Early history of quantum mechanics

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Introducing quantum theory...

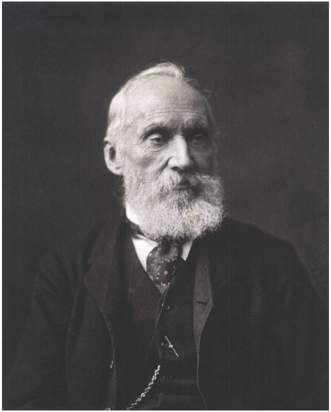
The following material draws heavily on J.P. McEnvoy and Oscar Zarate, *Introducing Quantum Theory*, Icon Books, 2004. In order to not overload the presentation, I refrain from giving proper citations each time.

- QT is arguably the most successful set of ideas ever devised by humans.
- Its predictions on the behavior and properties of subatomic particles and about the operation of lasers and microchips is astonishing.
- It explains the periodic chart of the elements and why chemical reactions take place.
- It predicts the stability of DNA and many things more...
- Let's start with a bit of classical physics in order to fully appreciate the novelty of QT.

Classical physics

- Mathematical formalism of classical physics of Isaac Newton (1642-1727)'s mechanics and James Clerk Maxwell (1831-79)'s electrodyamics was impeccable, and their thys well confirmed by many careful experiments.
- Newton's Law of Universal Gravitation has been used to predict the movement of planets w/ great accuracy, and helped predict the existence of Neptune.
- Maxwell predicted the existence of invisible "light" waves, and Heinrich Hertz (1857-94) detected the signals (radio waves) in 1888 in his Berlin laboratory.
- Radio waves reflect and refract just like light, as predicted by Maxwell.
- In short, classical physics was explanatorily powerful, predictively accurate, almost complete, s.t. most physicists thought that there were only a very few small mob-up operations left to finish the building of classical physics.
- It turns out they're wrong...

"Two dark clouds"



- Lord Kelvin (1824-1907), then at Glasgow University, spoke of only two dark clouds on the Newtonian horizon.
- One of these clouds would disappear only with the advent of Relativity and the other would lead to QT.

“Fill in the sixth decimal place”

- Albert Michelson (1852-1931), though he was paraphrasing Kevlin in a remark which he regretted for the rest of his life:
- “All that remains to do in physics is fill in the sixth decimal place.”
- Let’s look at the basic assumptions of classical physics, all of which would eventually prove to be in doubt...

The fundamental assumptions of classical physics

Assumption (Mechanism)

The universe was like a giant machine set in a framework of absolute time and space. Complicated movement could be understood as a simple movement of the machine's inner parts.

Assumption (Causality)

The Newtonian synthesis implied that all motion had a cause. If a body exhibited motion, one could always be figure out what was producing the motion. This is simply cause and effect.

Assumption (Determinism)

If the state of the universe was completely given at one moment in time (e.g. the present), together with all the dynamic laws, it could be determined at any other moment in the future or the past. This is (Laplacian) determinism.

Assumption (Light)

The properties of light are completely described by Maxwell's electromagnetic wave thy and confirmed by the interference patterns observed in a simple double-slit experiment by Thomas Yound in 1802.

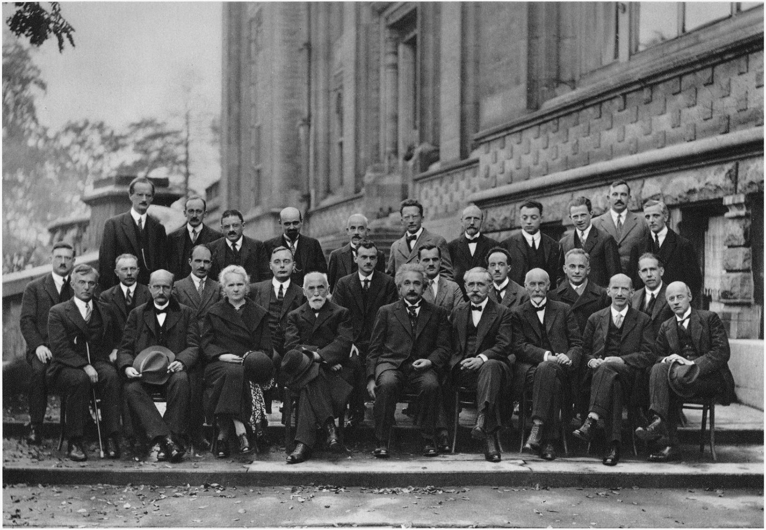
Assumption (Energy in motion)

There are two physical models to represent energy in motion: one a particle, represented by an impenetrable sphere (like a billiard ball), and the other a wave, like that which rides towards the shore in La Jolla Shores. They are mutually exclusive, i.e. energy must be either one or the other.

Assumption (Arbitrary accuracy of measurement)

It was possible to measure to any degree of accuracy the properties of a system, like its temperature or speed. Atomic systems were thought to be no exception.

Solvay Conference, Brussels, October 1927



The Solvay conference 1927

- Belgian industrialist Ernest Solvay (1838-1922) sponsored series of international meeting for which attendance was by invitation only, and participants were asked to concentrate on a pre-arranged topic.
- first five meetings held bw 1911 and 1927 chronicled in a most remarkable way the development of C20 physics
- 1927 meeting on QT, attended by nine physicists who were later awarded Nobel prize for their contributions to QT
- 17 of the 29 attendees were or became Nobel Prize winners, including Marie Curie (1867-1934) (only one with 2 NPs)
- McEnvoy: "There is hardly any period in the history of science in which so much has been clarified by so few in so short a time."
- 1927 meeting is famous as starting point of epic debate bw Albert Einstein (1879-1955) and Niels Bohr (1885-1962)

Thermodynamics

- We need some background in thermodynamics, which means "movement of heat".
- Heat flows from body of higher temperature to body of cooler temp, until the temps of the two bodies are the same ⇒ thermal equilibrium
- Mechanical models to explain the flow of heat developed quickly in C19 Britain, building on achievements of James Watt (1736-1819), who built a working steam engine.
- James Joule (1818-89) showed that a quantity of heat can be equated to a certain amount of mechanical work.

⇒ beginning of study of thermodynamics

The first law of thermodynamics

Hermann von Helmholtz (1821-94):

Law (Conservation of energy)

Whenever a certain amount of energy disappears in one place, an equivalent amount must appear elsewhere in the same system.

The second law of thermodynamics

Rudolf Clausius (1822-88):

Law

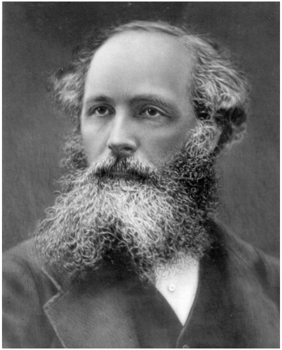
The entropy of an isolated system always increases, reaching a maximum at thermal equilibrium, i.e. when all bodies in the system are at the same temperature.

Reason: total entropy of a system increases when heat flows from a hot body to a cold one; but since heat had always been observed to flow from hot to cold, the second law follows

"If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations—then so much the worse for Maxwell's equations. If it is found to be contradicted by observation— well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation."

— Sir Arthur Eddington, 1915

Maxwell's distribution



- Maxwell developed his kinetic thy of gases by picturing the gas to consist of billions of molecules moving at random, colliding with each other and with the walls of the container.
- assumption: heating causes molecules to move faster and bang into the container walls more frequently.
- Maxwell's thy based on statistical averages and tried to recover macroscopic (measurable) properties from the microscopic model for a collection of gas molecules.

Maxwell's assumptions

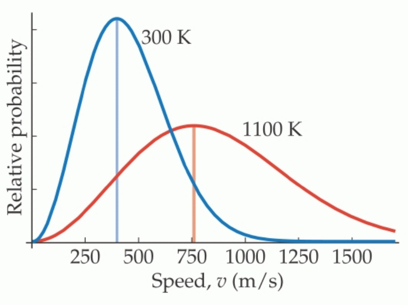
1. The molecules are like hard spheres with their diameters much smaller than the distance bw them.
2. The collisions bw molecules conserve energy.
3. The molecules move bw collisions without interacting at a constant speed in a straight line.
4. The positions and velocities of the molecules are initially at random. (most unusual and revolutionary)

The necessity of statistical averages

- Why did Maxwell use statistical averages rather than exact determinations of the particles' states?
- Number too large: one mole of gas (a few grams) contains 6×10^{23} molecules
- Just to get a feel for this number: check Isaacson bio for Avogadro's number
- Using these assumptions, Maxwell was able to show that temperature is a measure of the microscopic mean squared velocity, i.e. of the kinetic energy of the molecules

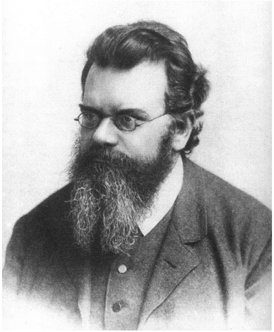
$\Rightarrow$ Heat is thus caused by the ceaseless random motion of molecules.

Relevance of Maxwell's analysis: Maxwell distribution



- Maxwell: prediction of the probable velocity distribution of the molecules
- gives probability that a molecule chosen at random would have a particular velocity

Ludwig Boltzmann (1844-1906)



- derived dynamical equation of velocity distribution of micro particles ("Boltzmann equation")
- Maxwell distribution is only possible stationary solution of this equation, i.e. the only possible dynamical equilibrium
- H-Theorem: entropy of ideal gas must increase, also at the level of micro particles

Boltzmann's new interpretation of the second law

Boltzmann gave a new interpretation to the second law:

- When energy in a system is “degraded”, the atoms in the system become more disordered and the entropy increases. But a measure of the disorder can be made...
- Boltmann entropy: $S = k \cdot \log W$, where k is the Boltzmann constant, and W is a measure for how many microscopic ways there are to produce the particular macroscopic state.
- Boltzmann argued that a system will evolve from a less probable state to a more probable state when agitated by heat or mechanical vibration, until thermal equilibrium is reached.
- At equil, system will be in its most probable state when the entropy is a maximum.
- A minuscule, but non-zero, probability exists that all the molecules of a system of confined gas might appear for an instant in just one corner of the container.
- This possibility must exist if the probabilistic interpretation of entropy is to be allowed. It's called an energy fluctuation.

Three critical experiments

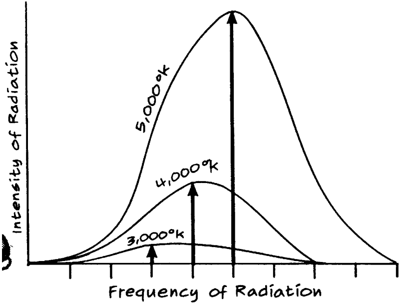
Experiments in pre-quantum era which classical physics failed to account for:

1. Black-body radiation and the ultraviolet catastrophe (Planck's quantum)
2. Photoelectric effect (Einstein's light particles)
3. Bright line optical spectra (Bohr's atom)

- each involved the interaction bw matter and radiation
- experiment engendered crisis in fundamental physics
- solutions offered by Max Planck (1858-1947), Einstein and Bohr
- Combined work of these three men, culminating in the Borh model of the atom in 1913, is known as the Old Quantum Theory

(1) Black-body radiation

- When an object is heated, it emits radiation consisting of electromagnetic waves with a broad range of frequencies.
- Measurements made on the radiation escaping from a small hole in a closed heated oven ("cavity") shows that the intensity of the radiation varies very strongly with the frequency of the radiation.
- The peak of the frequency distribution shifts to higher value as the temperature is increased, as shown in the graph drawn from measurements made in the late C19:



A black body

Definition (Black body)

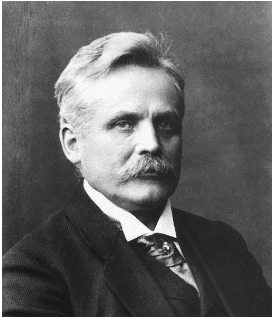
A black body is a body that completely absorbs all the electromagnetic radiation falling into it.

- Inside a cavity, the radiation has escape and is continually being absorbed and re-emitted by the inside of the walls.
- Small opening gives off radiation emitted by walls, not reflected.

$\Rightarrow$ radiation is characteristic of black body

- Important: frequency distribution of radiation only depends on temp (under equilibrium conditions)
- for high temps, oven glows in visible range: it appears red (at around 800°C, and regardless of what's inside, coal, glass, metal) although it's a black body!

Wilhelm Wien (1864-1928)



- recorded colour distribution of radiation (bw near infrared into violet) escaping through opening in the 1890s

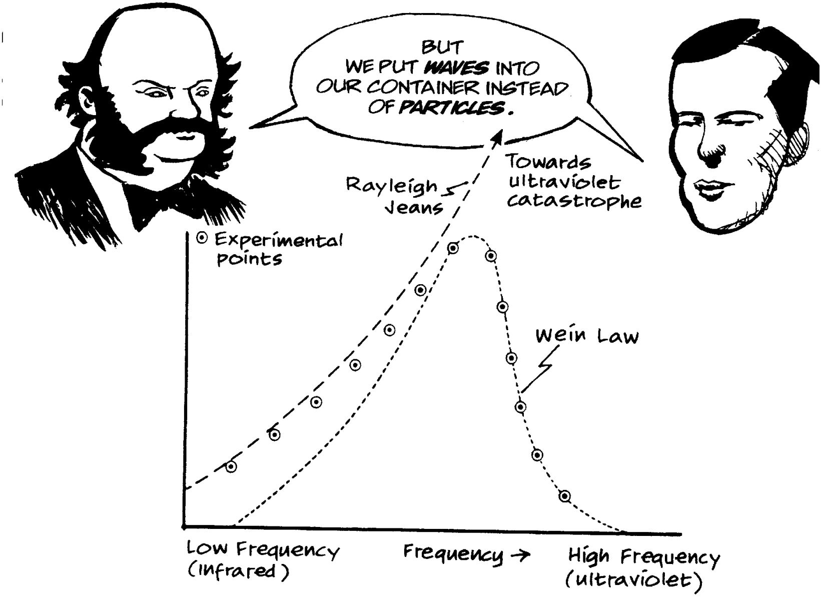
$\Rightarrow$ experimental distribution of frequencies of radiation as fct of T

- Wien derived formula (based on some dubious theoretical arguments) that agreed well with published experiments, but only at the high frequency part of spectrum.

Lord Rayleigh (1842-1919) and Sir James Jeans (1877-1946)

- Rayleigh and Jeans derived a different formula (putting waves rather than particles into the cavity).
- Their eq agreed well with the observed spectrum at low frequencies.
- Shock at high freqs: classical thy predicted an infinite intensity for the ultraviolett region and beyond.

$\Rightarrow$ "ultraviolett catastrophe"


BUT WE PUT WAVES INTO OUR CONTAINER INSTEAD OF PARTICLES.
Rayleigh Jeans
Towards ultraviolet catastrophe
Experimental points
Wein Law
Low Frequency (infrared)
Frequency →
High Frequency (ultraviolet)

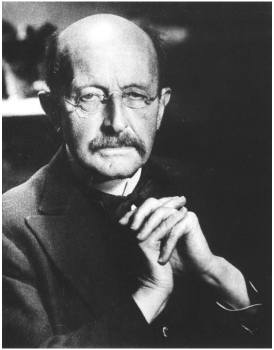
The ultraviolet catastrophe

- serious paradox in physics: if the Rayleigh-Jens formula were right, it would be dangerous even to sit in front of a fireplace; but everyone agreed that their method was sound...
- They applied the method from stat physics to the waves by analogy with Maxwell's gas particles using the equipartition of energy, i.e. that the total energy of radiation is distributed equally among all possible vibration frequencies.
- Problem: for waves, there's no limit on the number of modes of vibration that can be excited (bc one can fit more and more waves into the container at higher and higher frequencies)

$\Rightarrow$ Amount of radiation predicted by the thy quickly diverges as the temp is raised and the frequencies increase

Enter Max Planck (1858-1947)

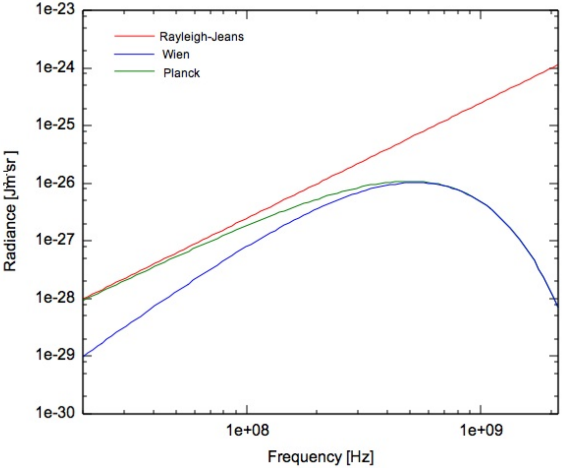
Enter Max Planck (1858-1947)



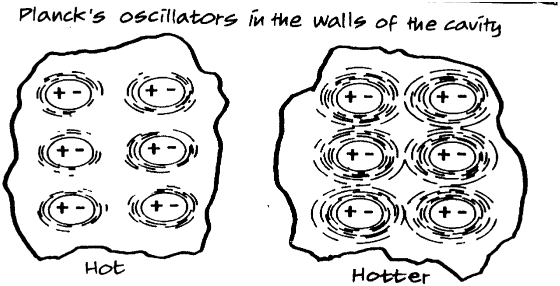
- Munich physics professor Philipp von Jolly advised him against going into physics, saying, "in this field, almost everything is already discovered, and all that remains is to fill a few holes."
- Planck replied that he didn't wish to discover new things, only to understand the known fundamentals of the field and began his studies in 1874 in Munich.
- 1879 PhD
- academic positions at Munich, Kiel, Berlin
- worked extensively on thermodynamics
- 1918 Nobel prize

Finding the correct radiation frequency distribution

In 1900, Planck successfully formulated the Black-Body Radiation Law, found to be in extraordinary agreement with data:



Pre-atomic model of matter



- Planck introduced idea of a collection of electric oscillators in the walls of the cavity, vibrating under thermal agitation.
- assumed that all possible frequencies would be present and expected the average frequency to increase for higher T

Planck's law

- Making further thermodynamic assumptions relating the average energy of the oscillators to their entropy, he eventually arrived at the correct formula, communicated at the Physics Seminar of the University of Berlin on 19 October 1900:

$$u(f, T) = \frac{c_1 f^3}{\exp(-c_2 f/T) - 1},$$

  where u is the energy density of the radiation, f its frequency, T the temp, and c_1 and c_2 two constants that he adjusted to the data.
- Planck had found the correct formula for the radiation law; but what was its physical meaning?

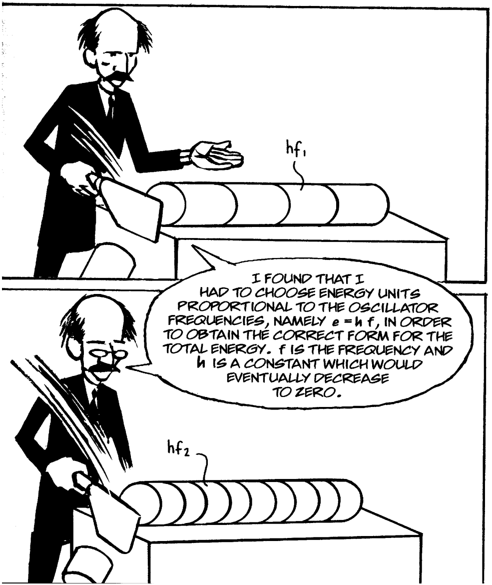
Interpreting Planck's law

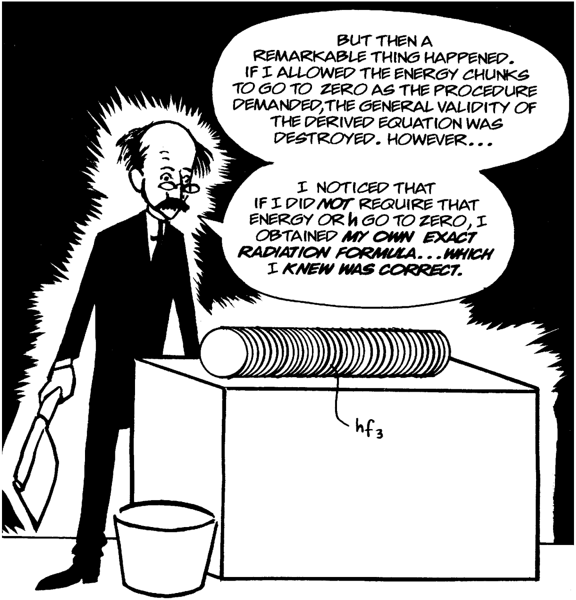
- After many futile attempts, Planck reluctantly turned to Boltzmann's statistical version of the second law, and applied three of Boltzmann's ideas about entropy:
  1. his statistical eq to calculate the entropy
  2. his condition that the entropy must be a maximum at equil
  3. his counting technique to determine the measure W in the entropy eq for how many microscopic ways there are to produce a macroscopic state

$\Rightarrow$ Planck divided the energy of the oscillators into arbitrarily small but finite chunks.

$\Rightarrow$ total energy $E = Ne$ where $N \in \mathbb{N}$ and e an arbitrarily small amount of energy.

- Planck's idea: let $e \rightarrow 0$ and $N \rightarrow \infty$ to get the correct result for E in the limit


hf₁
I FOUND THAT I HAD TO CHOOSE ENERGY UNITS PROPORTIONAL TO THE OSCILLATOR FREQUENCIES, NAMELY e = h f, IN ORDER TO OBTAIN THE CORRECT FORM FOR THE TOTAL ENERGY. f IS THE FREQUENCY AND h IS A CONSTANT WHICH WOULD EVENTUALLY DECREASE TO ZERO.
hf₂

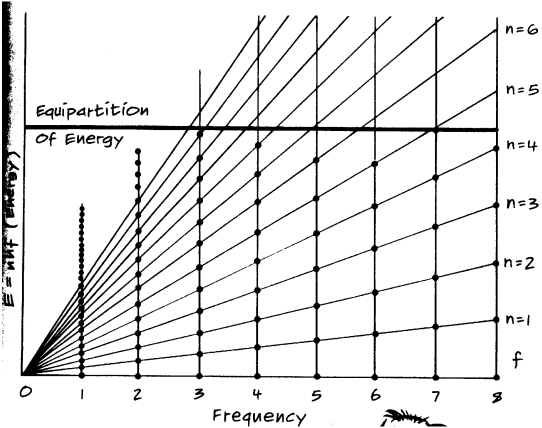

BUT THEN A REMARKABLE THING HAPPENED. IF I ALLOWED THE ENERGY CHUNKS TO GO TO ZERO AS THE PROCEDURE DEMANDED, THE GENERAL VALIDITY OF THE DERIVED EQUATION WAS DESTROYED. HOWEVER...
I NOTICED THAT IF I DID NOT REQUIRE THAT ENERGY OR h GO TO ZERO, I OBTAINED MY OWN EXACT RADIATION FORMULA... WHICH I KNEW WAS CORRECT.
hf3

A quantum of energy

- OK, so he had found a theoretical basis for his experimental radiation law, but only if he assumed that energy was discontinuous!
- If correct, this means that an oscillator cannot absorb and emit energy in a continuous range, but only is minuscule, indivisible units of hf.
- Planck called these units energy quanta.

$\Rightarrow$ theoretical explanation why the classical thy failed at high frequencies:

In this region, the quanta are so large that only a few vibration modes are excited. With a decreasing number of modes to excite, the radiation drops off to zero at the high frequency end.



⇒ ultraviolet catastrophe does not occur!

- Rayleigh-Jeans works well at low frequencies where all available vibrational modes can be excited.
- At high frequencies, even though plenty of modes are possible, not many are excited bc it costs too much energy to make a quantum at a high frequency ($e = hf$)
- During his early morning walk on 14 December 1900, he told his son that he may have produced a work as important as that of Newton.
- Later that day, he presented his results to the Berlin Physical Society signalling the birth of quantum physics.
- In early 1901, the constant h, "Planck's constant" appeared in print for the first time.
- $h = 6.626 \times 10^{-34}$ Js
- $h \neq 0$ ($\Rightarrow$ we can sit in front of a fire without getting burnt)

A revolutionary against his will

Helge Kragh, “Max Planck: the reluctant revolutionary”, *Physics World*, online 1 Dec 2000.

- The introduction of energy quanta in 1900 was “a purely formal assumption and I really did not give it much thought except that no matter what the cost, I must bring about a positive result.” (in a letter written in 1931)
- He considered the energy quanta as “a kind of mathematical hypothesis, an artefact that did not refer to real energy exchanges between matter and radiation.” (Kragh, p. 4)
- Only in 1908 “did Planck convert to the view that the quantum of action represents an irreducible phenomenon beyond the understanding of classical physics.” (ibid.)
- In a lecture given in 1911: “The hypothesis of quanta will never vanish from the world... I do not believe I am going too far if I express the opinion that with this hypothesis the foundation is laid for the construction of a theory which is someday destined to permeate the swift and delicate events of the molecular world with a new light.”

(2) The photoelectric effect

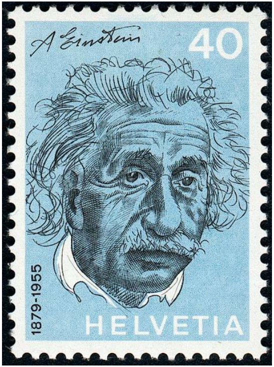
- Philipp Lenard (1862-1947) focused cathode rays (soon to be identified as electrons) at thin metal foils.
- In 1899, he started doing the same with light rays and discovered that the light ejects electrons from the metal.
- Tutored by his classical intuition, he expected that the emitted electrons would acquire their kinetic energy from the light beam. But this was not what he observed...

Lenard's observations

In fact, Lenard made several surprising observations:

1. In 1902, he discovered that the electron energies where entirely independent of the light intensity, but depended on the frequency (= colour) of the incident light.
2. Also, for a given frequency of the incident light, the rate at which electrons were ejected from the metal was directly proportional to the intensity of the light.
3. Furthermore, there was a certain threshold frequency below which no electrons were ejected, independently of the intensity of the light.

Enter Albert Einstein (1879-1955)



- At the time, Einstein was a young clerk at the Swiss Patent Office in Bern.
- In 1905, his Annus mirabilis, Einstein published five landmark essays that would forever change physics:
  1. photoelectric effect (finished 17 March) ($\Rightarrow$ Nobel 1921)
  2. dissertation, proving the existence of atoms (30 April)
  3. Brownian motion (11 May)
  4. special relativity (30 June)
  5. $E = mc^2$ (27 September)

"Never before and never since has a single human enriched science in such short time by so much as did Einstein enrich physics in this 'annus mirabilis'." (Albrecht Fölsing, 1993, p. 143)

Einstein's explanation of the photoelectric effect

- Einstein: $\exists$ deep theoretical asymmetry: Maxwell's electromagnetism treated continuous processes in space, but Boltzmann's (and Maxwell's!) statistical approach to thermodyn phenomena presupposed discrete particles.
- of paramount importance if one wanted to get a handle on the interaction bw radiation and matter
- Based on considerations on Boltzmann's second law and the statistical behavior of waves and particles, as well as on Wien's law, he derived an eq for the energy of the radiation: $E = nk\beta f$.

$\Rightarrow$ within the validity of Wien's law, radiation behaves thermodynamically as if it consists of mutually independent energy quanta of magnitude $k\beta f$.

- IOW, like light particles.

"On a heuristic viewpoint concerning the nature of light"

Annalen der Physik 17 (1905): 132-148

Einstein showed that the puzzling features discovered by Lenard are readily explained if one assumed that light consisted of particles or photons:

"According to the view that the incident light consists of energy quanta [photons] of magnitude [hf], it is possible to conceive of the ejection of electrons by light as follows. Energy quanta penetrate the surface layer of the metal of the target electrode. Their energy is transformed, at least in part, into the kinetic energy of the electrons." (145, my very liberal translation)

Imagine that a light quantum delivers its entire energy hf to the electron which then loses some of its energy to reach the surface of the metal, which means that those electrons closest to the surface will have the highest energy. The kinetic energy of the electrons will be given by $E_k = hf - P$, where P is the emission work.

$\Rightarrow$ simple eq that can be tested experimentally

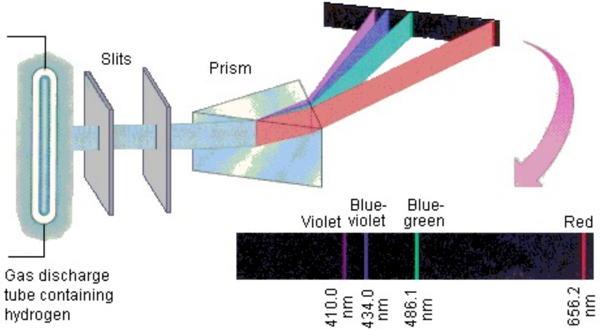
- Observation that energy of electrons does not respond to changes in intensity, but only depends on frequency was explained quite simply.
- Intensity only affects the number of electrons ejected and thus the magnitude of electron current.
- Finally, it was also clear why there would be threshold frequency below which no electrons would be ejected.

Robert Millikan (1868-1953)

- Ryerson Laboratories at the University of Chicago, Nobel Prize 1923
- tested Einstein's prediction, using various methods
- "I spent ten years of my life testing that 1905 equation of Einstein's, and, contrary to all my expectations I was compelled in 1915 to assert its unambiguous experimental verification in spite of its unreasonableness since it seemed to violate everything that we knew about the interference of light." (*Reviews of Modern Physics* 21 (1949): 1-13.)

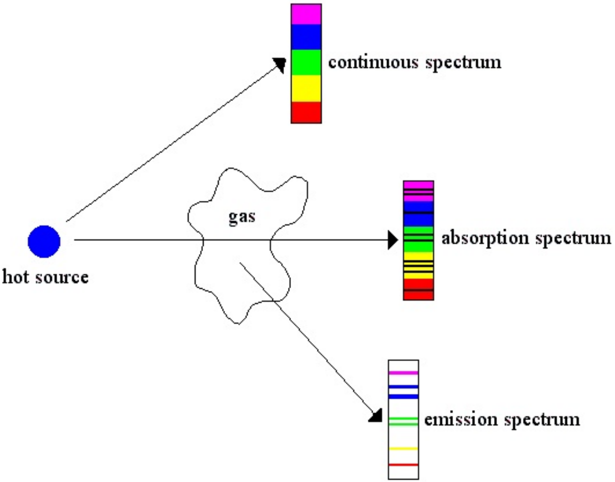
(3) Bright line optical spectra

Spectrum of light emitted from a hot gas when passed through a prism is very different from the rainbow-like spectrum of a glowing solid (e.g. the sun):



Different gases have different spectral lines.

Different types of spectra

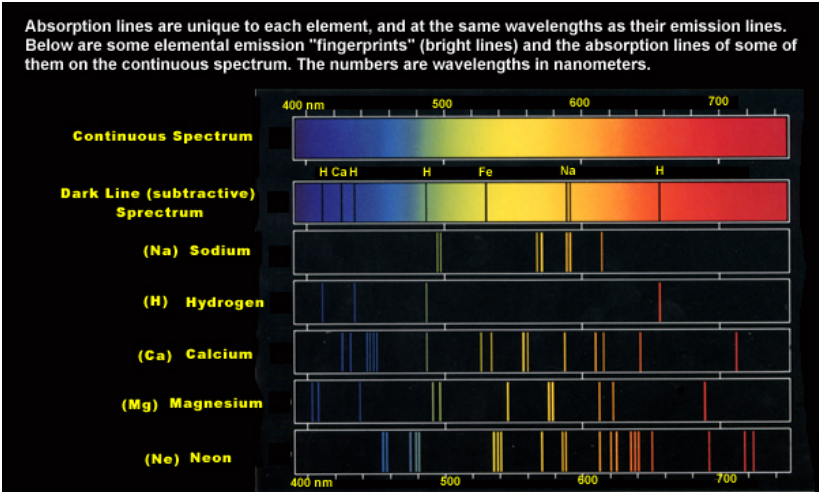


Bright line and dark line spectra

- Hot gases emit spectra with characteristic bright lines ("emission spectrum").
- But cool gases also absorb light of characteristic wavelengths, creating dark line spectra ("absorption spectrum").
- These lines (in both cases) can be photographed with a sensitive device called spectrometer.
- Amazing: the "missing" lines in a dark line spectrum exactly match the lines in a bright line spectrum if for both the exact same gas is used! (cf. figure on next page)

$\Rightarrow$ The cool (unexcited) gas is absorbing light at precisely the same frequencies at which this same gas emitted light when heated.

$\Rightarrow$ $\exists$ certain characteristic energy states in a gas that are reversible, i.e. it can take in or give off energy...


Absorption lines are unique to each element, and at the same wavelengths as their emission lines. Below are some elemental emission "fingerprints" (bright lines) and the absorption lines of some of them on the continuous spectrum. The numbers are wavelengths in nanometers.
400 nm
500
600
700
Continuous Spectrum
H Ca H
H
Fe
Na
H
Dark Line (subtractive) Sprectrum
(Na) Sodium
(H) Hydrogen
(Ca) Calcium
(Mg) Magnesium
(Ne) Neon
400 nm
500
600
700

Joseph von Fraunhofer (1787-1826)

Joseph von Fraunhofer
(1787-1826)

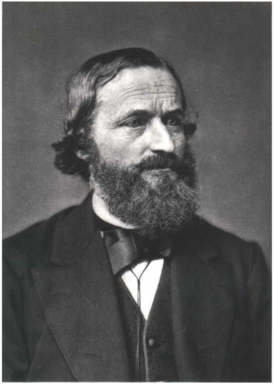
⇒ line spectra give precise information about a gas

- In 1814, he created the first spectroscope (combining a prism with a small viewing telescope focused on a distant narrow slit.
- When he looked at the sun's spectrum, he found an almost countless number of dark lines in the spectrum.

⇒ Fraunhofer lines, important in astrophysical spectroscopy


80
Fig. 6.
A a B C D E b F G
Sonnenspektrum mit Fraunhofer Linien
Joseph von Fraunhofer Optiker und Physiker 1787-1826 Deutsche Bundespost
1987

Gustav Kirchhoff (1824-87): the discovery of helium



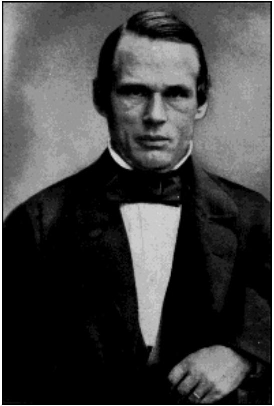
- studied Fraunhofer lines by superimposing the bright yellow lines of a salt (NaCl) solution onto the solar spectrum, and found an exact match

$\Rightarrow$ dark lines due to presence of cool vapours of NaCl in solar atmosphere

- When a previously unobserved pattern was found, he started a search in his earth-bound lab for this mysterious gas.
- The elusive element (odourless, colourless, chemically inert) was finally detected.

$\Rightarrow$ Helium, from Greek, *helios* = sun

Anders J Ångström (1814-74): hydrogen spectrum



- Ångström carefully analysed the spectrum of hydrogen, the simplest atom
- measured the four most prominent lines very accurately in 1862

Johann Jakob Balmer (1825-98)

- provided initial organization of the raw data collected in spectroscopy ("pure numerology")
- Miraculously, Balmer's formula predicted almost exactly the frequencies of the four hydrogen lines, as well as others later confirmed:

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

where R is Rydberg's constant and the four lines are reproduced when n_f (final) was chosen to be 2 and n_i (initial) was 3, 4, 5, and 6.

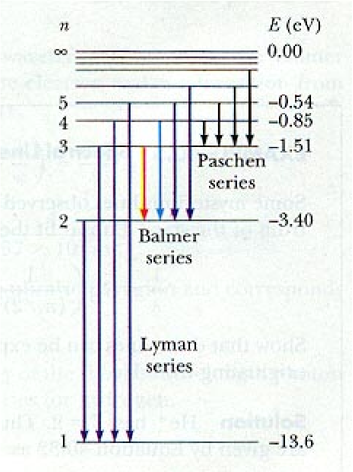
Hydrogen emission spectrum (Balmer, 1885)

Table: Compare the values for the frequencies (in 10^6 MHz) for $n_f = 2$:

Experimental values	From Balmer Formula	Value of n_i
457.170	457.171	3
617.190	617.181	4
691.228	691.242	5
731.493	731.473	6

Clearly, Balmer was onto something...

Hydrogen frequencies from Balmer's formula



- emission/absorption from atom corresponds to an decrease/ increase in atom's energy
- Notice: spectrum is generated using only whole numbers for n_f and n_i.

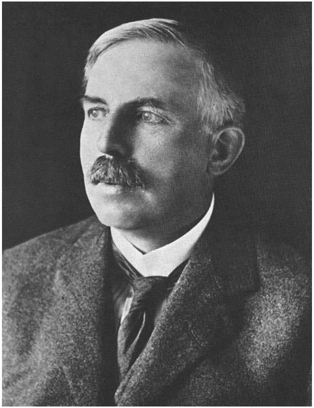
$\Rightarrow$ some rearrangement of parts of atom?

- constraint for any future thy of the atom: must accommodate Balmer's miraculous formula

J J Thomson (1856-1940): discovery of the electron

- demonstrated that the electron had a distinct charge-to-mass ratio and was thus a particle, not a cathode ray
- In fact, during the last five years of C19, other presumed rays were shown to behave like particles (alpha and beta rays $\Rightarrow$ alpha and beta particles)
- next step was to figure out how these particles formed atoms

Ernest Rutherford (1871-1937): the nuclear atom



- Rutherford, a former student of Thomson's, performed an important experiment in 1909 when he shot alpha particles on a thin gold foil with his students Hans Geiger (1882-1945) and Ernest Marsden (1889-1970), using scattering techniques he developed.
- He realized that these massive projectiles would be ideal probes to study the inner structure of atoms.
- Most alpha particles went through the foil without scattering, but some were scattered at large angles and few even came backward...

"It was quite the most incredible event that ever happened to me in my life. It was as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you. On consideration, I realized that this scattering backwards must be the results of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive center carrying a charge."

— Ernest Rutherford, 1937

$\Rightarrow$ Nobel prize 1908, birth of the modern concept of the nuclear model of the atom

Rutherford's nuclear atom

- atom is mostly empty, with the nucleus occupying about one billionth of the space

$\Rightarrow$ many new questions arose:

1. What is the arrangement of electrons about the nucleus?
2. What is the nucleus composed of and what keeps the it from exploding due to repulsion of its positive charges?
3. What keeps the negative electron from falling into a positive nucleus by electrical attraction?

$\Rightarrow$ Rutherford proposed a planetary model of the atom, with the electrons orbiting a positive nucleus.

- But if the electrons move around the center, they accelerate to stay on the orbits. What keeps them from radiating continuously as the classical electromagnetic thy would predict?

$\Rightarrow$ Rutherford's model was unstable!

Niels Bohr (1885-1962)

- grandfather of quantum physics, worked with just about everyone who made contributions to QT
- The "Great Dane" arrived in Cambridge, England, in 1911 with a dictionary and the complete works of Dickens from which to study English.
- In 1912, transferred to Manchester to study with Rutherford.
- Nobel 1922 (and his son got it in 1975)

Bohr on the constitution of atoms

- tried to solve the stability problem of Rutherford's model, and surmised that there might be special stable orbits which would keep the electrons from collapsing into the nucleus
- It was clear to Bohr that classical physics could not apply inside the atom.
- perhaps these orbits had something to do with the Planck/Einstein quantum relation bw the energy of a light photon and its frequency $E = hf$
- The great breakthrough came when he discovered Balmer's formula in early 1913, which led him to an interpretation of Balmer's formula in terms of the new model for the hydrogen atom.

$\Rightarrow$ This event marks the birth of the QT of atomic structure.

Quantized angular momentum

In 1912, J.W. Nicholson (1881-1955) quantizes angular momentum based on considerations that if Planck's constant h had an atomic significance, this may mean that the angular momentum of a particle can only rise or fall by discrete amounts when electrons leave or return:

$$L = mvR = \frac{nh}{2\pi},$$

where $n \in \mathbb{N}$, m the mass and v the tangential speed of the electron, and R the radius of its orbit.

(a) Linear momentum: Newton's first law

Law (Newton's first law)

A body continues to maintain its state of rest or of uniform motion unless acted upon by an external net force.

- sometimes also referred to as the law of inertia
- linear momentum: $p = mv$
- principle of the conservation of momentum: total linear momentum of a closed system of objects is constant

$\Rightarrow$ center of mass of any closed system will always continue with the same velocity unless acted on by a force from outside the system

(b) Angular momentum

- If a body is set in a rotational motion in a closed orbit w/out friction, it will continue undiminished with constant angular momentum until acted upon by external torque.
- The angular momentum is given by $L = mvr$, where m is the body's mass, v its speed, and r the radius of the orbit.

`Spinning ice skater`

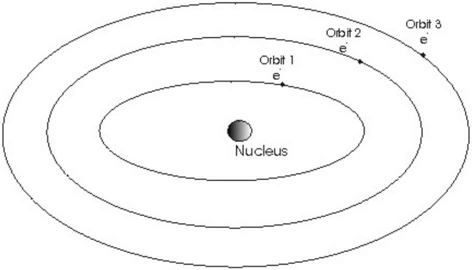
- In Bohr's model, if an electron is excited from its initial energy state, it can only "jump" to an orbit where its angular momentum will increase or decrease by some whole number times $h/2\pi$.
- This is the central premise of Bohr's scheme: the quantization of the electron orbits in the atom in units of Planck's constant.

The Bohr quantum postulates

Bohr's first postulate:

Postulate (Quantum orbital condition)

An atom can exist in any one of several special orbits with no emission of radiation, contrary to the expectations of classical physics. These orbits are called stationary states and are characterized by values of orbital angular momentum given by $L = mvr = n(h/2\pi)$.



- L cannot take on any value, but only certain values: $1(h/2\pi)$ in the first orbit, $2(h/2\pi)$ in the second, etc.
- n is called the principal quantum number
- Intriguing: energy seemed quantized in units of h ($E = hf$), but angular momentum is quantized in units of $h/2\pi$. Whence the difference?

The Bohr radius: mixing classical and quantum physics

Bohr used a combination of classical (from Newton's model of the solar system) and quantum physics to determine the radii of the stable electron orbits:

$$r = \left(\frac{h^2}{4\pi^2 m q^2}\right) n^2,$$

where q is the electronic charge.

Thus, we get $r_n = n^2 r_1$, where r_1 is the so-called Bohr radius, the radius of the smallest stable orbit in the hydrogen atom where the energy of the hydrogen atom is at a minimum and the atom is in its ground state. Bohr calculated a value of 5.3×10^{-9} m or 5.3 nanometers, which is close to contemporary estimates.

Bohr's second postulate:

Postulate (Quantum transition condition)

A sudden transition of the electron between two stationary states will produce an emission or absorption of radiation, with a frequency given by the Planck/Einstein relation $hf = E_i - E_f$. E_i and E_f are the energies of the atom in the initial and final stationary states, respectively.

Bohr derives the Balmer formula

In order to obtain the Balmer formula from first principles, he again mixed classical and quantum physics to get

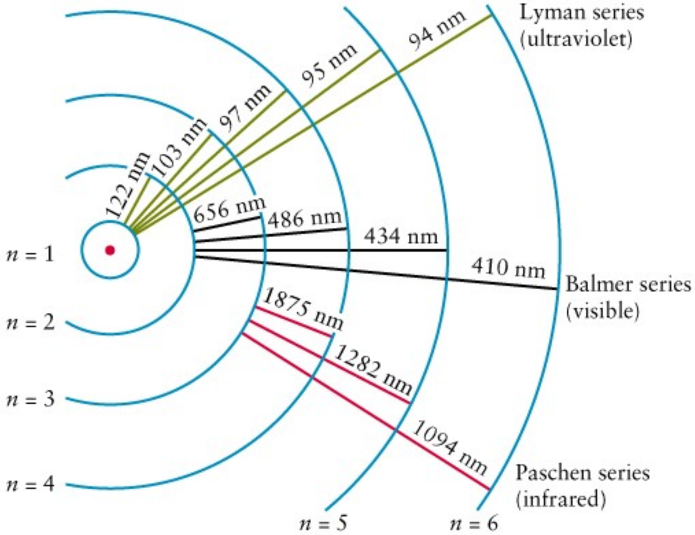
$$f = \frac{2\pi^2 mq^4}{h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$$

which was exactly the same formula Balmer had obtained if it could be shown that $R = (2\pi^2 mq^4/h^3)$ for Balmer's constant R.

With the values of m, q, h available then, Bohr came within a few percent of Balmer's values. (Drum rolls)

Bohr could now draw an energy diagram based on physical orbits in the atom to show how the various spectral series originate (see overleaf)

Had the young Dane solved the riddle of atomic structure? Would the model work, i.e. predict the spectra, for all other elements?


Lyman series
(ultraviolet)
94 nm
95 nm
97 nm
103 nm
122 nm
656 nm
486 nm
434 nm
410 nm
Balmer series
(visible)
1875 nm
1282 nm
1094 nm
Paschen series
(infrared)
$n = 1$
$n = 2$
$n = 3$
$n = 4$
$n = 5$
$n = 6$

This completes the Old Quantum Theory.

Arnold Sommerfeld (1868-1951): more spectral lines

- great theoretician and teacher of theoretical physics in Munich
- With better measurements, more spectral lines were discovered.

$\Rightarrow$ more structure needed

- extended Bohr's model s.t. each stationary orbit of a fixed value of n permits different elliptical shapes

$\Rightarrow$ slightly different values of energy of the stationary states with slightly larger or smaller energy transitions

$\Rightarrow$ multiple spectral lines

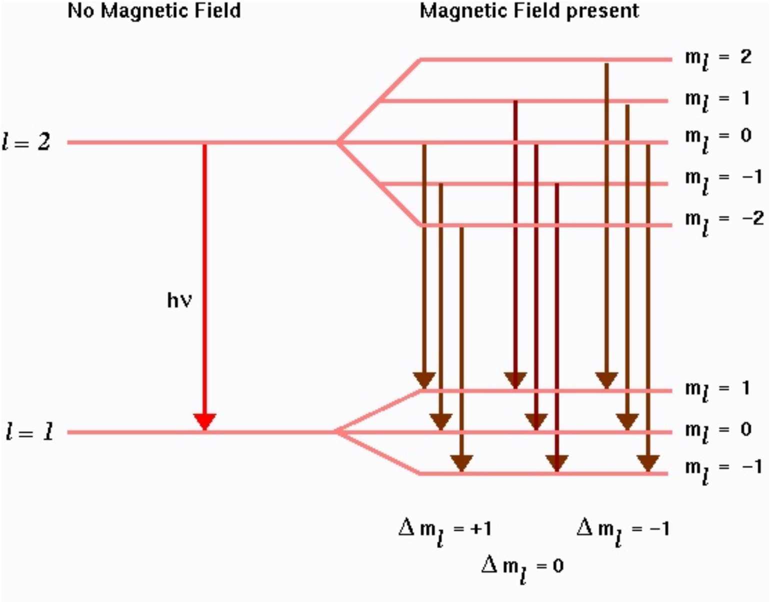
- another quantum number: k

Pieter Zeeman (1865-1943): still more lines

- 1890s: Zeeman showed that extraneous spectral lines appear if atom is placed in magnetic field

$\Rightarrow$ true atomic thy had to explain this Zeeman effect (Nobel 1902)

- Sommerfeld: the orientation of orbit important; when field is applied, the electron can select from more orbits pointing in various directions wrt the field, allowing different energies
- these directions also quantized: magnetic quantum number m


No Magnetic Field
Magnetic Field present
l = 2
l = 1
hv
m_l = 2
m_l = 1
m_l = 0
m_l = −1
m_l = −2
m_l = 1
m_l = 0
m_l = −1
Δ m_l = +1
Δ m_l = −1
Δ m_l = 0

Three quantum numbers: n, k, m

- Bohr incorporated Sommerfeld's calculations in his model: series of selection rules for atomic transitions on the basis of three quantum numbers:
    1. n: size of orbit
    2. k: shape of orbit
    3. m: direction in which orbit is pointing
- each separate energy state of the atom was now assigned a distinct set of these three numbers, and transition bw these states produce the observed spectral lines
- Was this enough to explain all lines in the spectra?
- As it turns out, no. Yet another quantum number was needed, but that's now part of the quantum mechanics proper.

Wolfgang Pauli (1900-1958)

- 1921, two months after getting his PhD, he published a 237-page review article of general relativity, of which Einstein said: “Whoever studies this mature and grandly conceived work might not believe its author is only 21 years old.”
- 1924: exclusion principle
- 1924/5: electron spin
- 1927: Pauli matrices
- 1930: predicted existence of neutrino
- 1945: Nobel
- important contributions to quantum field thy

Anomalous Zeeman effect (AZE)

- Anomalous Zeeman effect (AZE): yet more lines, for which nobody found an explanation
- In 1924/5, everyone was mystified by the AZE, not the least of whom was Pauli.
- Pauli effect: whenever he entered a laboratory, something would go badly wrong with the experimental apparatus.
- Example: experimentalist Otto Stern (1888-1969) at Hamburg would consult him only through the closed door leading to his laboratory...

Pauli's "hidden rotation" and the spinning electron

- Pauli's hypothesis (1924): a hidden rotation of the electron (and not a change in the orbit) produces the extra angular momentum responsible for AZE

⇒ proposed a fourth quantum number (w/ only two values, one for each orientation–clockwise and counter-clockwise)

- But he had no physical picture of this rotation process...
- Meanwhile, two young Dutch physicists, George Uhlenbeck and Sam Goudsmit, had the same idea.
- Their professor, Paul Ehrenfest (1880-1933), urged them to publish their idea.
- Angular mom of spinning electron turned out to be only one-half of the normal value $h/2\pi$ of atomic orbits, so-called spin 1/2.

⇒ electron seems to have to spin around *twice* to get back to its starting point

Pauli's exclusion principle

Why don't all of the electrons in atom simply tumble into the ground state?

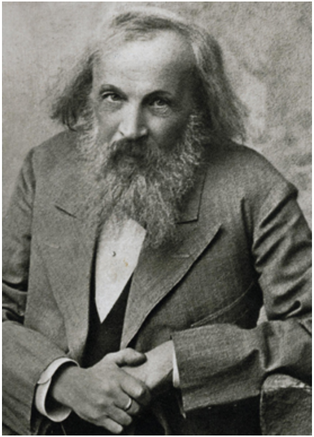
Pauli's idea: each atomic state (n, k, m) contains no more than two electrons and needs its own exclusive orbit ("space quantization")

Principle (Exclusion Principle)

Each quantum state in the atom is not limited to two electrons, but one. There are four quantum numbers, counting spin up or down, that uniquely specify the state. If a state is occupied, the next electron must go to an empty state, filling up the empty states from the lowest energy to higher energies. This is what keeps the atom from collapsing to its ground state and gives each element a characteristic structure.

This principle applies to all electrons in all atoms and is responsible for the solidity of tables!

Explaining Mendeleev's Periodic Table

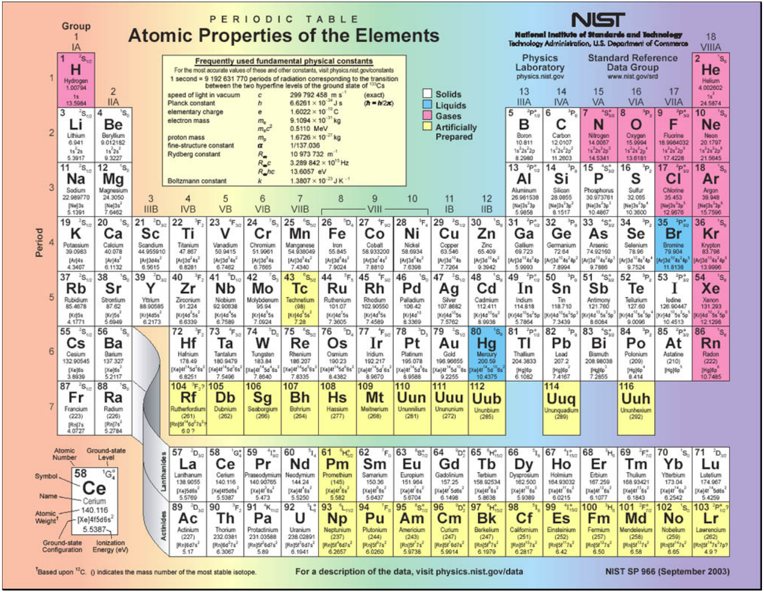


- Dimitri Mendeleev (1834-1907), Russian chemist, invented the preriodic table of chemical elements as visual aid for his struggling students
- He realized that the chemical properties of elements were repeated if arrayed in a table.

ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

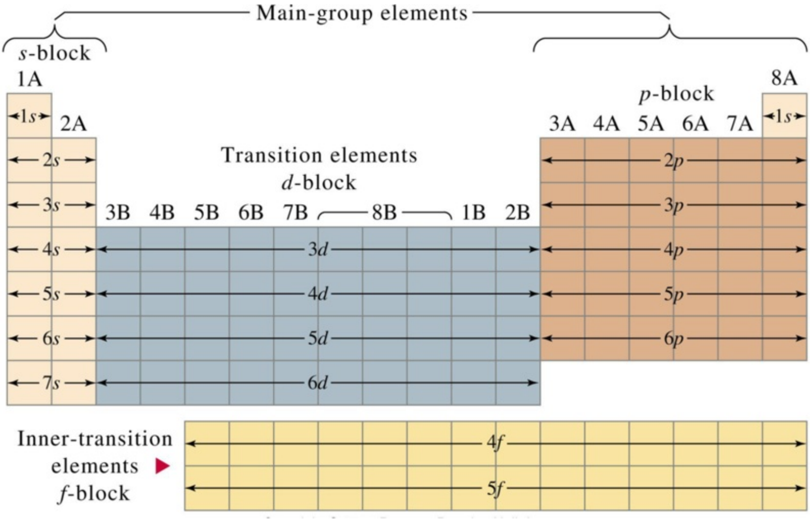
			Ti = 50	Zr = 90	? = 180.
			V = 51	Nb = 94	Ta = 182.
			Cr = 52	Mo = 96	W = 186.
			Mn = 55	Rh = 104,4	Pt = 197,4.
			Fe = 56	Rn = 104,4	Ir = 198.
			Ni = Co = 59	Pl = 106,6	Os = 199.
H = 1			Cu = 63,4	Ag = 108	Hg = 200.
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204.
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207.
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		


PERIODIC TABLE
Atomic Properties of the Elements
NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce
Physics Laboratory
physics.nist.gov
Standard Reference Data Group
www.nist.gov/srd
Frequently used fundamental physical constants
For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of 133Cs
speed of light in vacuum c 299 792 458 m s−1 (exact)
Planck constant h 6.6261 × 10−34 J s (ħ = h/2π)
elementary charge e 1.6022 × 10−19 C
electron mass me 9.1094 × 10−31 kg
mec2 0.5110 MeV
proton mass mp 1.6726 × 10−27 kg
fine-structure constant α 1/137.036
Rydberg constant R∞ 10 973 732 m−1
R∞c 3.289 842 × 1015 Hz
R∞hc 13.6057 eV
Boltzmann constant k 1.3807 × 10−23 J K−1
Solids
Liquids
Gases
Artificially Prepared
Group
Period
Lanthanides
Actinides
Atomic Number
Ground-state Level
Symbol
Name
Atomic Weight†
Ground-state Configuration
Ionization Energy (eV)
†Based upon 12C. () indicates the mass number of the most stable isotope.
For a description of the data, visit physics.nist.gov/data
NIST SP 966 (September 2003)

- periodicity remained mysterious until Pauli introduced his exclusion principle in 1925
- (Except for Bohr, who offered an alternative explanation a little earlier, this being his main motivation for the formulation of his atomic thy.)
- Pauli's exclusion principle automatically produced the numbers 2, 8, 18, ...

Table: Counting the states

	n	k	possible m	poss s	total states
1st shell	1	1	0	$\pm 1/2$	2 $= 2$
	2	1	0	$\pm 1/2$	2
2nd shell	2	2	-1, 0, 1	$\pm 1/2$	6 $= 8$
	3	1	0	$\pm 1/2$	2
3rd shell	3	2	-1, 0, 1	$\pm 1/2$	6 $= 18$
	3	3	-2, -1, 0, 1, 2	$\pm 1/2$	10


Main-group elements
s-block
1A
2A
1s
2s
3s
4s
5s
6s
7s
Transition elements
d-block
3B
4B
5B
6B
7B
8B
1B
2B
3d
4d
5d
6d
p-block
8A
3A
4A
5A
6A
7A
1s
2p
3p
4p
5p
6p
Inner-transition elements
f-block
4f
5f

The wave/particle duality

Question

Is the fundamental nature of radiation and matter described better by a wave or a particle representation? Or do we need both?

Does light consist of waves or particles?

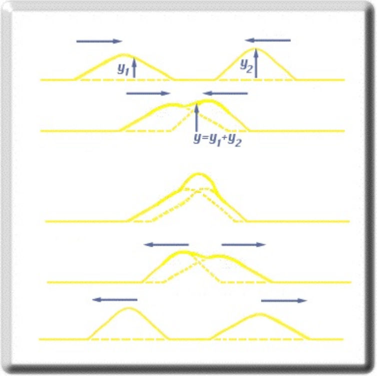
Christiaan Huygens (1629-95): waves

Isaac Newton (1643-1727): particles

Properties of waves: superposition

Law (Superposition)

If two waves (such as pulses on a string) travel past a particular point at the same time, the total wave (or displacement of the string) is the sum of the individual waves (or displacements).



Properties of waves: interference

Law

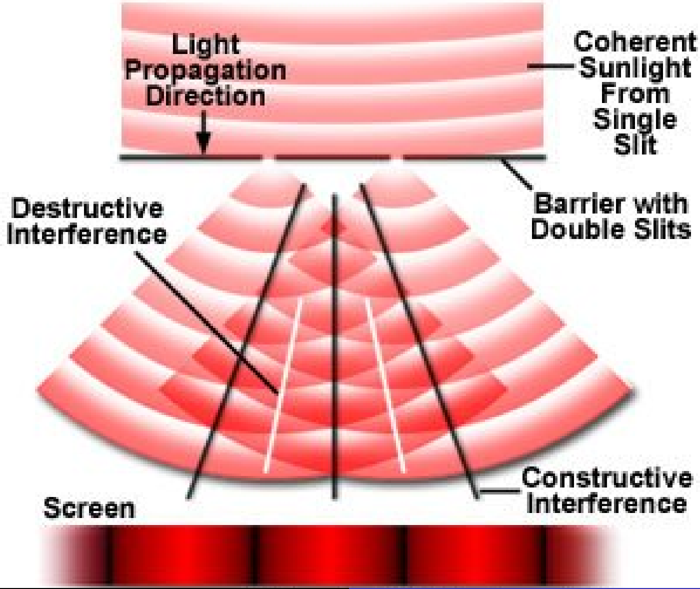
The speed v, wavelength λ and frequency f of a wave are related by $v = \lambda f$.

Double-slit experiment

If two identical periodic waves arrive at the same point "out of phase" in a classic double-slit experiment, i.e. separated by exactly one half of a wavelength, then destructive interference takes place and the wave is annihilated (light: dark spots occur). If the separation is exactly one whole wavelength, constructive interference takes place (light: very bright spot).

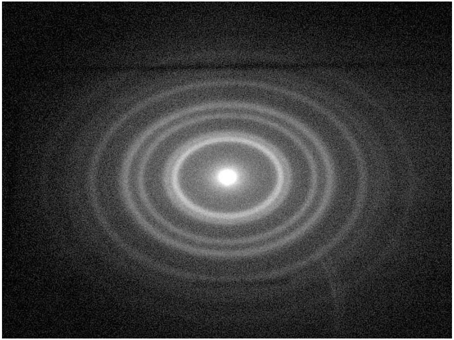
First performed by Thomas Young (1773-1829) in 1801.

$\Rightarrow$ clear evidence in favour of wave thy


Light Propagation Direction
Coherent Sunlight From Single Slit
Destructive Interference
Barrier with Double Slits
Constructive Interference
Screen

Properties of waves: diffraction

Diffraction pattern when light or another type of wave passes through a small circular hole (size similar to wavelength):



Further evidence for wave thy: Maxwell's electromagnetic wave thy of 1865.
⇒ in C19, physicists were convinced that light was a wave

Clouds in paradise...

- Einstein 1905: light as corpuscular photons, but only “heuristic viewpoint”
- Einstein 1909: “It is my opinion that the next phase in the development of theoretical physics will bring us a theory of light that can be interpreted as a kind of fusion of the wave and the [particle] theory.” (*Z Phys* **10**: 817)
- No physicist took this seriously at the time.
- But even Einstein wasn’t ready for the shock that came from Paris in 1924...

Louis-Victor-Pierre-Raymond, 7th duc de Broglie (1892-1987)

- Graduate student at the Sorbonne in Paris in 1923 when he introduced the astounding idea that particles may exhibit wave properties.
- Doctoral thesis 1924: "It would seem that the basic idea of the quantum theory is the impossibility of imagining an isolated quantity of energy without associating it with a certain frequency... However, it is difficult to understand precisely the physical sense of the frequency in the Einstein equation [$E = hf$]... But it apparently describes a certain internal 'cyclic process'."

In the first part of his thesis, de Broglie proposed one the great unifying principles in all of physics:

> *I am convinced that the wave-particle duality discovered by Einstein in his theory of light quanta is absolutely general and extends to all of the physical world, and it seems certain to me, therefore, that the propagation of a wave is associated with the motion of a particle of any sort—photon, electron, proton or any other. (My emphasis)*

- associated waves: de Broglie assigned a frequency to a wave that accompanied the particle through space and time

$\Rightarrow$ pilot waves which guide particle in its motion

- Can these pilot waves be measured? De Broglie: Yes.

Phase velocities and group velocities

- phase velocity: speed at which individual wave crest moves
- group velocity: speed of the reinforcement regions formed when many waves are superimposed (= speed of wave packet)

Phase and group velocities

- de Broglie: group velocity = velocity of particle
- reinforcement region displays all the mechanical properties (e.g. energy, momentum) normally associated w/ particle
- (Analogy: pulse that is produced by superposition of many waves of different frequencies)

Dramatic conclusions

Consider photons:

$$\begin{aligned} E &= mc^2 = (mc)(c), \\ &= (p)(c) = (p)(f\lambda), \\ (h)(f) &= (p)(f\lambda), \\ \Rightarrow \qquad h/p &= \lambda. \end{aligned}$$

$\Rightarrow$ If wavelength of light is decreased, the momentum of the photons is increased. In fact, this is true for all particles.

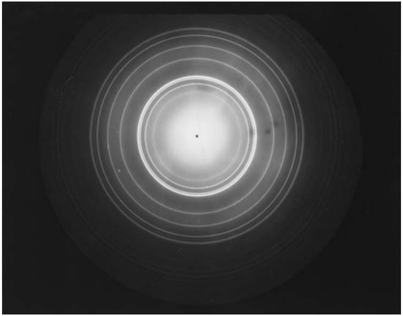
This result will later be used to show how Heisenberg explained his uncertainty principle.

The story of the thesis

- Unsurprisingly, de Broglie's PhD committee, chaired by the eminent Paul Langevin (1872-1946), was astounded and confounded.
- Langevin sent an advance copy to Einstein to obtain his opinion in the matter.
- Einstein read the thesis and informed Lorentz: "I believe de Broglie's hypothesis is the first feeble ray of light on this worst of our physics enigmas."
- ... and the thesis committee: "De Broglie has lifted the great veil."
- So they passed him for the PhD.

Confirmation of matter waves

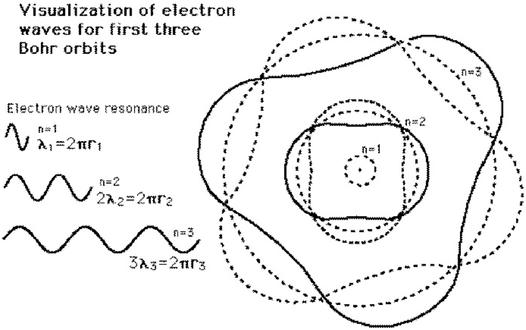
- In just a few years, all of de Broglie's predictions were confirmed by experiment.
- George P Thomson (1892-1975), Nobel 1937 for the "experimental discovery of the diffraction of electrons by crystals"



Electron waves in the atom

- For an electron in an atom, its associated wave is stationary, i.e. in a standing wave pattern (bf. wave moving along a violing string fixed at its ends).

⇒ only certain discrete frequencies are produced (music: the fundamental and its overtones): $2\pi r = n\lambda$, which was just what Bohr needed (remember the unexplained factor of 2π?)



A little algebra:

Using the standard wave equation and de Broglie's relation, we get:

$$\begin{aligned} n\lambda &= 2\pi r \\ n\,(h/mv) &= 2\pi r \\ n\,(h/2\pi) &= mvr \end{aligned}$$

which is just Bohr's quantum orbital postulate...

Finally, we are getting somewhere:

The old quantum theory, resulting in Bohr's orbital model of the atom (and Sommerfeld's modifications), could point to certain successes:

- hydrogen spectrum, i.e. the derivation of the Balmer formula
- quantum numbers and selection rules for energy states in the atom
- explanation of the periodic table of the elements
- Pauli's exclusion principle

But now we have a problem:

- Should we think of the electron in the hydrogen atom as a tiny charged particle orbiting the nucleus, jumping from one orbit to another...
- ... or as a closed standing wave that fits into one orbit with its electron charge somehow distributed around the circumference?

The birth of the new quantum theory

During the twelve-month period from June 1925 to June 1926, three independent developments of a complete quantum theory were published and ended 25 years of confusion:

1. Werner Heisenberg's matrix mechanics
2. Erwin Schrödinger's wave mechanics
3. Paul Dirac's quantum algebra

and then shown to be equivalent.

Let's look at the first two for today.

Werner Heisenberg (1901-1976)

- studied physics in Munich with Sommerfeld, where he met Pauli in 1920
- In 1922, Pauli and he were at Göttingen, where he first met Bohr
- 20 years old and a PhD student, he rose an objection after one of Bohr's lectures...
- Bohr asked him whether he would join him for a walk that afternoon. He would, and when they returned after three hours, Bohr told friends about Heisenberg:
- "Heisenberg understands everything. Now the solution is in his hands. He must find a way out of the difficulties of quantum theory."

Heisenberg's picture of the atom

- At the age of 22, Max Born (1882-1970) made him a *privatdozent* in Göttingen.
- Starting point: thought of atom not as little solar system, but as simple virtual oscillators which could produce all the frequencies of the spectrum (like Planck in 1900)
- Using semi-classical methods, he found the "code" for connecting the quantum numbers and the energy states in an atom with the experimentally determined frequencies and intensities of the light spectra.
- At this point, he made a startling discovery: unlike in classical physics, where factors such as q and p commute ($qp = pq$), they may not commute in quantum physics!

$\Rightarrow$ law of the commutativity of multiplication no longer valid...

The night of Helgoland

- In order to obtain the correct frequencies and intensities of the spectral line, Heisenberg had to assume a quantum postulate, which was to have profound implications:

Postulate (Non-commutativity)

$pq - qp = h/2\pi i.$

- This postulate allowed him to show that energy states were quantized and time independent, i.e. they were stationary as in the Bohr atom.
- Heisenberg finished the derivation at around 3am one night on the island of Helgoland, where he was recovering from severe hay fever, and was so excited that he couldn't sleep. So instead he took a walk on the top of a hill where he awaited the sunrise...

$\Rightarrow$ "The night of Helgoland"

Max Born (1882-1970) and matrix mechanics

- taught at Göttingen, Cambridge, Edinburgh
- 1954 Nobel in physics
- When Heisenberg gave him his paper, he started to think hard about the non-commutativity in Heisenberg's thy.
- Together with his talented, though politically misguided, student Pascual Jordan (1902-80), Born transposed Heisenberg's thy into a systematic matrix language (incl. the non-cummutativity postulate).

$\Rightarrow$ Matrix mechanics

Pauli and what was left of intuition

- Pauli then quickly proved that not only can the spectrum of hydrogen be deduced from matrix mechanics, but also the additional lines produced by electric and magnetic fields.
- Problem: with the electron orbits gone, physicists were left with an abstract mathematical formalism that worked remarkably well, but whose physical meaning they couldn't interpret.
- Whether atoms consisted of waves or particles became irrelevant in matrix mechanics, and visual aids didn't exist...

Erwin Schrödinger (1887-1961): wave mechanics

- taught at Breslau, Zürich, Berlin, Oxford, Graz, Institute for Advanced Studies at Dublin
- 1933 Nobel in physics
- in 1925, set out to develop another version of quantum physics based on de Broglie's concept of matter waves
- He thought that his approach would
    1. be more acceptable to physicsts, and
    2. mark a return to continuous, visualizable world of classical physics

he was right only about the first part...

Schrödinger's equation

Schrödinger found an equation which can be applied to a particle with mass m in one dimension in which the potential $V(x)$ is known:

$$i\hbar\frac{\partial}{\partial t}\Psi(t,x) = -\frac{\hbar^2}{2m}\nabla^2\Psi(x) + V(t,x)\Psi(t,x), \qquad (1)$$

where the function $\Psi(t,x)$ is a wave that describes–in a sense yet to be clarified–the quantum aspects of the particle. For a general physical system, the Schrödinger eq is

$$i\hbar\frac{\partial}{\partial t}\Psi(t,x) = \hat{H}\Psi(t,x), \qquad (2)$$

where $\hat{H}$ is the so-called Hamiltonian operator.

Schrödinger's wave mechanics

- Schrödinger reduced the problem of the energy states in an atom to a so-called eigenvalue problem
- He was able to give a complete description of the spectral lines in the hydrogen atom, reproducing the Balmer formula.
- He thought his wave mechanics was a return to classical physics of continuum processes undisturbed by sudden jumps; he was proposing an essentially classical thy of matter waves that would stand to mechanics as Maxwell's thy em waves stood to optics.
- He even doubted the existence of particles and instead assumed that they really are wave groups with small dimensions in every direction (= "wave packet")
- Henrik Lorentz (1853-1928) criticized him for this interpretation, arguing that a free particle as wave packet will disperse over time

$\Rightarrow$ from summer 1926, Schrödinger's original conception of matter as wave packets began to waver

- But what was the relationship bw a particle's wave fct and the particle itself?

Schrödinger meets Heisenberg

- Schrödinger hated Heisenberg's matrix mechanics due to its lack of "Anschaulichkeit" (intuitiveness), yet he was able to show the complete mathematical equivalence of matrix and wave mechanics!
- How could that be if one was based on a conceptual wave model of atomic structure that the other rejected?
- In July 1926, Schrödinger and Heisenberg met for the first time in Munich, when WH challenged ES to explain quantized processes such as the photoelectric effect and black-body radiation on the basis of his continuum wave model.
- ES had no good answer for him and realized that his model failed to account for these effects.

Born's probabilistic interpretation of Ψ

In the summer of 1926, Born developed his ideas of a quantum mechanical probability:

- Ψ is a probability amplitude for an electron in the state *n* to scatter into the direction *m*
- $|\Psi^2|$ is a "physical probability of the associated particle's presence"
- new thy's probability is not due to ignorance, but represents a fundamental, principled limit to what can be known
- reconciliation of particles and waves: wave Ψ determines the likelihood that the particle will be in particular position (and has not physical reality, unlike the em field)

Heisenberg's uncertainty principle

- recall the non-cummutativity of position and momentum: $pq - qp = h/2\pi i$
- Interpreting q and p as operators, does this mean that the order of position and momentum measurements might be relevant?
- To locate an object, the radiation used must have smaller wavelength than the size of the object. (For an e^-, waves must thus be smaller than the ultraviolet, as the diameter of the entire hydrogen atom is only a fraction of the wavelength of visible light)
- imprecision in the position measurement is $\Delta x \geq \lambda$
- imprecision in momentum measurement is at least the momentum imparted to e^- by a single photon used to illuminate e^-: $\Delta p \geq h/\lambda$ (from de Broglie/Einstein relation)

Principle (Heisenberg's uncertainty principle)

The uncertainty in a simultaneous measurement of momentum and position is always greater than a fixed amount, approximately equal to Planck's constant:

$$\Delta x \cdot \Delta p \geq h. \tag{3}$$

- $\Rightarrow$ to measure both x and p accurately at the same time is impossible
- $\Rightarrow$ one cannot be pinpointed exactly, unless we are willing to be quite uncertain about the other