and a nephew of Heinrich Rudolf Hertz. At the end of 1934, he was forced to resign his position at BTH, as he was classified as a "second degree part-Jew". He then took a position at Siemens, as director of Research Laboratory II. While there, he continued his work on atomic physics, but he eventually discontinued his work on isotope separation. He held this position until he departed for the Soviet Union in 1945. Hertz remained in the Soviet Union until 1955. Upon return from the Soviet Union, Hertz became ordinarius professor at the University of Leipzig. From 1955 to 1967, he was also the chairman of the Physical Society of the Deutsche Demokratische Republik; he was honorary chairman from 1967 to 1975.

Baroque tower upon Gothic base

Baroque Tower

Gothic Base

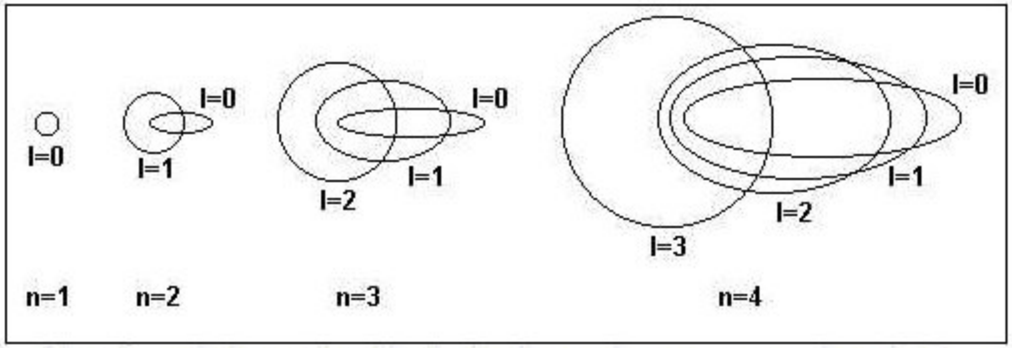


As Henry Margenau later phrased it, "Bohr's atom sat like a baroque tower upon the Gothic base of classical electrodynamics."[2] Bohr himself was well aware of the apparent inconsistency, but he saw it as a necessity and resource rather than a weakness. In the end, the inconsistency became the basis of quantum mechanics.

Henry Margenau (B.1901 – D.1997) was a German-U.S. physicist, and philosopher of science.

Improve Bohr's model

Sommerfeld investigated the Bohr model of the atom but considered the possibility of new energy levels arising from the existence of elliptical orbits in addition to the circular orbits. This necessitated two quantum conditions, one specifying the radial component of the angular momentum of the electron about the nucleus; and the other the azimuthal component. When non-relativistic mechanics are used, the theory shows no new energy levels for the hydrogen atom; but introduces the concept of degeneracy: orbits of differing eccentricity in which the electron has the same energy. This gives the possibility of splitting the energy levels in a magnetic field



The allowed electronic orbits for the four main quantum numbers by the Bohr-Sommerfeld model.

Sommerfeld quantization condition

Sommerfeld generalized the quantization conditions: $J_k \equiv \oint p_k dq_k = n_k h$

In the Kepler problem one has three quantum numbers: ***n, l, m*.**

$n = n_r + n_\theta + n_\varphi$, $l = n_\theta + n_\varphi$, $m = n_\varphi$

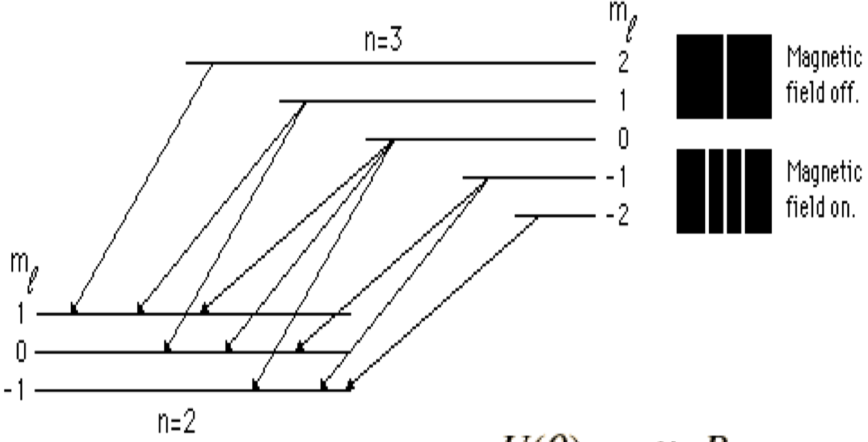
$n = 1, 2, \ldots l = 0, 1, 2 \ldots n-1,\ m = -l, -(l-1), \ldots (l-1),\ l$

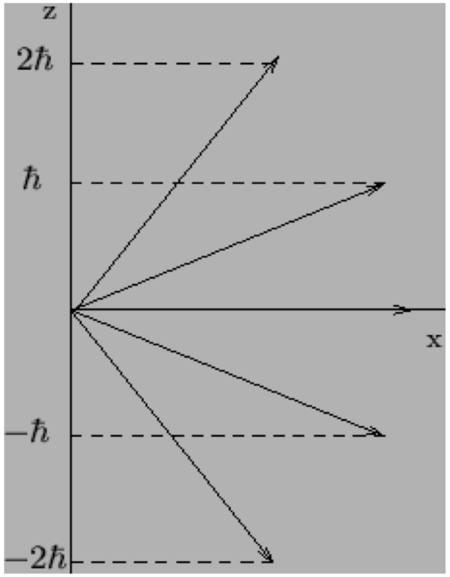
n: Principle Quantum Number
l:Azimathual Quantum Number
m:Magnetic Quantum Number

→

n: Energy of the orbit
l: Angular momentum of the orbit
m: Orient direction of the orbit

Normal Zeeman effect





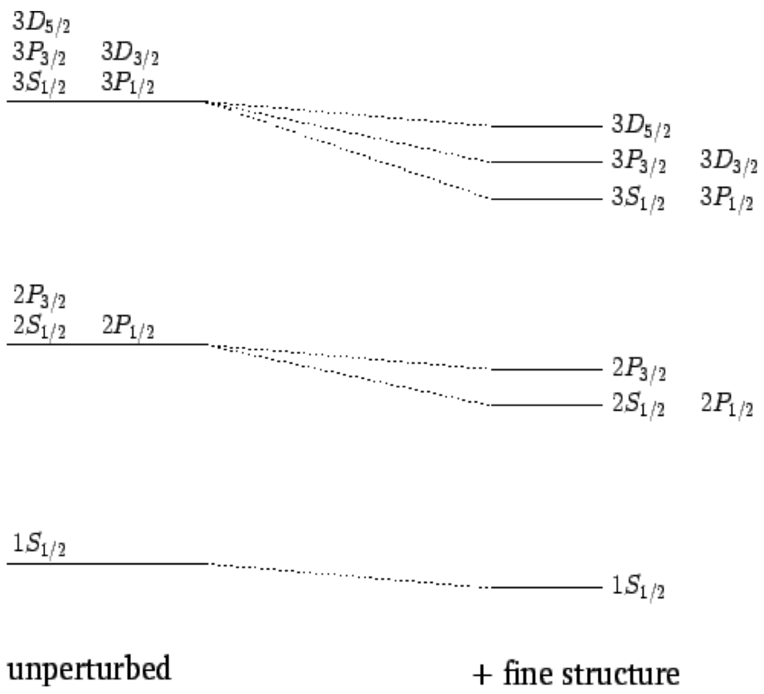
$$U(\theta) = -\mu \cdot B \qquad \mu_{orbital} = \frac{-e}{2m_e} L$$

$$U = \frac{e}{2m} L_z B = m_\ell \frac{e\hbar}{2m} B$$

It explains the Zeeman effect

$$\Delta E = m_\ell \frac{e\hbar}{2m} B = m_\ell \mu_B B \qquad \mu_B = \ Bohr \ \ magneton$$

Fine structure of Hydrogen



$$\Delta E_{nlm} = E_n \frac{\alpha^2}{n^2}\left(\frac{n}{l+1/2} - \frac{3}{4}\right),$$

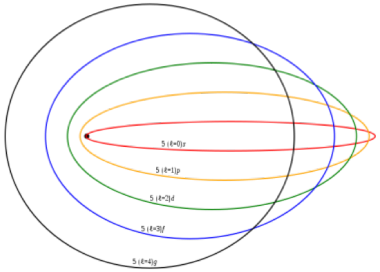
$$\alpha = \frac{e^2}{4\pi\,\epsilon_0\,\hbar\,c} \simeq \frac{1}{137}$$

In 1887, Michelson and Morley discovered a fine structure of some of these lines. Sommerfeld showed in 1916 that the fine structure of Bohr's energy levels was caused by relativistic corrections.

Bohr-Sommerfeld Theory

Arnold Johannes Wilhelm Sommerfeld (1868 – 1951)

Sommerfeld was nominated for the Nobel Prize 81 times, more than any other physicist, he never received the award.



Considering the ellipse orbit
and including the relativistic effectit

$$u = \frac{1}{r}$$

$$W = m_0c^2\left(\frac{1}{\sqrt{1-\frac{v^2}{c^2}}} - 1\right) - k\frac{Ze^2}{r} \Longrightarrow \frac{1}{\sqrt{1-\frac{v^2}{c^2}}} = 1 + \frac{W}{m_0c^2} + k\frac{Ze^2}{m_0c^2}u$$

Quantization Condition:

$$\oint p_\varphi d\varphi = 2\pi p_\varphi = n_\varphi h \qquad \oint p_r dr = p_\varphi \oint \left(\frac{1}{r}\frac{dr}{d\varphi}\right)^2 d\varphi = n_r h$$

$$\Longrightarrow \boxed{\frac{W}{m_0c^2} = \left(1 + \frac{\alpha^2 Z^2}{(n_r + \sqrt{n_\varphi^2 - \alpha^2 Z^2})^2}\right)^{-1/2} - 1}$$

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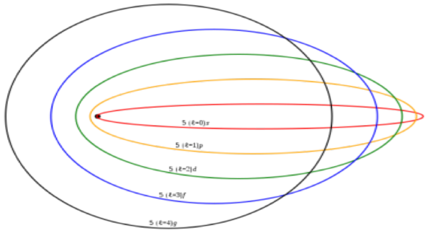

$$p_r = m\dot{r} \qquad p_\varphi = mr^2\dot{\varphi}$$

$$\frac{p_r}{p_\varphi} = -\frac{du}{d\varphi}$$

$$\frac{du}{d\varphi} = \frac{du}{dt}\frac{dt}{d\varphi}$$

$$= \frac{du}{dt}\left(\frac{d\varphi}{dt}\right)^{-1} = \frac{1}{\dot{\varphi}}\frac{du}{dt} = \frac{1}{\dot{\varphi}}\left(-\frac{\dot{r}}{r^2}\right) = \frac{mr^2}{p_\varphi}\left(-\frac{p_r}{mr^2}\right)$$

$$\frac{d^2u}{d\varphi^2} = \frac{d}{dt}\left(\frac{du}{d\varphi}\right)\frac{dt}{d\varphi} = \frac{d}{dt}\left(\frac{du}{d\varphi}\right)\left(\frac{d\varphi}{dt}\right)^{-1} = \frac{1}{\dot{\varphi}}\frac{d}{dt}\left(\frac{du}{d\varphi}\right) = \frac{1}{\dot{\varphi}}\frac{d}{dt}\left(-\frac{p_r}{p_\varphi}\right) = \frac{1}{\dot{\varphi}}\left(-\frac{\dot{p_r}}{p_\varphi} + \frac{p_r}{p_\varphi^2}\dot{p_\varphi}\right)$$

$$\dot{p_\varphi} = -\frac{\partial H}{\partial \varphi} = 0$$

$$\dot{p_r} = -\frac{\partial H}{\partial r} = \frac{p_\varphi^2}{mr^3} - \frac{kZe^2}{r^2}$$

$$\frac{d^2u}{d\varphi^2} = \frac{mr^2}{p_\varphi}\left(-\frac{1}{p_\varphi}\right)\left[\frac{p_\varphi^2}{m}u^3 - kZe^2u^2\right]$$

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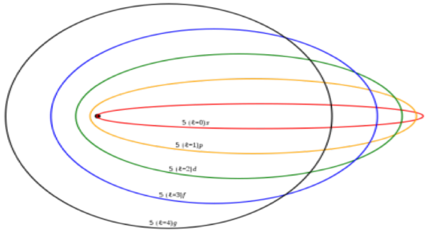

$$\frac{d^2u}{d\varphi^2} = \frac{mr^2}{p_\varphi}\left(-\frac{1}{p_\varphi}\right)\left[\frac{p_\varphi^2}{m}u^3 - kZe^2u^2\right] = -\frac{mr^2}{p_\varphi^2}\frac{p_\varphi^2}{mr^3} + \frac{mr^2}{p_\varphi^2}kZe^2u^2$$

$$= -u + \frac{mkZe^2}{p_\varphi^2}$$

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}}$$

$$\frac{d^2u}{d\varphi^2} = -u + \frac{m_0kZe^2}{p_\varphi^2}\frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$$

$$= -u + \frac{m_0kZe^2}{p_\varphi^2}\left(1 + \frac{W}{m_0c^2} + \frac{kZe^2}{m_0c^2}u\right)$$

$$\frac{1}{\sqrt{1-\frac{v^2}{c^2}}} = 1 + \frac{W}{m_0c^2} + k\frac{Ze^2}{m_0c^2}u$$

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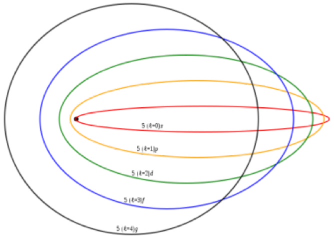


$$\frac{d^2u}{d\varphi^2} = -u + \frac{m_0 kZe^2}{p_\varphi^2}\left(1+\frac{W}{m_0c^2}+\frac{kZe^2}{m_0c^2}u\right)$$

$$\frac{d^2u}{d\varphi^2} = -\left(1-k^2\frac{Z^2e^4}{c^2p_\varphi^2}\right)u + \frac{m_0kZe^2}{p_\varphi^2}\left(1+\frac{W}{m_0c^2}\right) = -\omega_0^2u + K$$

➡

$$u = \frac{1}{r} = \frac{K}{\omega_0^2} + A\cos\omega_0\varphi$$

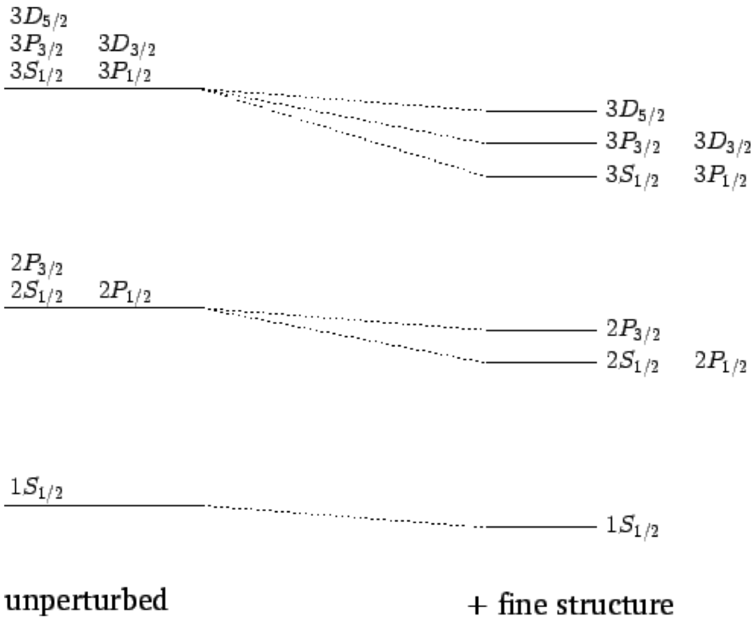
$$\boxed{\int_0^{2\pi}\frac{\sin^2(x)}{a+b\cos(x)}\,dx = \frac{2\pi}{b^2}\left(a-\sqrt{a^2-b^2}\right)}$$

Quantization Condition: $\oint p_\varphi d\varphi = 2\pi p_\varphi = n_\varphi h$ $\qquad \oint p_r dr = p_\varphi \oint \left(\frac{1}{r}\frac{dr}{d\varphi}\right)^2 d\varphi = n_r h$

➡

$$\boxed{\frac{W}{m_0c^2} = \left(1+\frac{\alpha^2Z^2}{(n_r+\sqrt{n_\varphi^2-\alpha^2Z^2})^2}\right)^{-1/2} - 1}$$

Fine structure of Hydrogen



$$E_{jn} = -m_e c^2 \left[1 - \left(1 + \left[\frac{\alpha}{n - j - \frac{1}{2} + \sqrt{\left(j + \frac{1}{2}\right)^2 - \alpha^2}} \right]^2 \right)^{-1/2} \right]$$

$$\approx -\frac{m_e c^2 \alpha^2}{2n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right],$$

$$\Delta E_{nlm} = E_n \frac{\alpha^2}{n^2} \left(\frac{n}{l + 1/2} - \frac{3}{4} \right), \qquad \alpha = \frac{e^2}{4\pi \, \epsilon_0 \, \hbar \, c} \simeq \frac{1}{137}$$

Arnold Sommerfeld

Arnold Johannes Wilhelm Sommerfeld
(B.1868 – D.1951)

was a German theoretical physicist who pioneered developments in atomic and quantum physics, and also educated and groomed a large number of students for the new era of theoretical physics.

Sommerfeld was a great theoretician, and besides his invaluable contributions to the quantum theory, he worked in other fields of physics. Also, as a mark of the prowess of Sommerfeld's school of theoretical physics and the rise of theoretical physics in the early 1900s, as of 1928, nearly one-third of the ordinarius professors of theoretical physics in the German-speaking world were students of Sommerfeld.

Sommerfeld at Munich

Over his 32 years of teaching at Munich, Sommerfeld taught general and specialized courses, as well as holding seminars and colloquia. The general courses were on mechanics, mechanics of deformable bodies, electrodynamics, optics, thermodynamics and statistical mechanics, and partial differential equations in physics. They were held four hours per week, 13 weeks in the winter and 11 weeks in the summer, and were for students who had taken experimental physics courses from Röntgen and later by Wilhelm Wien. There was also a two-hour weekly presentation for the discussion of problems. From 1942 to 1951, Sommerfeld worked on putting his lecture notes in order for publication. They were published as the six-volume *Lectures on Theoretical Physics*.

Lecture of Theoretical Physics

During his emeritus period Arnold Sommerfeld compiled his «Lectures in theoretical physics» which were published in six volumes between 1943 and 1953.

Vol 1. Mechanics
Vol 2. Mechanics of Deformable Bodies
Vol 3. Electrodynamics
Vol 4. Optics
Vol 5. Thermodynamics and Statistical Mechanics
Vol 6. Partial Differential Equations in Physics

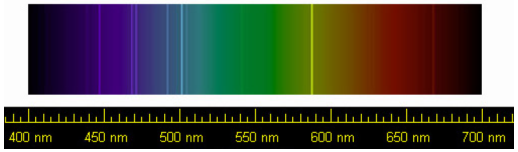
Seminar of Sommerfeld

Wolfgang Pauli with his teacher and mentor Arnold Sommerfeld at the "Metallkongress" (conference on physics of metals) in Geneva, October 1934.

The specialized courses were of topical interest and based on Sommerfeld's research interests; material from these courses appeared later in the scientific literature publications of Sommerfeld. The objective of these special lectures was to grapple with current issues in theoretical physics and for Sommerfeld and the students to garner a systematic comprehension of the issue, independent of whether or not they were successful in solving the problem posed by the current issue or not. For the seminar and colloquium periods, students were assigned papers from the current literature and they then prepared an oral presentation.

What Bohr-Sommerfeld Theory cannot tell you…

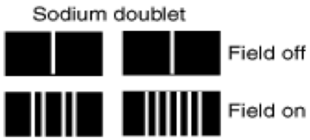
- Bohr-Sommerfeld theory fails to explain Helium spectrum.
- Bohr-Sommerfeld theory also fails to explain Anomalous Zeeman effect
- But the most serious shortcoming is Bohr-Sommerfeld theory cannot tell anything about the intensity of the spectral lines even for hydrogen.

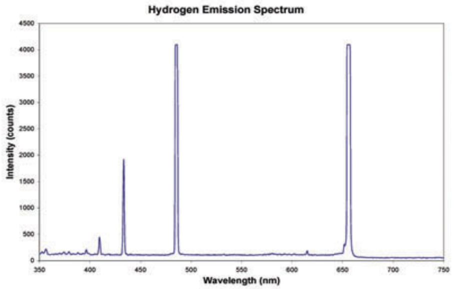


Helium Spectrum

Normal Zeeman Effect

Anomalous Zeeman Effect

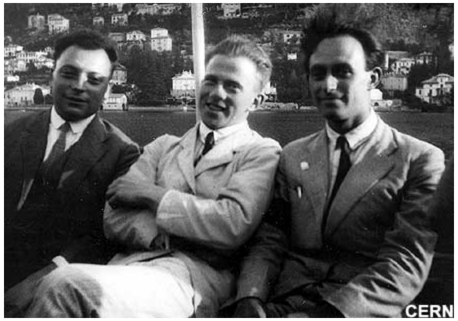




Intensity of Hydrogen spectral lines

Pauli and Heisenberg

- The difficulty of Anomalous Zeeman effect is solved by Wolfgang Pauli, one of Sommerfeld's student.
- The difficulty of intensity of spectral line is solved by Werner Heisenberg, another student of Sommerfeld. Later he also solved the Helieum problem.
- Both of them were Ph. D students of Sommerfeld and went to Gottingen to be assistants of Born and Copenhagen as assistants of Bohr.



CERN

Scanned at the American Institute of Physics

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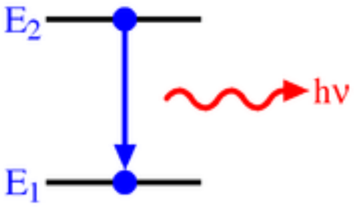
The crucial questions

- Pauli solve the anomalous Zeeman effect problem by introduing the non-classical degree of freedom, spin.
- Heisenberg solve the mystery of intensity by creating Matrix Mechanics!
- The spectrum of Helium was understood by combining the spin and matrix mechanics.

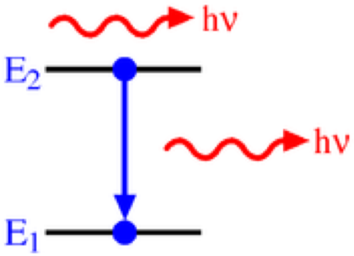
Einstein’s A and B coefficients

Spontaneous emission



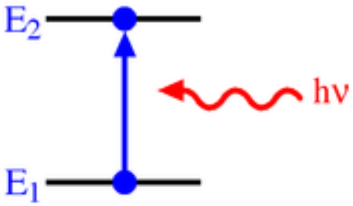
$$\left(\frac{dn_1}{dt}\right)_{A_{21}} = A_{21} n_2$$

Stimulated emission



$$\left(\frac{dn_1}{dt}\right)_{B_{21}} = B_{21} n_2 \rho(\nu); \qquad \rho(\nu) = \frac{2h\nu^3}{c^2(e^{h\nu/kT}-1)}$$

Photo absorption



$$\left(\frac{dn_1}{dt}\right)_{B_{12}} = -B_{12} n_1 \rho(\nu)$$

Thermal equilibrium between emission and absorption

Detailed balance: $0 = A_{21}n_2 + B_{21}n_2 I(\nu) - B_{12}n_1 I(\nu)$

$$\frac{n_i}{n} = \frac{g_i e^{-E_i/kT}}{Z}$$

g_i: degeneration factor

$$I(\nu) = \frac{F(\nu)}{e^{h\nu/kT} - 1} \qquad F(\nu) = \frac{8\pi h\nu^3}{c^3}$$

Plank's Law of Black body radiation

$$A_{21}g_2e^{-h\nu/kT} + B_{21}g_2e^{-h\nu/kT}\frac{F(\nu)}{e^{h\nu/kT} - 1} = B_{12}g_1\frac{F(\nu)}{e^{h\nu/kT} - 1}$$

$$\boxed{\frac{B_{21}}{B_{12}} = \frac{g_1}{g_2} \qquad \frac{A_{21}}{B_{21}} = F(\nu)}$$

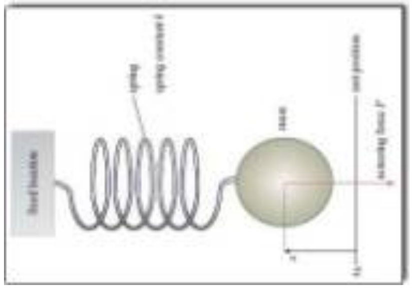
But how to calculate the A and B coefficients ?

Why Bohr-Somerfeld theory cannot explain the intensity of the spctrum line?

- It fails to explain why classical electrodynamics becomes invalid at the special orbits.
- Hence it provide no mechanism of emitting and absorbing the light of the electron, so it cannot provide any mean to calculate its strength.
- The frequency of light emitted is determined by the initial and final orbits, this is an extremely non-classical behaviour.
- The success of classical theory of dispersion causes the anxiety of the inconsistency .

Dispersion theory of Lorentz

$E=E_0 \cos \omega t$



$$m\ddot{x} = -m\omega_0^2 x - eE\cos\omega t,$$

$$\Delta x_{\mathrm{coh}}(t) = A\cos\omega t, \qquad A = \frac{eE}{m(\omega^2-\omega_0^2)}.$$

$$p(t) = -e\Delta x_{\mathrm{coh}}(t) = \frac{e^2E}{4\pi^2 m(\nu_0^2-\nu^2)}\cos 2\pi\nu t.$$

$$p(t) \equiv -e\Delta x_{\mathrm{coh}}(t)$$

Assume the system containing n_i dispersion electrons of the kind i

$$\boxed{P(t) = \frac{e^2E}{4\pi^2 m}\sum_i \frac{n_i}{\nu_i^2-\nu^2}\cos 2\pi\nu t.}$$

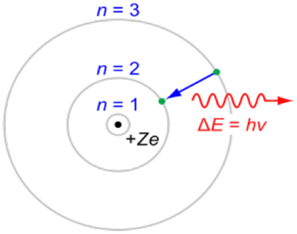
$$\vec{\mathrm{P}} = \alpha\vec{\mathrm{E}}$$

$$\boxed{\alpha = \frac{e^2}{4\pi^2 m}\sum_i \frac{n_i}{\nu_i^2-\nu^2}}$$

Correspondence principle

Quantization Condition:
$$\frac{m_e v^2}{r} = \frac{k_e e^2}{r^2}$$

$$L = n\frac{h}{2\pi} = n\hbar \Rightarrow m_e v r = n\hbar \Rightarrow r_n = \frac{n^2\hbar^2}{k_e e^2 m_e}$$



Angular velocity at the nth orbit:
$$\omega_n^c = 2\pi f_n^c = \frac{nh}{2\pi m_e r_n^2} = \frac{8\pi^3 m_e e^4 k_e^2}{n^3 h^3}$$

Quantization of energy:
$$E = -\frac{k_e e^2}{2r_n} = -\frac{(k_e e^2)^2 m_e}{2\hbar^2 n^2} = \frac{-13.6\text{eV}}{n^2}$$

Transition frequency:
$$\nu_{m,n} = \frac{-2\pi^2 k_e^2 e^4 m_e}{h^3}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

$$\nu_{n+1,n} = \frac{-2\pi^2 k_e^2 e^4 m_e}{h^2}\frac{1}{n^2}\left((1+\frac{1}{n})^{-2} - 1\right) \Longrightarrow \frac{4\pi^2 k_e^2 e^4 n}{n^3 h^3} \quad f_n^c = \lim_{n\to\infty} \nu_{n+1,n} = \frac{4\pi^2 k_e^2 e^4 m_e}{n^3 h^3}$$

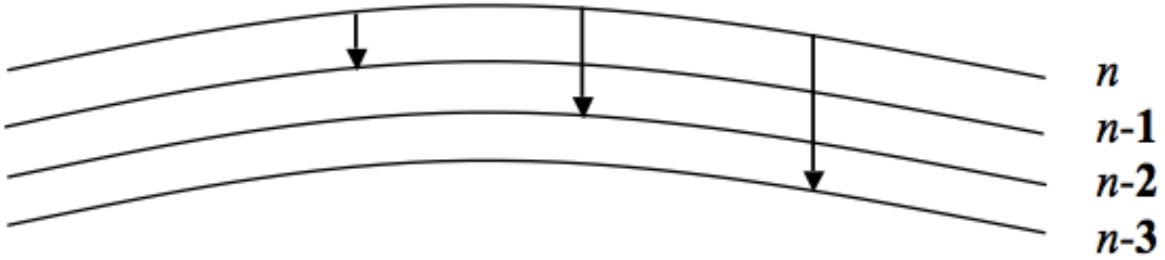
Classical theory = Quantum theory at large quantum number limit

Another interpretations

There is the *intensity interpretation* of correspondence principle. It is a statistical agreement in the limit of large quantum numbers between the quantum intensity, understood in terms of the probability of a quantum transition, and the classical intensity, understood as the square of the amplitude of one component of the classical motion.

There is the *selection rule interpretation*, it is the statement that each allowed quantum transition between stationary states corresponds to one harmonic component of the classical motion.

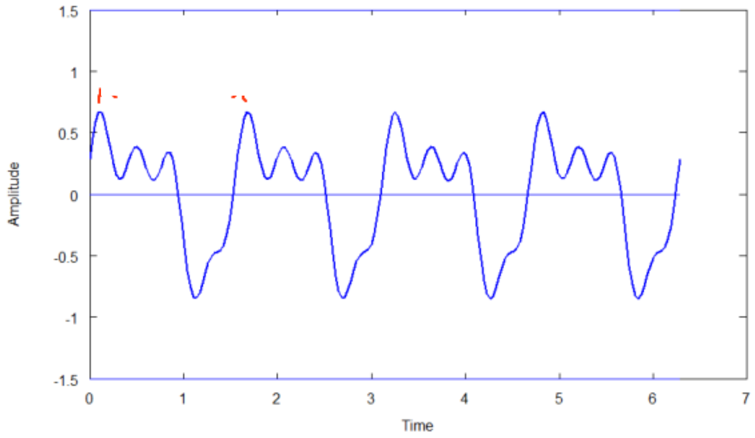
$$x(t) = a_1 \cos \mathbf{1}\omega t + a_2 \cos \mathbf{2}\omega t + a_3 \cos \mathbf{3}\omega t$$



An example: 1-D periodic motion

Consider a simplified model of the atom as a one-dimensional system, where the electron is undergoing simply periodic motion. Classically the trajectory of the electron is given by **$x(t)$**, which is the solution to Newton's equation of motion, and is periodic, which means it simply retraces its steps over and over again with a frequency, ω, known as the fundamental frequency. Because the motion is periodic, the position of the electron can be represented by a Fourier series as follows:

$$x(t) = C_1\cos(\omega t) + C_2\cos(2\omega t) + C_3\cos(3\omega t) + \ldots$$



An example: 1-D system

According to the *intensity interpretation*, the correspondence principle is defined as the agreement, in the limit of large quantum numbers, between the probability, $P_{n' \rightarrow n''}$, of a transition between two stationary states separated by **τ** and the square of the amplitude, C_τ, of the τ^{th} harmonic component of the classical motion:

$$P_{n' \rightarrow n''} \propto |C_\tau(n)|^2 \text{ for large } n$$

According to the *selection rule interpretation*, correspondence principle is best understood as the statement that *each allowed quantum transition between stationary states corresponds to one harmonic component of the classical motion*. In other words, the transition from a stationary state n' to another stationary state n'' is allowed *if and only if* there exists a τ^{th} harmonic in the classical motion of the electron in the initial stationary state; if there is no τ^{th} harmonic in the classical motion, then transitions between stationary states whose separation is τ are not allowed quantum mechanically.

Challenges for physicists

- What is the relation between the characteristic frequencies in dispersion and the transition frequencies in Bohr model?
- How to calculate Einstein's A and B coefficients by using corresponding principle?
- How to apply the quantization condition into dispersion? In other word, how to derive the formula of dispersion which is consistent with the "new" quantum theory?

Ladenburg's formula (1921)

Rudolf W.Ladenburg
(1882 – 1952)

When the wave of German emigration began in 1933, he was the principal coordinator for job placement of exiled physicist in the United States.

J_{CL}: Energy radiated per second according to classical electrodynamics

N: oscillatory electrons per unit volume

U: mean energy per unit volume

τ: decay time of oscillator

$$J^x_{CL} = J^y_{CL} = J^z_{CL} = \frac{\pi e^2}{3m} N u_{\nu 0}$$

$$\boxed{J_{CL} = \frac{UN}{\tau} \qquad \tau = \frac{3mc^3}{8\pi^2 e^2 \nu_0^2} \qquad U = \frac{3c^3 u_{\nu_0}}{8\pi^2 \nu_0^2}} \Longrightarrow \boxed{J_{CL} = \frac{\pi e^2}{m} N u_{\nu_0}}$$

$$\boxed{J_{QU} = \sum_{E_k > E_i} h\nu_{ik} N_k (B_{k\to i} + A_{k\to i}) u_{ik} = \sum_{E_k > E_i} h\nu_{ik} N_i B_{i\to k} u_{ik}}$$

$$h\nu_{ik} = E_k - E_i$$

$$A_{k\to i} = \frac{8\pi h \nu_{ik}^3}{c^3} B_{i\to k}$$

Ladenburg’s formula (1921)

$$J_{QU} = J_{CL}$$

➡

$$N = N_i \frac{mc^3}{8\pi^2 e^2 \nu_{ik}^2} A_{k\to i}$$

➡

$$N/N_i = n_i = \frac{mc^3}{8\pi^2 e^2 \nu_{ik}^2} A_{k\to i}$$

n_i: extracted from dispersion data; $A_{k\to i}$ absorption data

What Ladenburg didn’t do is to replace n_i by A in the dispersion formula:

$$\alpha = \frac{e^2 c^3}{32\pi^4} \sum_i \sum_{E_k > E_i} \frac{A_{k\to i}}{\nu_{ik}^2 (\nu_{ik}^2 - \nu^2)}$$

or

$$\alpha = \sum_{E_k > E_i} A_{k\to i} \tau_{ik} \frac{e^2}{4\pi^2 m} \frac{1}{\nu_{ik}^2 - \nu^2}$$

$$\tau_{ik} = \frac{3mc^3}{8\pi^2 e^2 \nu_{ik}^2}$$

Who is Ladenburg?

Rudolf Walter.Ladenburg
(B. 1882 – D. 1952)
was a German atomic physicist. Ladenburg earned his doctorate in 1906 at Heidelberg under the direction of Wilhelm Röntgen. After working at the physics institute at the University of Breslau, Ladenburg became the chief of the physics division at the Kaiser Wilhelm Institute. His research explored dispersion lines in atomic spectra. He emigrated from Germany as early as 1932 and became a Brackett Research Professor at Princeton University When the wave of German emigration began in 1933, he was the principal coordinator for job placement of exiled physicist in the United States.

EINSTEIN AND WIGNER (second from left) both considered symmetry principles to be of fundamental importance. Einstein's theories of special relativity (1905) and general relativity (1915) are classic examples of symmetry principles constraining and even dictating dynamics. Wigner's great contribution in the late 1920s and 1930s was to discover the fundamental role symmetry plays in quantum theories, from explaining atomic spectra to classifying types of elementary particles. Pictured here at Einstein's 70th birthday celebration in 1949 at the Institute for Advaced Study in Princeton are (from left to right) Howard Robertson, Wigner, Herman Weyl, Kurt Gödel, I. I. Rabi, Einstein, Rudolf Ladenburg, J. Robert Oppenheimer and G. M. Clemence. **FIGURE 1.**

Kramer’s formula

Hendrik Anthony Kramers
(B. 1894 – D.1952)

In the world of human thought generally, and in physical science particularly, the most important and fruitful concepts are those to which it is impossible to attach a well-defined meaning

It is Kramers who first realized the implication of Ladenburg’s formula and derive the “quantum” dispersion relation in probably 1923 winter. But he just submit two-pages note to Nature in March 1924.

$$\alpha = \sum_{E_k>E_i} A_{k\to i}\tau_{ik}\frac{e^2}{4\pi^2 m}\frac{1}{\nu_{ik}^2-\nu^2} - \sum_{E_i>E_j} A_{i\to j}\tau_{ij}\frac{e^2}{4\pi^2 m}\frac{1}{\nu_{ij}^2-\nu^2}$$

New term given by Kramers

More common form of this formula:

$$\alpha = \frac{e^2}{4\pi^2 m}\left(\sum_{E_k>E_i}\frac{f_{ki}}{\nu_{ik}^2-\nu^2} - \sum_{E_i>E_j}\frac{f_{ij}}{\nu_{ij}^2-\nu^2}\right)$$

Many Contributions of Kramers

- Kramers-Heisenburg dispersion formula
- Wentzel–Kramers–Brillouin approximation
- Kramers-Kronig relation
- Kramers–Wannier duality
- Kramers-Anderson superexchange
- Kramers degeneracy theorem
- Kramers' Law, a formula for the spectral distribution of X-rays produced by an electron hitting a solid target

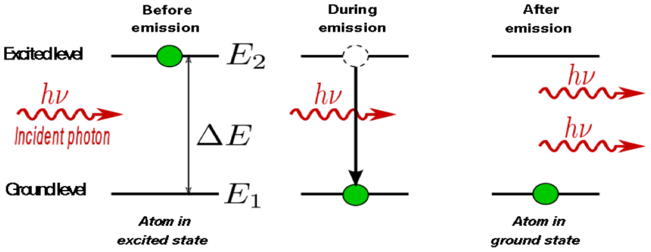
Slater’s idea: Virtual Oscillation

John Clarke Slater
B. 1900 – D.1976

- Slater suggested an atom in a stationary state generates a classical field which can be described formally as the electromagnetic field produced by a set of oscillators with Bohr frequencies v_{ij} .
- The probability that an atom emits a photon is determined by the surface integral of the Poynting vector of the virtual field around the atom. Once the photon is emitted the atom change into new state.
- The local energy density of the virtual field at a point is the probability to find a photon at that point.
- Once a photon is emitted the virtual field guides the photon along its path.

Bohr-Kramers-Slater’s Theory

- Slater arrived Copenhagen on Dec 21, 1923 and three weeks he and Bohr and Kramers submitted a article to philosophical Magazine on January 21, 1924.
- Bohr and Kramers convinced Slater to eliminate photon , the price is to pay is the conservation of energy and momentum becomes statistical.
- Consequently any causal connection between transition in distant atoms becomes impossible.
- Furthermore the distinction between spontaneous emission and simulated emission.



$$E_2 - E_1 = \Delta E = h\nu$$

Kramer’s derivation of his dispersion formula

- Kramers was passionately believing BKS theory. He sent his two pages note to Nature about his dispersion formula on March 25, 1924.
- He then sent second note to Nature on July 22, 1924 to explain his formula briefly.
- Kramers finished the article with Heisenburg on the complete formal derivation of dispersion formula on Dec 24 1924 and Heisenburg had left Copenhagen two days before. Zeitschrift für Physik received the manuscript on January 5, 1925.
- On April 1925 the coincidence experiment of Bothe and Geiger showed BKS theory was disapproved. It was a heavy blow to Kramers.

Kramer’s derivation of his dispersion formula

- Kramers first applied the contact transformation and action-angle variables to derive the polarizability in classical mechanics.
- Then Kramers replaced the differential coefficients by difference quotients which was also suggested by Born in June 1924.
- Identify the radiated energy emitted by a dipole classically and quantum-theoretically and obtain the relation between Classical Fourier coefficients and the Einstein’s A coefficients.

Contact Transformation

$$\boxed{\text{contact transformation } (q_i, p_i) \to (q_i', p_i')}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}. \qquad \Longleftrightarrow \qquad \dot{q}_i' = \frac{\partial H'}{\partial p_i'}, \quad \dot{p}_i' = -\frac{\partial H'}{\partial q_i'}.$$

$$\delta \int_{t_1}^{t_2} \left(\sum_i p_i \dot{q}_i - H(q_i, p_i) \right) dt = 0, \quad \delta \int_{t_1}^{t_2} \left(\sum_i p_i' \dot{q}_i' - H'(p_i', q_i') \right) dt = 0$$

$$\left(\sum_i p_i \dot{q}_i - H(q_i, p_i) - \sum_i p_i' \dot{q}_i' + H'(p_i', q_i') \right) dt = dF,$$

$$\boxed{\frac{\partial F}{\partial t} = H' - H, \quad \frac{\partial F}{\partial q_i} = p_i, \quad \frac{\partial F}{\partial q_i'} = -p_i'.}$$

Application of Action-Angle variables: Simple Harmonic Oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2.$$

$$F = \frac{1}{2}m\omega_0 q^2 \cot q'.$$

$$p = \frac{\partial F}{\partial q} = m\omega_0 q \cot q', \qquad p' = -\frac{\partial F}{\partial q'} = \frac{1}{2}m\omega_0 q^2 \csc^2 q'.$$

$$q = \sqrt{\frac{2p'}{m\omega_0}}\sin q'. \qquad p = \sqrt{2m\omega_0 p'}\cos q'.$$

⇒

$$H = \omega_0 p'.$$

$$\dot{q}' = \frac{\partial H}{\partial p'} = \omega_0, \qquad \dot{p}' = -\frac{\partial H}{\partial q'} = 0,$$

Application of Action-Angle variables: Simple Harmonic Oscillator

$$J \equiv 2\pi p', \quad w \equiv \frac{1}{2\pi} q'.$$

(J,w) Action-Angle Variable

$$\dot{w} = \frac{\partial H}{\partial J} = \nu_0, \quad \dot{J} = -\frac{\partial H}{\partial w} = 0.$$

Generalize to arbitrary system with period

$$J = \oint p dq.$$

$$q(t) = D\cos 2\pi\nu_0 t = D\cos 2\pi w,$$

$$\oint \left(\sqrt{2m\omega_0 p'}\cos q'\right) d\left(\sqrt{\frac{2p'}{m\omega_0}}\sin q'\right) = \int_0^{2\pi} 2p'\cos^2 q' dq' = 2\pi p',$$

$$D = \sqrt{\frac{J}{m\pi\omega_0}}.$$

Application of Action-Angle variables: Oscillator driven by electric field (I)

$$H = H_0 + H_{\text{int}} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 + eEx\cos\omega t.$$

When H=H_0: $x(t) = \sum_{\tau=\pm1} A_\tau(J)e^{2\pi i\tau w},$ $\Longrightarrow$ $0 = -\dot{J} = \frac{\partial H_0}{\partial w}, \qquad \frac{\partial H_0}{\partial J} = \dot{w} = \nu_0.$

Add H_{int}: $\Delta x = \frac{\partial x}{\partial J}\Delta J + \frac{\partial x}{\partial w}\Delta w.$ $\Longrightarrow$ $\Delta x = \sum_{\tau=\pm1}\left(\frac{\partial A_\tau}{\partial J}\Delta J + 2\pi i\tau A_\tau\Delta w\right)e^{2\pi i\tau w}.$

$$\Delta J = \int_0^t \Delta\dot{J}dt, \quad \Delta w = \int_0^t \Delta\dot{w}dt, \qquad \dot{J} = -\frac{\partial H_0}{\partial w} - eE\frac{\partial x}{\partial w}\cos 2\pi\nu t = -eE\frac{\partial x}{\partial w}\cos 2\pi\nu t.$$

$$\Delta\dot{J} = -\pi ieE\sum_{\tau=\pm1}\tau A_\tau\left(e^{2\pi i(\tau w+\nu t)} + e^{2\pi i(\tau w-\nu t)}\right).$$

$$\Big\Downarrow$$

$$\boxed{\Delta J = \int_0^t \Delta\dot{J}dt = \frac{eE}{2}\sum_{\tau=\pm1}\tau A_\tau\left\{\frac{1-e^{2\pi i(\tau\nu_0 t+\nu t)}}{\tau\nu_0+\nu} + \frac{1-e^{2\pi i(\tau\nu_0 t-\nu t)}}{\tau\nu_0-\nu}\right\}.}$$

Application of Action-Angle variables: Oscillator driven by electric field (II)

$$\begin{aligned}\dot{w} &= \frac{\partial H_0}{\partial J} + eE\frac{\partial x}{\partial J}\cos 2\pi\nu t \\ &= \nu_0 + \frac{eE}{2}\sum_{\tau=\pm1}\frac{\partial A_\tau}{\partial J}\left(e^{2\pi i(\tau w+\nu t)} + e^{2\pi i(\tau w-\nu t)}\right).\end{aligned}$$

$$\boxed{\Delta w = \int_0^t \Delta\dot{w}\,dt = \frac{ieE}{4\pi}\sum_{\tau=\pm1}\frac{\partial A_\tau}{\partial J}\left\{\frac{1-e^{2\pi i(\tau\nu_0 t+\nu t)}}{\tau\nu_0+\nu} + \frac{1-e^{2\pi i(\tau\nu_0 t-\nu t)}}{\tau\nu_0-\nu}\right\}}$$

$$\Delta x = \frac{\partial x}{\partial J}\Delta J + \frac{\partial x}{\partial w}\Delta w. \quad \Rightarrow \quad \boxed{\begin{aligned}\Delta x = \frac{eE}{2}\sum_{\tau'=\pm1}\sum_{\tau=\pm1}&\left\{\frac{\partial A_{\tau'}}{\partial J}\tau A_\tau - \tau' A_{\tau'}\frac{\partial A_\tau}{\partial J}\right\}\frac{1-e^{2\pi i(\tau\nu_0 t-\nu t)}}{\tau\nu_0-\nu}e^{2\pi i\tau'\nu_0 t} \\ &+ (\nu \to -\nu),\end{aligned}}$$

Application of Action-Angle variables: Oscillator driven by electric field (III)

$$\begin{aligned}\Delta x_{\mathrm{coh}} &= \frac{eE}{2}\sum_{\tau=\pm1}\left\{\left(\frac{\partial A_{-\tau}}{\partial J}\tau A_\tau + \tau A_{-\tau}\frac{\partial A_\tau}{\partial J}\right)\frac{-e^{-2\pi i\nu t}}{\tau\nu_0-\nu} + (\nu\to-\nu)\right\}\\ &= \frac{eE}{2}\sum_{\tau=\pm1}\tau\frac{\partial|A_\tau|^2}{\partial J}\left\{\frac{e^{-2\pi i\nu t}}{\nu-\tau\nu_0} - \frac{e^{2\pi i\nu t}}{\nu+\tau\nu_0}\right\}.\end{aligned}$$

$$\begin{aligned}\Delta x_{\mathrm{coh}} &= \frac{eE}{2}\sum_{\tau}\tau\frac{\partial|A_\tau|^2}{\partial J}\left(\frac{1}{\nu-\tau\nu_0} - \frac{1}{\nu+\tau\nu_0}\right)\cos 2\pi\nu t\\ &= \frac{eE}{2}\sum_{\tau}\tau\frac{\partial|A_\tau|^2}{\partial J}\left(\frac{2\tau\nu_0}{\nu^2-\tau^2\nu_0^2}\right)\cos 2\pi\nu t.\end{aligned}$$

$$\Delta x_{\mathrm{coh}} = 2eE\frac{\partial}{\partial J}\left(\frac{\nu_0}{\nu^2-\nu_0^2}|A_\tau|^2\right)\cos 2\pi\nu t.$$

Generalization to many-period system

$$x = \frac{1}{2}\sum C_{\tau_1\tau_2\ldots\tau_f}\exp[2\pi i(\tau_1 w_1 + \tau_2 w_2 + \tau_f w_f)] \qquad w_i = \nu_i t + \delta_i$$

$$\omega = \tau_1\nu_1 + +\tau_2 w_2 + \tau_f w_f \qquad \frac{\partial}{\partial J} = \sum_k \tau_k \frac{\partial}{\partial J_k}$$

⇓

$$\boxed{\Delta x = eERe\left[\exp[2\pi i\nu t]\sum_\tau \frac{1}{4}\frac{\partial}{\partial J}\left(\frac{C_\tau^2}{\omega-\nu} + \frac{C_\tau^2}{\omega+\nu}\right)\right]}$$

From Classical to Quantum

$$\left.\frac{\partial F(w,J)}{\partial J}\right|_{J=rh} \to \frac{1}{h}(F(r+1)-F(r)),$$

Here Planck constant is introduced.

$$\Delta x = eERe\left[\exp[2\pi i\nu t]\sum_{\tau}\frac{1}{4}\frac{\partial}{\partial J}\left(\frac{C_\tau^2}{\omega-\nu}+\frac{C_\tau^2}{\omega+\nu}\right)\right]$$

$$\Downarrow$$

$$\Delta x = eERe\left[\exp[2\pi i\nu t]\sum_{\nu_{ki}>0}\frac{1}{4h}\left(\frac{C_{ki}^2}{\nu_{ki}-\nu}+\frac{C_{ki}^2}{\nu_{ki}+\nu}\right)-\sum_{\nu_{ij}>0}\frac{1}{4h}\left(\frac{C_{ij}^2}{\nu_{ij}-\nu}+\frac{C_{ij}^2}{\nu_{ij}+\nu}\right)\right]$$

From classical to Quantum

$$\frac{dE}{dt} = \frac{2}{3}\frac{e^2}{c^3}\dot{v}^2 \Longrightarrow \frac{dE}{dt} = \frac{2}{3}\frac{e^2}{c^3}\omega^4|C_\omega|^2$$

Quantum=Classical

$$h\nu_{rs}A_{r\to s} = \frac{4}{3}\frac{e^2}{c^3}(2\pi\nu_{rs})^4|C_{rs}|^2 \Longrightarrow |C_{rs}|^2 = \frac{3hc^3}{64\pi^4 e^2\nu_{rs}^3}A_{r\to s}$$

$$\Delta x = eERe\left[\exp[2\pi i\nu t]\sum_{\nu_{ki}>0}\frac{1}{4h}\left(\frac{C_{ki}^2}{\nu_{ki}-\nu}+\frac{C_{ki}^2}{\nu_{ki}+\nu}\right)-\sum_{\nu_{ij}>0}\frac{1}{4h}\left(\frac{C_{ij}^2}{\nu_{ij}-\nu}+\frac{C_{ij}^2}{\nu_{ij}+\nu}\right)\right]$$

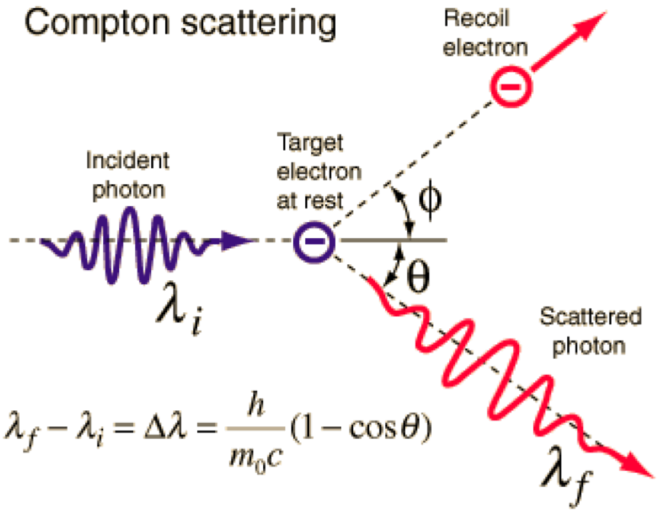
$$\Downarrow$$

$$\alpha = \sum_{E_k>E_i} A_{k\to i}\tau_{ik}\frac{e^2}{4\pi^2 m}\frac{1}{\nu_{ik}^2-\nu^2} - \sum_{E_i>E_j} A_{i\to j}\tau_{ij}\frac{e^2}{4\pi^2 m}\frac{1}{\nu_{ij}^2-\nu^2}$$

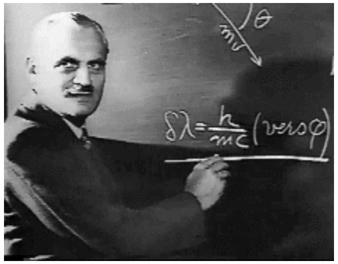
It is long way but I get it!

$$\tau_{ik} = \frac{3mc^3}{8\pi^2 e^2\nu_{ik}^2}$$

Test of BKS theory



$$\lambda_f - \lambda_i = \Delta\lambda = \frac{h}{m_0 c}(1-\cos\theta)$$



Arthur Holly Compton (B.1892 – D.1962) was an American physicist and Nobel laureate in physics for his discovery of the Compton effect. He served as Chancellor of Washington University in St. Louis from 1945 to 1953.

By simultaneously measure the scattered photon and the recoiled electron shows that the exact conservation of energy and momentum.

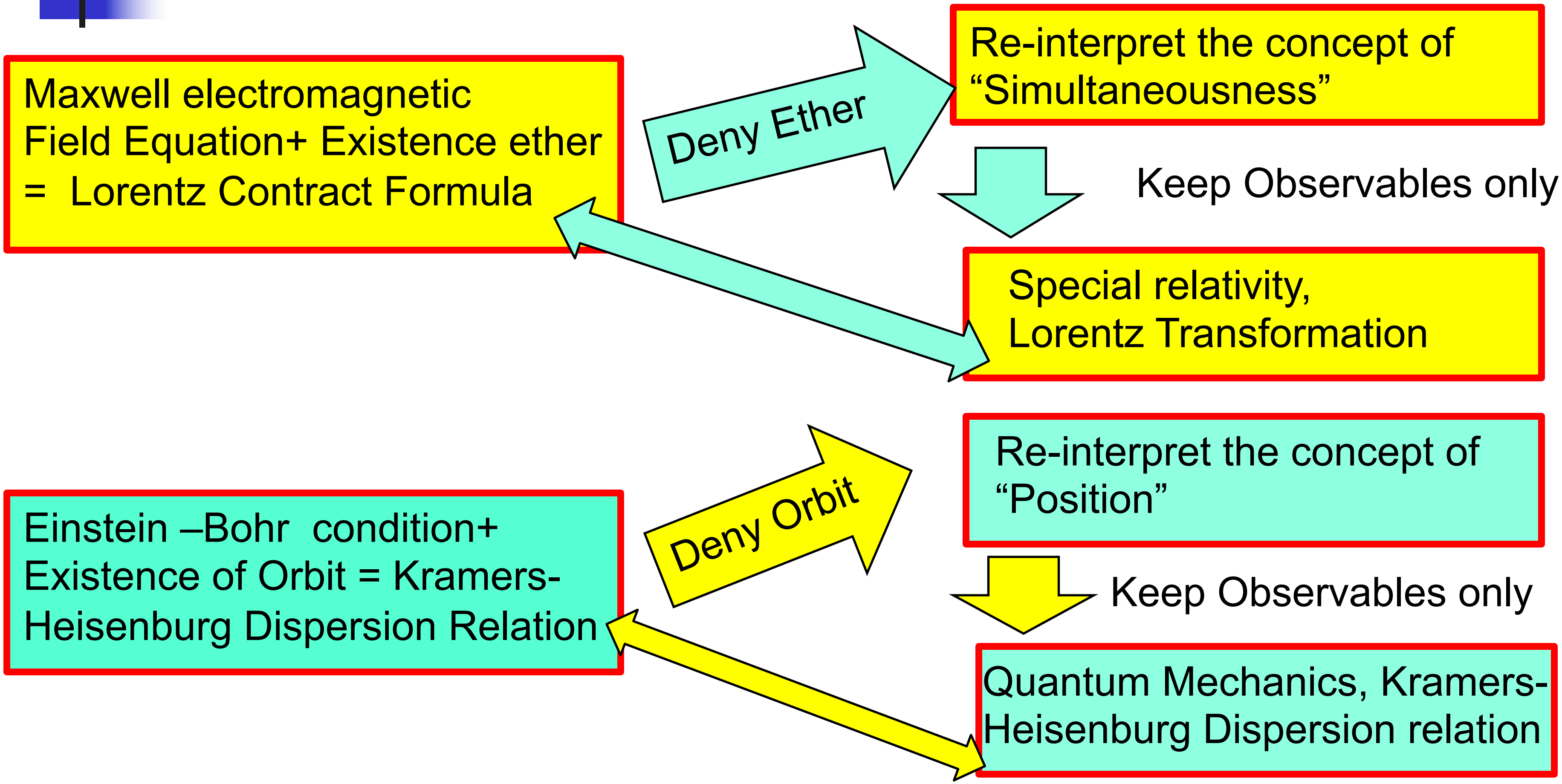
Epiphany at Heligoland

- In 1925 Werner Heisenberg was working in Göttingen on the problem of calculating the spectral lines of hydrogen. By May 1925 he began trying to describe atomic systems by observables only.
- On June 7, to escape the effects of a bad attack of hay fever, Heisenberg left for the pollen free North Sea island of Heligoland. While there, in between climbing and learning by heart poems from Goethe's West-östlicher Diwan, he continued to ponder the spectral issue and eventually realized that adopting non-commuting observables might solve the problem, and he later wrote:
- *"It was about three o' clock at night when the final result of the calculation lay before me. At first I was deeply shaken. I was so excited that I could not think of sleep. So I left the house and awaited the sunrise on the top of a rock."*

Epiphany at Heligoland

- On June 9 Heisenberg returned to Gottingen and sent a copy of his results to Wolfgang Pauli, commenting in the accompanying letter: *"Everything is still vague and unclear to me, but it seems as if the electrons will no more move on orbits".*
- On July 25, Heisenberg's paper announcing the invention of quantum mechanics is received by the Zeitschrift fur Physik .
- Before that he had also given a copy of the paper to Max Born commenting "*that he had written a crazy paper and did not dare to send it in for publication, and that Born should read it and advice him on it."*

What is his “Crazy idea” ?



Maxwell electromagnetic Field Equation+ Existence ether = Lorentz Contract Formula

Deny Ether

Re-interpret the concept of “Simultaneousness”

Keep Observables only

Special relativity,
Lorentz Transformation

Einstein –Bohr condition+ Existence of Orbit = Kramers-Heisenburg Dispersion Relation

Deny Orbit

Re-interpret the concept of “Position”

Keep Observables only

Quantum Mechanics, Kramers-Heisenburg Dispersion relation

What is his “Crazy idea” ?

Classical Aspect

Resonant frequencies

$$\nu(n,\alpha) = \alpha\nu(n)$$

$$\nu(n,\alpha) + \nu(n,\beta) = \nu(n,\alpha+\beta)$$

$$X(t) = \sum_{\alpha} C_{\alpha}(n)\exp(2\pi i\nu(n)\alpha t)$$

⟺

Quantum Aspect

$$\nu(n,n-\alpha) = \frac{E_n - E_{n-\alpha}}{h}$$

$$\nu(n,\alpha) + \nu(n,\beta) = \nu(n,\alpha+\beta)$$

$$\nu(n,n-\alpha) + \nu(n-\alpha,n-\alpha-\beta)$$

$$= \nu(n,n-\alpha-\beta)$$

$$X(t) = \sum_{\alpha} C_{n,n-\alpha}\exp(2\pi i\nu(n,n-\alpha)t)$$

Where the matrix from?

Classical :

$$X(t)X(t)=\sum_{\beta}D_{\beta}(n)\exp(2\pi i\nu(n)\beta t)=\sum_{\alpha}C_{\alpha}(n)C_{\beta-\alpha}(n)\exp(2\pi i\nu(n)(\beta)t)$$

$$D_{\beta}(n)=\sum_{\alpha}C_{\alpha}(n)C_{\beta-\alpha}(n)$$

Quantum:

$$X(t)X(t)=\sum_{\beta}D_{n,n-\beta}\exp(2\pi i\nu(n,n-\beta)t)=\sum_{\alpha}C_{n,n-\alpha}C_{n-\alpha,n-\alpha-\beta}\exp(2\pi i\nu(n,n-\beta)t)$$

$$D(n,n-\beta)=\sum_{\alpha}C_{n,n-\alpha}C_{n-\alpha,n-\alpha-\beta}$$

Quantum Condition of Heisenburg

$$\int p dq = \int m\dot{x} dx = \int m\dot{x}^2 dt = J = nh$$

$$\boxed{nh = 4\pi^2 m \sum_{\alpha=-\infty}^{\infty} |C_\alpha(n)|^2 \alpha^2 \nu(n)} \Rightarrow \boxed{h = 4\pi^2 m \sum_{\alpha=-\infty}^{\infty} \alpha \frac{d}{dn} \left[C_\alpha(n)|^2 \alpha \nu(n) \right]}$$

$$\Downarrow$$

$$\boxed{h = 8\pi^2 m \sum_{\alpha=0}^{\infty} \left[|C(n, n+\alpha)|^2 \nu(n, n+\alpha) - |C(n, n-\alpha)|^2 \nu(n, n-\alpha) \right]}$$

Some tests of Heisenburg

$$\frac{d^2X}{dt^2} + \omega_0^2 X + \lambda X^2 = 0 \quad \Longrightarrow \quad E_n = (n + \frac{1}{2})\frac{h\omega_0}{2\pi}$$

$$\frac{d^2X}{dt^2} + \omega_0^2 X + \lambda X^3 = 0$$

$$\Big\Downarrow$$

$$E_n = (n + \frac{1}{2})\frac{h\omega_0}{2\pi} + \lambda(n^2 + n + 1)\frac{3h^2}{32\pi^2\omega_0^2 m} - \lambda^2(17n^3 + \frac{51}{2}n^2 + \frac{59}{2}n + \frac{21}{2})\frac{h^3}{512\pi^3\omega_0^5 m^2}$$

Rotator in 2D: $h = 4\pi^2 m(a^2\nu(n+1, n) - a^2\nu(n, n-1)$

$$\nu(n, n-1) = \frac{nh}{2\pi m a^2} \qquad E_n = \frac{h^2}{8\pi^2 m a^2}(n^2 + n + 1)$$

Born-Jordan's work

- Born and his assistant, Pascal Jordan recognize the strange algebra developed by Heisenberg is matrix algebra.
- Furthermore they found that the quantum condition of Heisenberg can be written in a very simple form.

$$p = \sum_{\tau=-\infty}^{\infty} p_\tau \exp(2\pi i \nu \tau t), \quad q = \sum_{\tau=-\infty}^{\infty} q_\tau \exp(2\pi i \nu \tau t)$$

$$J = \int_0^{1/\nu} p\dot{q}\,dt = -2\pi i \sum_{\tau=-\infty}^{\infty} \tau p_\tau q_{-\tau} \quad \Longrightarrow \quad 1 = -2\pi i \sum_{\tau=-\infty}^{\infty} \tau \frac{\partial}{\partial J}(p_\tau q_{-\tau})$$

$$1 = \frac{-2\pi i}{h} \sum_{\tau=-\infty}^{\infty} p(n, n+\tau)q(n+\tau, n) - p(n, n-\tau)q(n-\tau, n)$$

Born-Jordan’s work

$$\frac{h}{2\pi i} = \sum_{\tau=-\infty}^{\infty} p(n, n-\tau)q(n-\tau, n) - q(n, n+\tau)p(n+\tau, n)$$

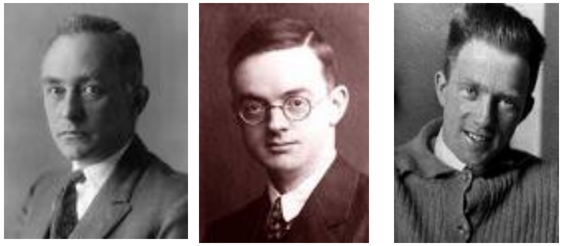
$$\sum_{m} \mathbf{P}_{nm}\mathbf{Q}_{mn} - \mathbf{Q}_{nm}\mathbf{P}_{mn} = \frac{h}{2\pi i}$$

$$p = m\dot{q}$$

$$\frac{h}{2\pi i} = 2\pi i m \sum_{\tau=-\infty}^{\infty} \nu(n, n-\tau)q(n, n-\tau)q(n-\tau, n) - \nu(n, n+\tau)q(n, n+\tau)q(n+\tau, n)$$

$$h = 4\pi^2 m \sum_{\tau=-\infty}^{\infty} \nu(n, n+\tau)|q(n, n+\tau)|^2 - \nu(n, n-\tau)|q(n, n-\tau)|^2$$

Dreimännarbeit



- In winter of 1925, Born, Jordan and Heisenburg wrote a long paper which basically complete the framework of matrix mechanics.
- They also developed the quantum theory of angular momentum based on $M_x M_y - M_y M_x = \frac{h}{2\pi i} M_z$
- They even quantize the wave field and obtain the Einstein mean square deviation relation:

$$\Delta = E - \bar{E} \qquad \bar{\Delta}^2 = h\nu\bar{E} + \frac{\bar{E}^2}{z_\nu V} \qquad z_\nu = \frac{8\pi\nu^2}{c^3}$$

Dirac’s deep insight

- Almost at same time, a young Britain Ph.D student in Cambridge named Dirac found that the novel relations discovered by Born and Jordan is a natural generalization of Poisson bracket in classical Mechanics.

$$\{f,g\} = \sum_{i=1}^{N}\left[\frac{\partial f}{\partial q_i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q_i}\right].$$

$$pq - qp = \frac{ih}{2\pi}[p,q]_{cl}$$

- He furthermore found the similarity between new “Quantum Mechanics” and old “classical Mechanics”.

$$\dot{p}_r = [p_r, H], \quad \dot{q}_s = [q_s, H]$$

- He also derived the Einstein-Bohr relation easily.

$$x_{nm}H_{mm} - H_{nn}x_{nm} = \frac{ih}{2\pi}\dot{x}_{nm} = -h\nu_{nm}x_{nm}$$

$$h\nu_{nm} = H_{nn} - H_{mm}$$

Pauli’s calculation on hydrogen spectrum

- Also in the winter of 1925, Pauli derived the hydrogen spectrum formula of Bohr.
- By matrix mechanics with the help of Laplace–Runge–Lenz vector.

$$\mathbf{F}(r) = \frac{-k}{r^2}\hat{\mathbf{r}} \qquad \mathbf{A} = \mathbf{p} \times \mathbf{L} - mk\hat{\mathbf{r}}$$

- The effect of electric and magnetic field on the atom were also studied.
- Pauli’s paper was received on january 17th, 1926 but the main part of the paper has been obtained before Nov 3,1925.

Wave theory strike back

- In 1924, Louis-Victor de Broglie formulated the de Broglie hypothesis, claiming that all matter, not just light, has a wave-like nature; he related wavelength (*λ*), and momentum (*p*) by the relation: $\lambda = \frac{h}{p}$
- In January 1926, Schrödinger published in the Annalen der Physik the paper "*Quantisierung als Eigenwertproblem*" [English. *Quantization as an Eigenvalue Problem*] on wave mechanics and what is now known as the Schrödinger equation.

Wave theory strike back

- In 1924, Louis-Victor de Broglie formulated the de Broglie hypothesis, claiming that all matter, not just light, has a wave-like nature; he related wavelength (λ), and momentum (p) by the relation: $\lambda = \frac{h}{p}$

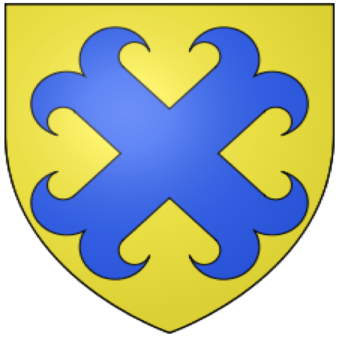
Suppose now the electron, having momentum *p*, is moving in a circular orbit of radius *r*. Then for a standing wave, a whole number of wavelengths must fit around the circle, so for some integer *n*, $n\lambda = 2\pi r$. Putting this together with $p = h/\lambda$, we find: $2\pi r = n\lambda = nh/p \Longrightarrow L = pr = nh/2\pi$

The "standing wave" condition immediately gives Bohr's quantization of angular momentum

Who is de Broglie?

Louis-Victor-Pierre-Raymond, 7th duc de Broglie (B1892 – D 1987) was a French physicist and a Nobel laureate . De Broglie had originally intended a career in humanities, and received his first degree in history. Afterwards, he turned his attention toward mathematics and physics. His 1924 doctoral thesis, *Recherches sur la théorie des quanta* (Research on Quantum Theory), introduced his theory of electron waves. The thesis examiners, unsure of the material, passed his thesis to Einstein for evaluation who endorsed his wave-particle duality proposal wholeheartedly; de Broglie was awarded his doctorate. This research culminated in the de Broglie hypothesis stating that *any moving particle or object had an associated wave*. For this he won the Nobel Prize in Physics in 1929.

House of Broglie



Coat of Arms of the House of Broglie

The **House of Broglie** is the name of a noble French family, originally Piedmontese, who emigrated to France in the year 1643. The family patriarch, François-Marie created for himself the title of *Comte de Broglie*. His son, Victor-Maurice, comte de Broglie (1647–1727), becoming marechal de camp in 1676, lieutenant-general in 1688, and finally marshal of France in 1724. His grandson, François-Marie, was made duc de Broglie and a peer of France in 1742. The family counts among its members three marshals of France, a Nobel Prize laureate, several members of the Institut de France. All junior members of the House of Broglie bear the title of *prince of Broglie*, while the head of the family is *duke of Broglie*.

François-Marie de Broglie, 1er duc de Broglie

Family of Broglie

Victor-François, 2ème duc de Broglie (B.1718 – D. 1804) was a French aristocrat and soldier and a marshal of France. He played a prominent part in the French Revolution, which he opposed with determination. Since the duke's eldest son died in the Terror, the succession fell to his grandson, who became the third duc de Broglie.

Achille-Léonce-Victor-Charles, 3rd duc de Broglie (B. 1785 – D.1870) was a French statesman and diplomat. His literary works, though few of them have been published, were rewarded in 1856 by a seat in the Académie française.

Jacques-Victor-Albert, 4th duc de Broglie (B.1821 – D. 1901) was a French monarchist politician. He had already published a translation of the religious system of Leibniz (1846). These, and other contributions, brought him the seat in the Académie française in 1862. He was Prime Minister of France from 17 May 1877 to 23 November 1877.

Brother, Duc and physicist

Louis-César-Victor-Maurice, 6th duc de Broglie (B. 1875–D.1960), was a French physicist. Having graduated from naval officer's school, Maurice de Broglie spent nine years in the French Navy. While serving, he became interested in physics, and began doing research on electromagnetism. Broglie defied his family's wishes and left the navy in 1904 to pursue a scientific career. He studied under Paul Langevin, receiving his doctorate in 1908. Broglie made advances in the study of X-ray diffraction and spectroscopy. After Louis de Broglie's rise to prominence in the 1920s, building on some of their shared research, the elder Broglie physicist continued his own research. While Louis was primarily a theoretician, Maurice himself was always the experimental physicist *par excellence.* In 1934 he was elected to the Académie française. He had the unique honor of welcoming his own brother into the Academy on the latter's induction.

Isn’t that crazy?

….I was in Zurich in 1925. Debye was Professor in Zurich at that time, and Schrodinger was also. I knew Debye pretty well and spoke with him, and he said, “What do you think, Lande, of this crazy idea -- Schrödinger thinks to solve the quantum problem by waves. Isn’t that crazy?”…

Interview with Dr. Alfred Lande By Thomas S. Kuhn and John Heilbron In Berkeley, California
March 5, 1962. Niels Bohr Library & Archives, American Institute of Physics, College Park, MD USA, www.aip.org/history/ohilist/LINK

Who is Schrödinger ?

Erwin Rudolf Josef Alexander Schrödinger
(B.1887– D. 1961)
was an Austrian theoretical physicist who achieved fame for his contributions to quantum mechanics, especially the Schrödinger equation, for which he received the Nobel Prize in 1933. In 1935, after extensive correspondence with personal friend Albert Einstein, he proposed the Schrödinger's cat thought experiment.

Wave theory strike back

- In January 1926, Schrödinger published in the Annalen der Physik the paper "*Quantisierung als Eigenwertproblem*“

  [English. *Quantization as an Eigenvalue Problem*]

  on wave mechanics and what is now known as the Schrödinger equation. In this paper he gave a "derivation" of the wave equation for time independent systems, and showed that it gave the correct energy eigenvalues for the hydrogen-like atom.

Quotation: The scientist only imposes two things, namely truth and sincerity, imposes them upon himself and upon other scientists. (**Erwin Schrödinger**)

How he created his equation?

The following is taken from *The God Particle* by Leon Lederman:

Leaving his wife at home, Schrödinger booked a villa in the Swiss Alps for two weeks, taking with him his notebooks, two pearls, and an old Viennese girlfriend. Schrödinger's self-appointed mission was to save the patched-up, creaky quantum theory of the time. The Viennese-born physicist placed a pearl in each ear to screen out any distracting noises. Then he placed the girlfriend in bed for inspiration. Schrödinger had his work cut out for him. He had to create a new theory and keep the lady happy. Fortunately, he was up to the task.

His derivation of his equation

Schrodinger started from Hamilton-Jacobi Equation in Classical Mechanics.

$$H\left(q, \frac{\partial S}{\partial q}\right) = E$$

Then he replaced the action function S as follows:

$$S = K \log \psi$$

Hence he arrived this equation:

$$H\left(q, \frac{K}{\psi}\frac{\partial \psi}{\partial q}\right) = E$$

For an electron moving in the Coulomb potential, The Hamilton-Jacobi equation becomes as follows:

$$-\frac{e^2}{r} + \frac{1}{2m}\left[\left(\frac{\partial S}{\partial x}\right)^2 + \left(\frac{\partial S}{\partial y}\right)^2 + \left(\frac{\partial S}{\partial z}\right)^2\right] = E$$

$$\left(\frac{\partial \psi}{\partial x}\right)^2 + \left(\frac{\partial \psi}{\partial y}\right)^2 + \left(\frac{\partial \psi}{\partial z}\right)^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2 = 0$$

His derivation of his equation

The next step is the most crucial one, he made a variation problem as follows:

$$\delta J = \delta \int dxdydz \left[\left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi^2 \right] = 0$$

Using part integration one easily obtains the following relation:

$$\delta\left(\frac{\partial\psi}{\partial x}\right)^2 = 2\frac{\partial\psi}{\partial x}\frac{\partial}{\partial x}(\delta\psi) = \frac{\partial}{\partial x}\left(2\frac{\partial\psi}{\partial x}\delta\psi\right) - 2\frac{\partial^2\psi}{\partial x^2}\delta\psi$$

Inserting these relation he then discovered the following equation:

$$\frac{1}{2}\delta J = \int df\,\delta\psi\frac{\partial\psi}{\partial n} - \int dxdydz \left[\bigtriangledown^2\psi + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi\right]\delta\psi = 0$$

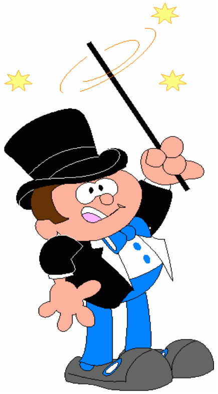
His derivation of his equation

$$\frac{1}{2}\delta J = \int df\,\delta\psi\frac{\partial\psi}{\partial n} - \int dxdydz\left[\nabla^2\psi + \frac{2m}{K^2}\left(E+\frac{e^2}{r}\right)\psi\right]\delta\psi = 0$$

If ψ vanishes at infinitely far away then the surface term vanishes, and one obtains the famous equation:

$$\boxed{\nabla^2\psi + \frac{2m}{K^2}\left(E+\frac{e^2}{r}\right)\psi = 0}$$

Then we set the value of K: $K = \frac{h}{2\pi}$



$$\boxed{E = -\frac{2\pi^2 me^4}{n^2h^2}, n = 1, 2, 3...}$$

Now the magic comes! When we require ψ vanishes at infinity then the energy values are no longer arbitrary, only the certain values are acceptable!

Incomprehensible….

Kuhn: **….**In the early Schrodinger papers there are about three different ways of getting the wave equation, the first of them still almost incomprehensible. Did this bother people? You know, in the first paper he uses a variational method and I still don't know anybody who feels he's quite made sense out of the variational method.

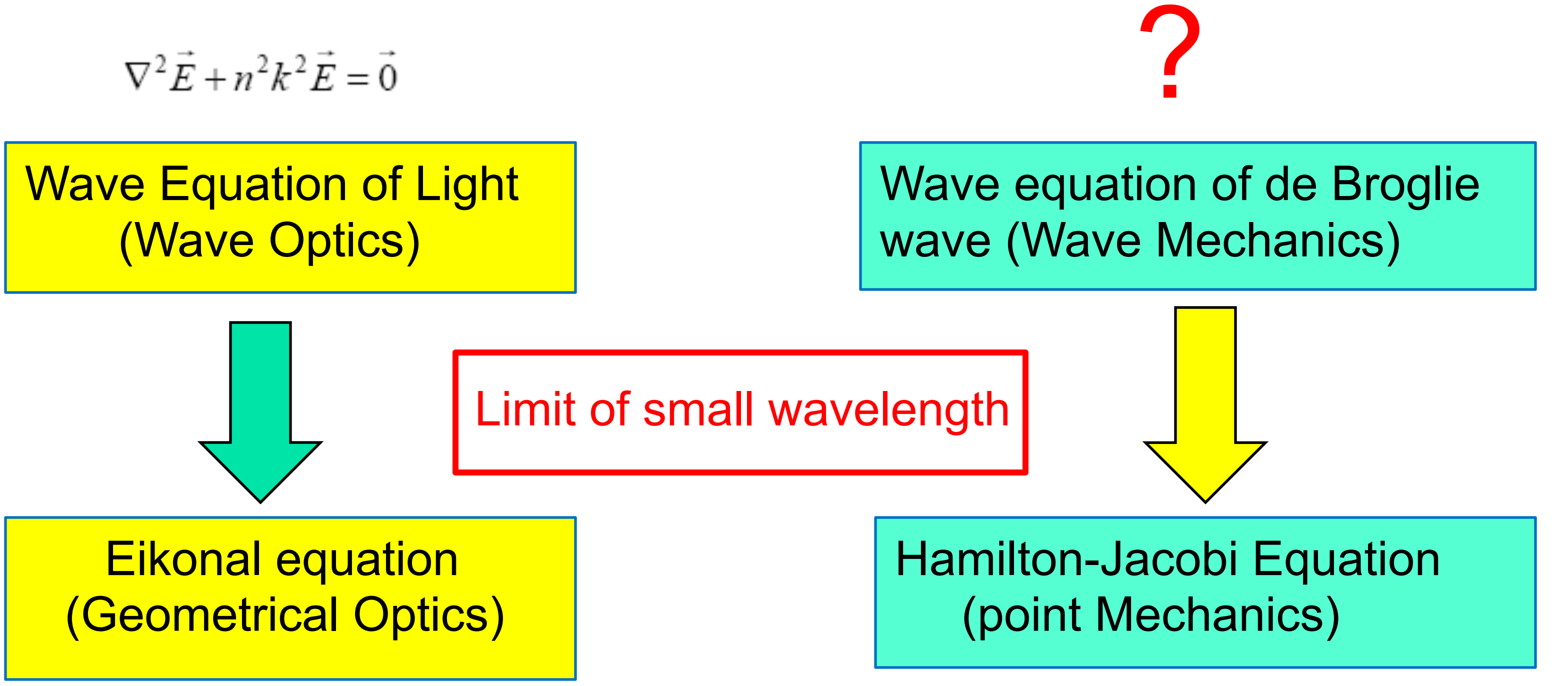
Bethe: Which is different from the way the variational method is now --?

Kuhn: Yes, in part because it's pulled very much out of the hat and in part because it depends on some very odd substitutions and variance conditions. No, it is not what one would now call a straightforward variational derivation of it. Then he later gets very deeply involved with the question of the parallel between wave optics and geometries, doing classical versus wave mechanics as the parallel to geometric versus wave optics….

Scanned at the American Institute of Physics

Interview with Hans Albrecht Bethe
by Thomas S. Kuhn
At Kuhn's office, Dwinelle Hall, UC, Berkeley
17 January 1964

Optical-Mechanical analogy



$$\nabla^2 \vec{E} + n^2 k^2 \vec{E} = \vec{0}$$

?

Wave Equation of Light (Wave Optics)

Wave equation of de Broglie wave (Wave Mechanics)

Limit of small wavelength

Eikonal equation (Geometrical Optics)

Hamilton-Jacobi Equation (point Mechanics)

$$(\nabla S)^2 = n^2$$

$$H\left(q_1, \ldots, q_N; \frac{\partial S}{\partial q_1}, \ldots, \frac{\partial S}{\partial q_N}; t\right) + \frac{\partial S}{\partial t} = 0.$$

Optical-Mechanical analogy

Wave Equation of Light
(Wave Optics)

Schrödinger's
↔
Completion

Wave equation of de Broglie wave (Wave Mechanics)

$$\nabla^2 \vec{E} + n^2 k^2 \vec{E} = \vec{0}$$

$$\nabla^2 \psi + \frac{2m}{K^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

Eikonal equation
(Geometrical Optics)

Hamilton's
↔
Analogy

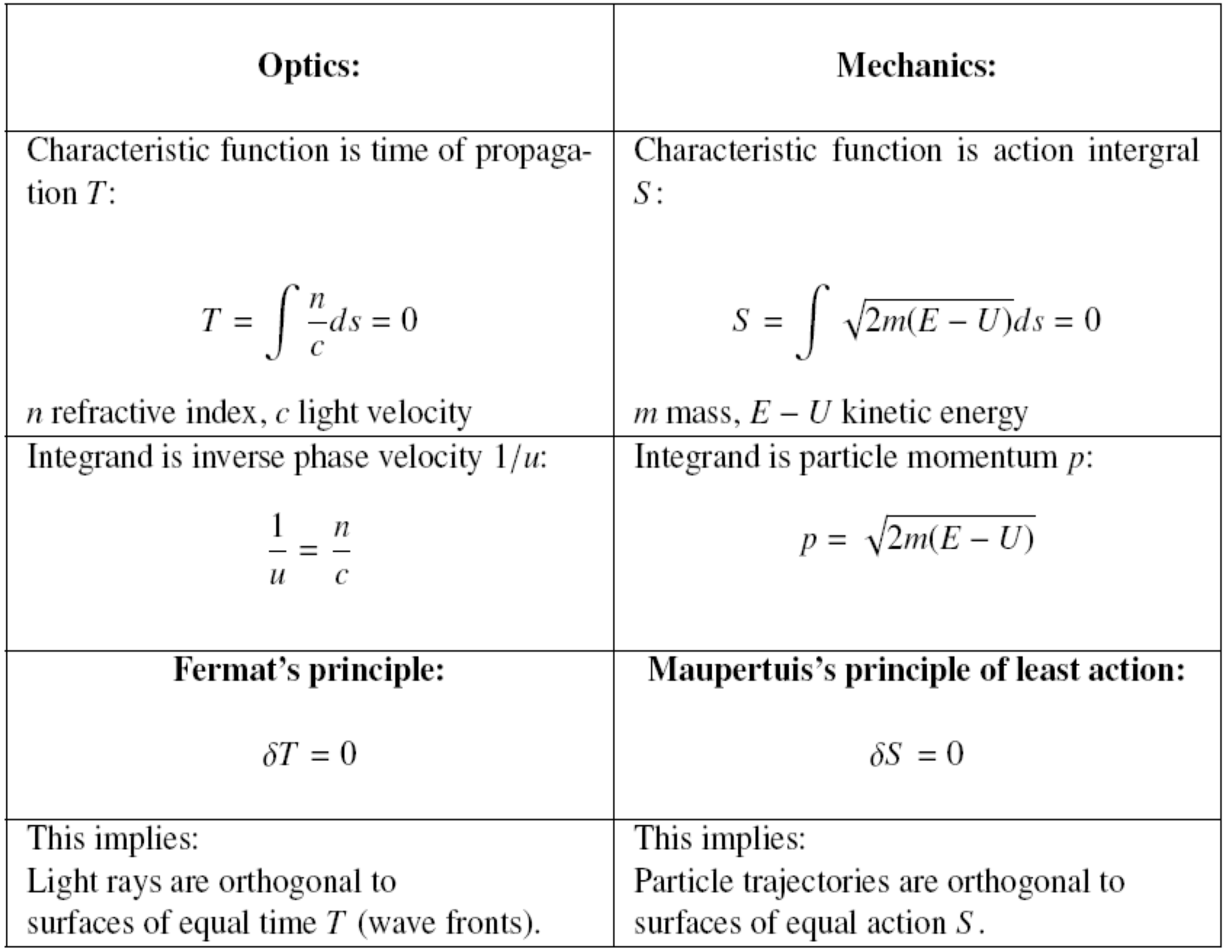
Hamilton-Jacobi Equation
(point Mechanics)

$$(\nabla S)^2 = n^2$$

$$H\left(q_1, \ldots, q_N; \frac{\partial S}{\partial q_1}, \ldots, \frac{\partial S}{\partial q_N}; t\right) + \frac{\partial S}{\partial t} = 0.$$

Hamilton’s analogy

William Rowan Hamilton (B.1805 – D.1865) was an Irish physicist, astronomer, and mathematician, who made important contributions to classical mechanics, optics, and algebra. His studies of mechanical and optical systems led him to discover new mathematical concepts and techniques.



Optics:	**Mechanics:**
Characteristic function is time of propagation T: $T = \int \frac{n}{c} ds = 0$ n refractive index, c light velocity	Characteristic function is action intergral S: $S = \int \sqrt{2m(E-U)} ds = 0$ m mass, $E - U$ kinetic energy
Integrand is inverse phase velocity $1/u$: $\frac{1}{u} = \frac{n}{c}$	Integrand is particle momentum p: $p = \sqrt{2m(E-U)}$
Fermat’s principle: $\delta T = 0$	**Maupertuis’s principle of least action:** $\delta S = 0$
This implies: Light rays are orthogonal to surfaces of equal time T (wave fronts).	This implies: Particle trajectories are orthogonal to surfaces of equal action S.

Schrödinger’s completion

He again started from Hamilton-Jacobi Equation: $2\mathscr{T}\left(q, \frac{\partial S}{\partial q}\right) = 2(E-V).$

On the other, the linear element is written as: $ds^2 = \sum_{i,k=1}^{4} dq_i dq_k = 2\mathscr{T}(q_k, \dot{q}_k)dt^2.$

Assuming a relation between the trajectory of the particle and the propagation of the wave front Schrödinger started from the wave front equation: $S = \text{const.},$

IF one puts the following condition on S: $|\text{grad } S| = \sqrt{2(E-V)},$

Then the propagation of the wave front in the phase velocity u: $u = \frac{ds}{dt} = \frac{E}{\sqrt{2(E-V)}},$

Identity between Fermat optical principle and Maupertuis mechanical least action principle is established:

$$O = \delta \underset{\text{(Fermat)}}{\int_{P_1}^{P_2}} \frac{ds}{u} = \delta \int_{P_1}^{P_2} \frac{ds\sqrt{2(E-V)}}{E} = \delta \underset{\text{(Maupertuis)}}{\int} \frac{2\mathscr{T}}{E}\, dt.$$

Schrödinger’s completion

Let us come back to the Wave Equation: $\nabla^2\psi - \frac{1}{u^2}\ddot{\psi} = 0$

Assuming the time-dependence of the wave front is as follows: $\psi = \exp(i2\pi\nu t)\psi_q$

Now you insert the phase velocity found previously: $u = \frac{ds}{dt} = \frac{E}{\sqrt{2(E-V)}}$,

Insert the phase velocity into wave equation: $\nabla^2\psi_q + \frac{8\pi^2\nu^2}{E^2}(E-V)\psi_q = 0$

The frequency of “matter wave” is given by $\nu = \frac{E}{h}$

Once again we reach the famous equation! $\nabla^2\psi_q + \frac{8\pi^2}{h^2}(E-V)\psi_q = 0$

Wave theory strike back

- A second paper was submitted just four weeks later that solved the quantum harmonic oscillator, the rigid rotor and the diatomic molecule, and gives a new derivation of the Schrödinger equation.
- A third paper in May showed the equivalence of his approach to that of Heisenberg and gave the treatment of the Stark effect.
- A fourth paper in this most remarkable series showed how to treat problems in which the system changes with time, as in scattering problems.

Why Wave Mechanics is popular?

Bethe: …Nobody ever, to my recollection, said, "There is a calculus of the matrix mechanics." Nobody to my knowledge mentioned how Heisenberg got matrix mechanics, that it had something to do with the spectral resolution of the dipole moment of an oscillator or something like that -- never. At a much later time, I think it must have been in early '28 or so, Sommerfeld said, "Well, of course we really believe that Heisenberg knows better about the physics, but we calculate with Schrodinger."……………

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by Thomas S. Kuhn
At Kuhn's office, Dwinelle Hall, UC, Berkeley
17 January 1964

Schrödinger vs. Nazi

University of Graz

Karl-Franzens-Universität Graz

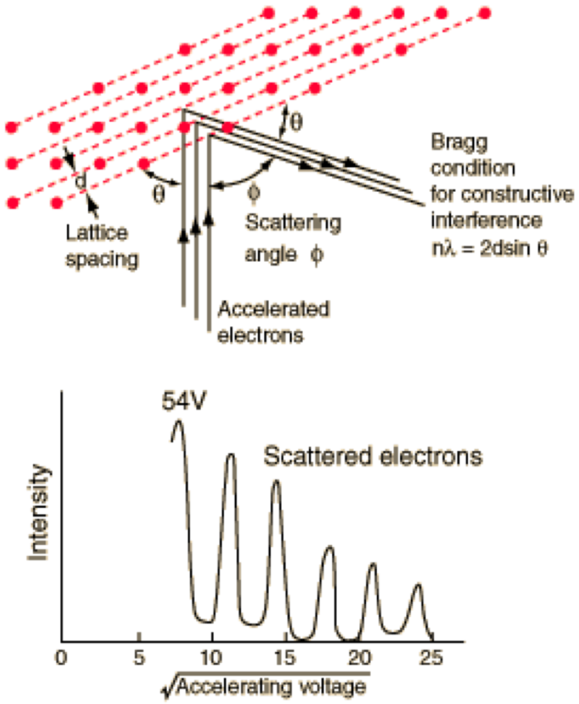
In 1927, he succeeded Max Planck at the Friedrich Wilhelm University in Berlin. In 1933, however, Schrödinger decided to leave Germany; he disliked the Nazis' anti-semitism. He became a Fellow of Magdalen College at the University of Oxford. His position at Oxford did not work out; his unconventional personal life (Schrödinger lived with two women) was not met with acceptance. In 1934, Schrödinger lectured at Princeton University; he was offered a permanent position there, but did not accept it. Again, his wish to set up house with his wife and his mistress may have posed a problem. He had the prospect of a position at the University of Edinburgh but visa delays occurred, and in the end he took up a position at the University of Graz in Austria in 1936.

Schrödinger vs. Nazi

In 1939, after the Anschluss, Schrödinger had problems because of his flight from Germany in 1933 and his known opposition to Nazism. He issued a statement recanting this opposition (he later regretted doing so, and he personally apologized to Einstein). However, this did not fully appease the new dispensation and the university dismissed him from his job for political unreliability. He suffered harassment and received instructions not to leave the country, but he and his wife fled to Italy. From there he went to visiting positions in Oxford and Ghent Universities.

In 1940 he received an invitation to help establish an Institute for Advanced Studies in Dublin, Ireland. He moved to Clontarf, Dublin and became the Director of the School for Theoretical Physics and remained there for 17 years, during which time he became a naturalized Irish citizen.

Davisson-Germer Experoment



Davisson and Germer built a vacuum apparatus for the purpose of measuring the energies of electrons scattered from a metal surface. Electrons from a heated filament were accelerated by a voltage and allowed to strike the surface of nickel metal. 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.

Who is Davisson?

Clinton Joseph Davisson
(B. 1881 – D. 1958), was an American physicist who won the 1937 Nobel Prize in Physics for his discovery of electron diffraction. Davisson shared the Nobel Prize with George Paget Thomson, who independently discovered electron diffraction at about the same time as Davisson.

Lester Halbert Germer (B.1896 – D. 1971) was an American physicist. With Clinton Davisson, he proved the wave-particle duality of matter in the Davisson-Germer experiment, which was important to the development of the electron microscope. These studies supported the theoretical work of De Broglie.

George Thomson

Sir George Paget Thomson,
(B.1892 – D1975) was an English physicist and Nobel laureate in physics. George Thomson was jointly awarded the Nobel Prize for Physics in 1937 for his work in Aberdeen in discovering the wave-like properties of the electron. Whereas his father had seen the electron as a particle (and won his Nobel Prize in the process), Thomson demonstrated that it could be diffracted like a wave, a discovery proving the principle of wave-particle duality which had first been posited by Louis-Victor de Broglie in the 1920s as what is often dubbed the de Broglie hypothesis. In the late 1930s and during the Second World War Thomson specialised in nuclear physics, concentrating on practical military applications. In particular Thomson was the chairman of the crucial MAUD Committee in 1940-1941 that concluded that an atomic bomb was feasible. In later life he continued this work on nuclear energy but also wrote works on aerodynamics and the value of science in society.

Pauli and von Neumann

I remember a talk between Pauli and von Neumann much later, in which this opposition between the two possibilities came out quite clearly. Pauli himself was definitely, in this sense, a pupil of Sommerfeld; he was not interested in proofs. And von Neumann, being an excellent mathematician, of course was very interested in having rigorous proofs. Von Neumann told Pauli, "I can prove this and this," and then Pauli said, "Well, if a proof was important in physics, you would be a great physicist." You know, Pauli was always very shocking in this way…

Interview with Werner Heisenberg
by T. S. Kuhn at the Max Planck Institute,
Munich, Germany
February 7, 1963

Inclusion of spin

In 1927 Wolfgang Pauli invited a way to accommodate spin in the quantum mechanics. The first step he invited 2x2 matrix called Pauli matrices:

$$
\begin{aligned}
S_i &\equiv \frac{\hbar}{2}\sigma_i \\
\vec{S} &= \frac{\hbar}{2}\vec{\sigma}
\end{aligned}
$$

$$
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
$$

$$
\begin{aligned}
[\sigma_i, \sigma_j] &= 2i\epsilon_{ijk}\sigma_k \\
\sigma_i^2 &= 1
\end{aligned}
$$

Those matrices satisfies the anti-commutation relations:

$$
\sigma_x\sigma_y = -\sigma_y\sigma_x \qquad \sigma_x\sigma_z = -\sigma_z\sigma_x \qquad \sigma_z\sigma_y = -\sigma_y\sigma_z
$$

$$
\{\sigma_i, \sigma_j\} = 2\delta_{ij}
$$

Pauli Equation

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

The usual basis states are the eigenstates of S_Z.We know from our study of angular momentum, that the eigenvalues of Sz are +1/2ħ and-1/2 ħ We will simply represent the +1/2ħ eigenstate as the upper component of a 2-component vector. The -1/2ħ eigenstate amplitude is in the lower component.

The extended Schrödinger Equation with spin is

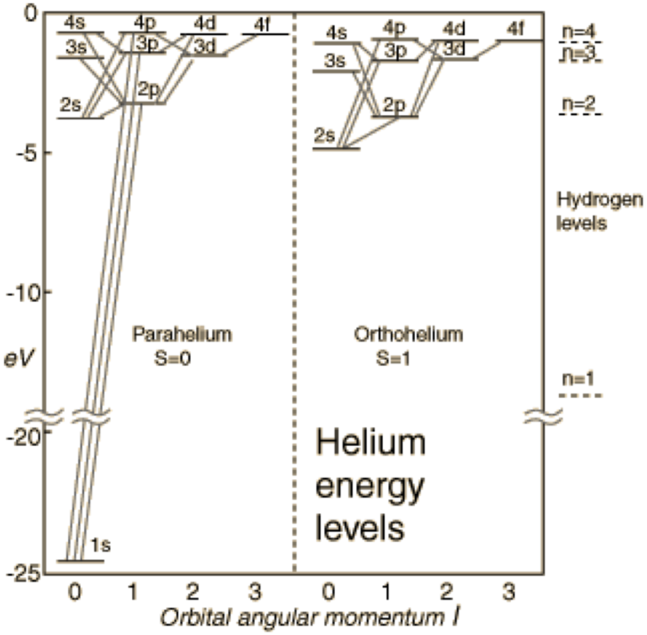
$$\left[\frac{1}{2m}\left(\sum_{n=1}^{3}(\sigma_n(-i\hbar\frac{\partial}{\partial x_n}-qA_n))\right)^2+q\phi\right]\begin{pmatrix}\psi_0\\ \psi_1\end{pmatrix}=i\hbar\begin{pmatrix}\frac{\partial\psi_0}{\partial t}\\ \frac{\partial\psi_1}{\partial t}\end{pmatrix}$$

With an external electromagnetic field the **full Pauli equation** reads

$$\underbrace{i\hbar\partial_t\vec{\varphi}_\pm=\left(\frac{(\vec{p}-q\vec{A})^2}{2m}+q\phi\right)\hat{1}\vec{\varphi}_\pm}_{\text{Schrödinger equation}}-\underbrace{\frac{q\hbar}{2m}\vec{\sigma}\cdot\vec{B}\vec{\varphi}_\pm}_{\text{Stern Gerlach term}}$$

Helium spectrum and spin

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$



Helium energy levels

$$E = E_{n_1} + E_{n_2} = -\frac{1}{2} Z^2 \alpha^2 m_e c^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right) = -54.4 \text{ eV} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right).$$

$$E_{11} = E_{gs} = -108.8 \text{ eV}$$

$$\Delta E_{gs} = \langle u_0 | V | u_0 \rangle = \int d^3 r_1 d^3 r_2 |\phi_{100}(\vec{r}_1)|^2 |\phi_{100}(\vec{r}_2)|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{5}{8} \frac{Ze^2}{a_0} = \frac{5}{4} Z (\frac{1}{2} \alpha^2 mc^2) = \frac{5}{4} (2)(13.6) = 34 \text{ eV}$$

$$E_{gs} = -108.8 + 34 = -74.8 \text{ eV}$$

First electron: $-54.4 \text{ eV} = Z^2 \ (-13.6 \text{ eV})$; $Z = 2$

Second electron: $-24.6 \text{ eV} = Z_{\text{eff}}^2 \ (-13.6 \text{ eV})$; $Z_{\text{eff}} = 1.34$

Spin exchange force

If you have two electrons, then the state in which their spins are parallel (S=1, triplet state) will be lower in energy than the state in which their spins are antiparallel (S=0, singlet state). Why? The interaction between magnetic dipole is too small to explain it. Heisenberg resolved this problem by Pauli exclusion principle:

$$\Psi_{2e(\text{antisymmetric})} = \underset{(\text{symmetric})}{\Psi_{\text{spin}}} \times \underset{(\text{antisymmetric})}{\Psi_{\text{space}}}$$

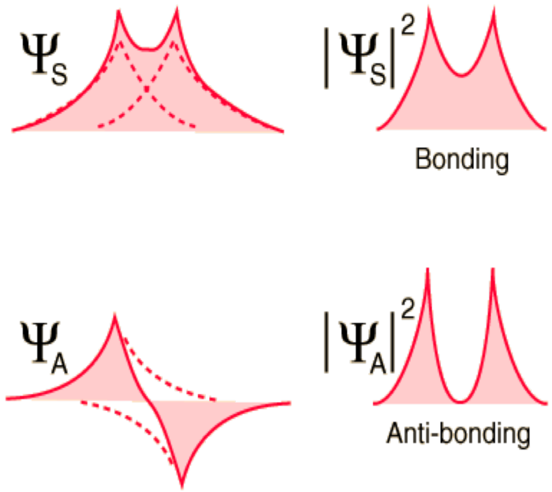
$$\psi_A = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)\right]$$

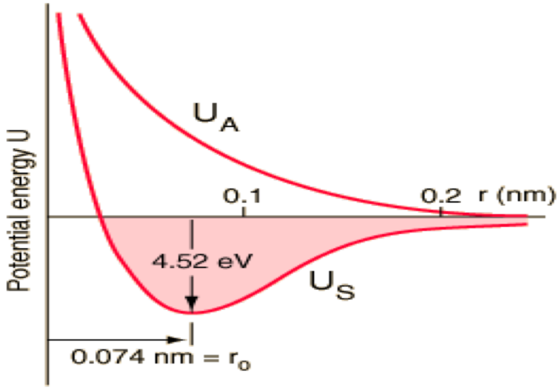
$$\psi_S = \frac{1}{\sqrt{2}}\left[\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)\right]$$

$$\begin{aligned}
\chi_{s=1,m=1} &= \chi_+^{(1)}\chi_+^{(2)} \\
\chi_{s=1,m=0} &= \frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_+^{(2)}\right) \\
\chi_{s=1,m=-1} &= \chi_-^{(1)}\chi_-^{(2)}
\end{aligned}$$

$$\chi_{s=0,m=0} = \frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right)$$

Spin Exchange Force





The fact that the spins are parallel makes the spin part of the wavefunction symmetric, and forces the space part to be antisymmetric. An anti-symmetric space wavefunction for the two electrons implies a larger average distance between them than a symmetric function of the same type. The probability is the square of the wavefunction, and from a simple functional point of view, the square of an antisymmetric function must go to zero at the origin. So in general, the probability for small separations of the two electrons is smaller than for a symmetric space wavefunction. If the electrons are on the average further apart, then there will be less shielding from the nucleus by the other electron, and a given electron will therefore be more exposed to the nucleus. This implies that it will be more tightly bound and of lower energy.

Heisenberg vs. Schrödinger

The more I think about the physical portion of Schrödinger's theory, the more repulsive I find it...What Schrödinger writes about the visualizability of his theory 'is probably not quite right,' in other words it's crap.
--Heisenberg, writing to Pauli, 1926

knew of [Heisenberg's] theory, of course, but I felt discouraged, not to say repelled, by the methods of transcendental algebra, which appeared difficult to me, and by the lack of visualizability.
Schrödinger in 1926

Double faces of Quantum mechanics

Early quantum theory had two approaches: Matrix mechanics proposed by Heisenberg and wave mechanics developed by Schrödinger. Heisenberg found the physical ideas of Schrödinger's theory "disgusting," and Schrödinger was "discouraged and repelled" by lack of visualization in Heisenberg's method

The underlying mathematical framework is Hilbert space developed Hilbert.

When his colleague Richard Courant wrote the now classic Methods of Mathematical Physics including some of Hilbert's ideas, he added Hilbert's name as author even though Hilbert had not directly contributed to the writing

Hilbert said "Physics is too hard for physicists", the Courant-Hilbert book made it easier for them.

Firm as a rock, at last

John von Neumann
(B 1903 – D 1957)
was an Austro-Hungarian-born
American mathematician

After hearing Heisenberg lecture on matrix mechanics, von Neumann decided to develop his own version of quantum mechanics--the matrices of Heisenberg were "too imprecise."

In his book (1932), The *mathematical Foundations of Quantum Mechanics*, von Neumann invented operator theory (now called Neumann algebras) to explain certain aspects of quantum mechanics.

Largely because of his work, quantum physics and operator theory can be viewed as two aspects of the same subject. von Neumann's new mathematics proved Schrödinger and Heisenberg theories equivalent mathematically.

Pauli and von Neumann

I remember a talk between Pauli and von Neumann much later, in which this opposition between the two possibilities came out quite clearly. Pauli himself was definitely, in this sense, a pupil of Sommerfeld; he was not interested in proofs. And von Neumann, being an excellent mathematician, of course was very interested in having rigorous proofs. Von Neumann told Pauli, "I can prove this and this," and then Pauli said, "Well, if a proof was important in physics, you would be a great physicist." You know, Pauli was always very shocking in this way…

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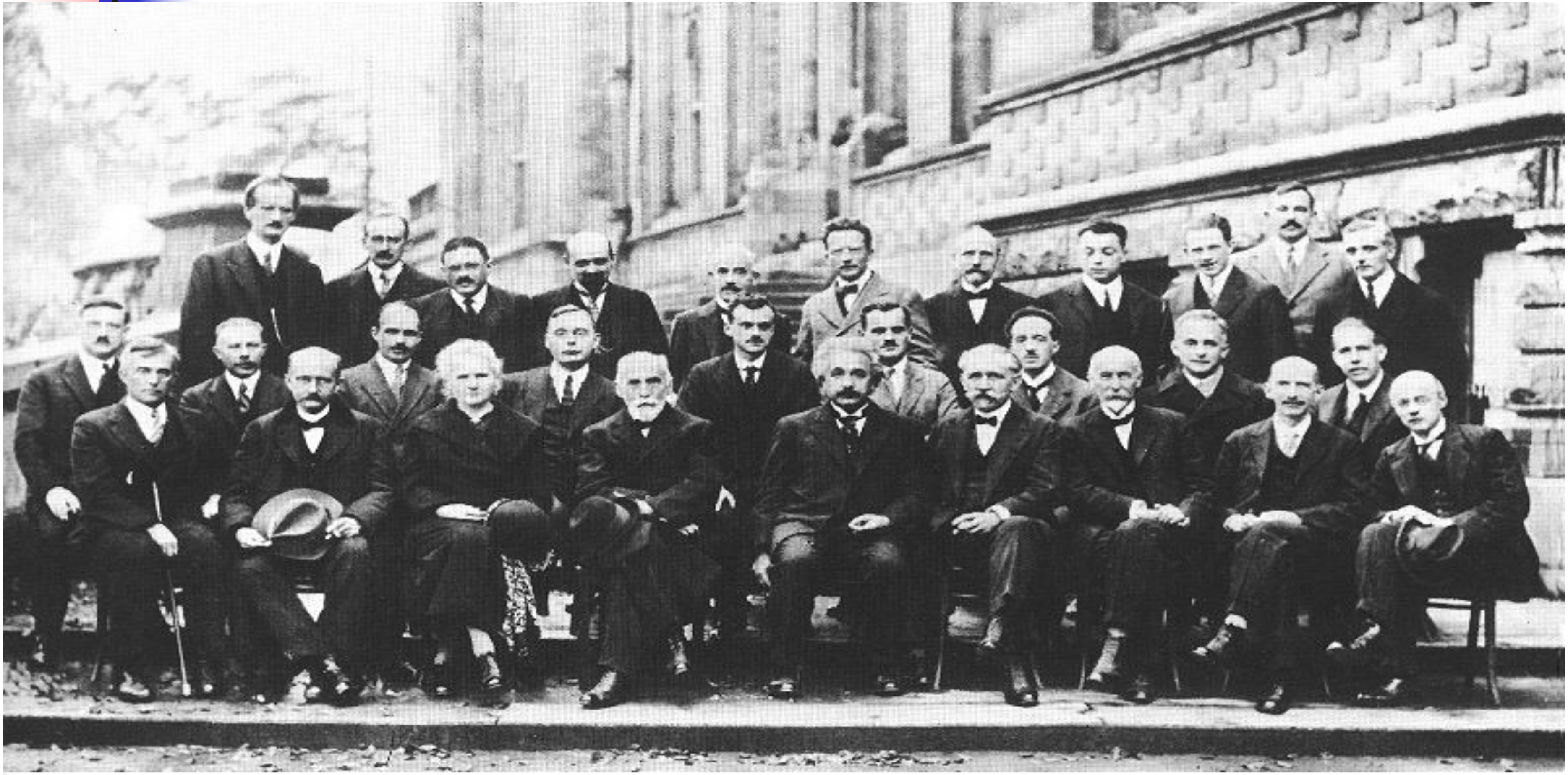
Era for Heroes –Young and Old
1927 Solvay Conference



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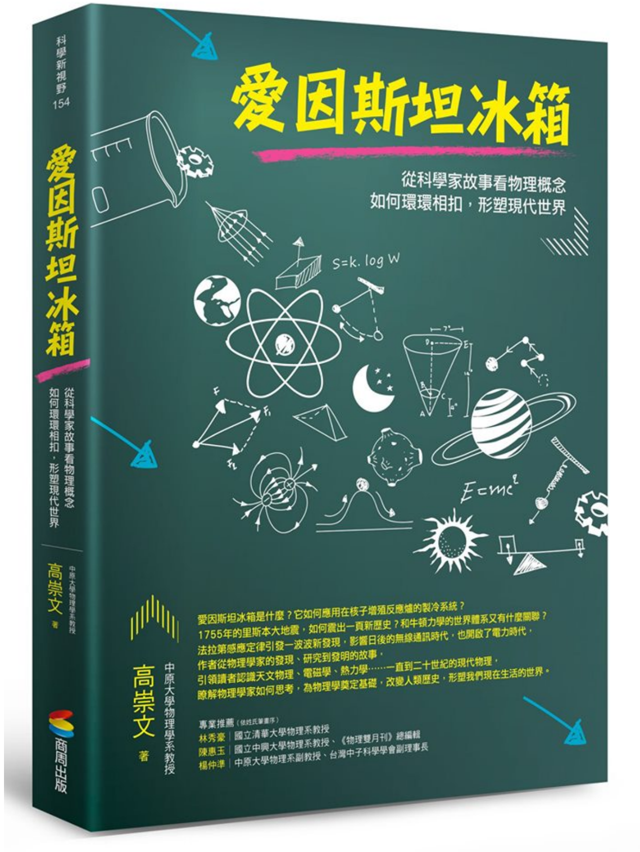

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