Modern Physics

Contents:

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Spectrum Hydrogen Atom

Early atomic physics

- The electron and the elementary charge
- The nucleus
- The spectrum of the hydrogen atom
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- The spectra of the alkali metals
- X-ray spectra
- The Frank-Hertz experiment

The spectrum of the hydrogen atom 1

Johannes Balmer (1885): spectral lines of hydrogen in the visible range of the spectrum (WasserstoffSpektrallampe.mp4)

$$\underline{\lambda_\mathrm{n} = A\frac{n^2}{n^2-4}} \quad \text{and} \quad n = 3, 4, 5\ldots$$

With $A = 364.568$ nm one finds the energy of the photons $\Delta E_n = hc/\lambda_n$

$$\Delta E_n = \frac{hc}{A}\left(1-\frac{4}{n^2}\right) = \frac{4hc}{A}\left(\frac{1}{2^2}-\frac{1}{n^2}\right) = R_y\left(\frac{1}{2^2}-\frac{1}{n^2}\right) = \underline{13.6\,\mathrm{eV}\left(\frac{1}{2^2}-\frac{1}{n^2}\right)}$$

The spectrum of the hydrogen atom 1 Comment 1

The video shows a discharge tube that is filled with hydrogen gas.

If a high voltage is applied, the H_2 molecules disintegrate through electron impact and atomic hydrogen is formed.

Excited hydrogen atoms give off their energy through spontaneous emission of photons and return to the ground state.

The figure shows the spectral lines in the visible range of the electromagnetic spectrum.

In 1885 Johannes Balmer found the simple formula underlined in red with which the wavelengths of the spectral lines of hydrogen in the visible spectral range can be calculated.

The spectrum of the hydrogen atom 1 Comment 2

The comparison with the experimental data determines the constant A: $A = 364.568$ nm.

The energy of the transitions can be calculated from the wavelength using Planck’s law $E = h\nu = hc/\lambda$.

The constant $R_y = \frac{4hc}{A} = 13.6$ eV is called the Rydberg energy.

The spectrum of the hydrogen atom 2

Theodore Lyman (1906): hydrogen spectral lines in the ultraviolet range

$$\lambda_n = \frac{A}{4}\frac{n^2}{n^2-1} \quad \text{and} \quad n = 2, 3, 4, 5\ldots$$

With Balmer's constant $A = 364.568$ nm and Planck's law $\Delta E_n = hc/\lambda_n$

$$\Delta E_n = 13.6\,\text{eV}\left(1 - \frac{1}{n^2}\right)$$

The spectrum of the hydrogen atom 2

Comment

In 1906 Theodore Lyman observed the spectral lines of the hydrogen atoms in the ultraviolet region of the spectrum.

The wavelength of the spectral lines can be calculated with a small modification of the Balmer formula.

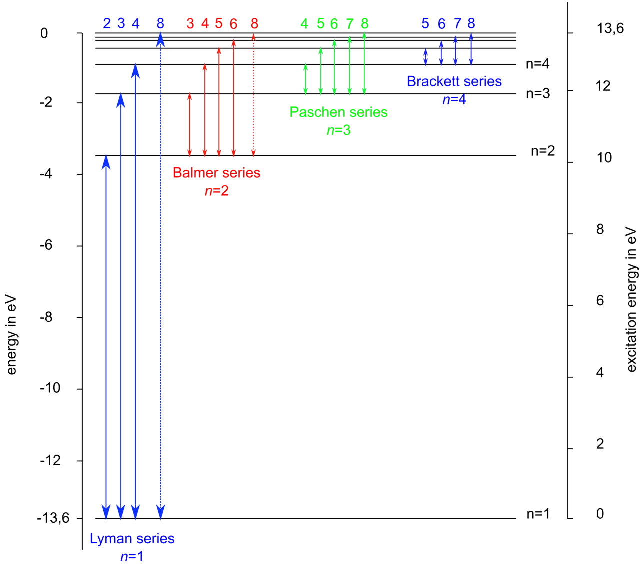
If the transition energy is calculated from the wavelength using Planck’s law, the formula below, underlined in red, results.

The infrared range of the spectrum was examined by Friedrich Paschen in 1908.

The wavelength of the spectral lines can also be calculated with a small modification of the Balmer formula.

Obviously, the transition energy results from the difference between two energy terms.

The spectrum of the hydrogen atom 3



$$\boxed{E_n = -13.6\,\mathrm{eV}\,\frac{1}{n^2}}$$

e.g. for the Paschen series

$$\Delta E_n = E_n - E_3$$

$$\Delta E_n = -13.6\,\mathrm{eV}\left(\frac{1}{n^2} - \frac{1}{3^2}\right)$$

and $n = 4, 5, 6, \ldots$

The spectrum of the hydrogen atom 3 Comment 1

With the energy of the photons, it is easy to find the underlying energy level scheme of the hydrogen atom.

The formula outlined in red indicates the quantized energy of the electron in the hydrogen atom.

This makes it easy to calculate the respective transition energy.

The transition energy of the Lyman series is given by $\Delta E_n = E_n - E_1$, the transition energy of the Balmer series is given by $\Delta E_n = E_n - E_2$ and the Paschen series by $\Delta E_n = E_n - E_3$.

The figure shows the energy levels scheme of the hydrogen atom with the various series of spectral lines.

The ground state with the quantum number $n = 1$ has the lowest energy.

The spectrum of the hydrogen atom 3 Comment 2

For $n \to \infty$ the ionization energy results, which is 13.6 eV above the ground state.

The right scale of the figure gives the excitation energy above the ground state.

If the ionization energy is assigned the value zero, then the left-hand scale of the figure results.

The energy of the ground state is then -13.6 eV.

If the excitation energy is increased above 13.6 eV, the electron is no longer bound to the proton.

The blue double arrows show the transitions of the Lyman series in the ultraviolet range of the spectrum.

The spectrum of the hydrogen atom 3 Comment 3

The red double arrows show the transitions of the Balmer series in the visible range of the spectrum.

The green double arrows show the transitions of the Paschen series in the infrared range of the spectrum.

The second group of blue double arrows is the Brackett series, which is also in the infrared range of the spectrum and was first detected in 1922.

Bohr’s model

Early atomic physics

- The electron and the elementary charge
- The nucleus
- The spectrum of the hydrogen atom
- Bohr’s model of the hydrogen atom
- The spectra of the alkali metals
- X-ray spectra
- The Frank-Hertz experiment

Bohr's model of the hydrogen atom 1

What was known in 1913 about atoms?

1. Lorentz (1889): electromagnetic radiation of atoms is due to electrons.
2. Planck (1900): the energy of electromagnetic radiation is quantised:

$$\underline{E = h\nu = hc/\lambda}$$

3. Balmer (1885), Lyman (1906), Paschen (1908): the binding energy of electrons in hydrogen atoms is given by the formula

$$\underline{E_n = -13.6\,\mathrm{eV}\frac{1}{n^2}} \quad \text{and} \quad n = 1, 2, 3...$$

4. Rutherford (1913): The mass and the positive charge are concentrated in the atomic nucleus.

Bohr’s model of the hydrogen atom 1 Comment

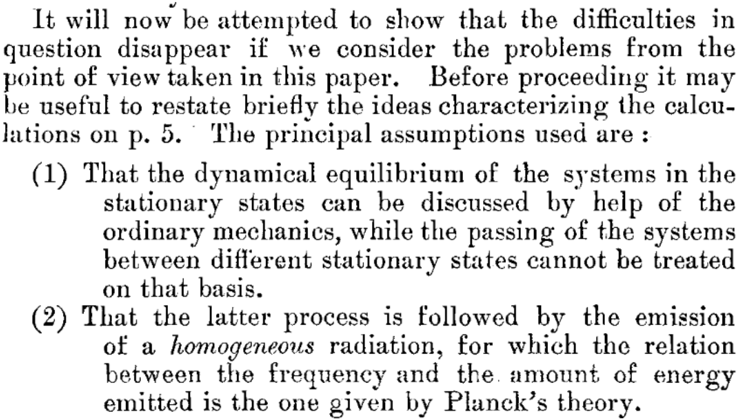
The slide summarizes the state of knowledge from 1913.

Nils Bohr used this information to formulate a first theoretical model of the atom.

Bohr’s model is very simple and yet allows precise predictions of atomic properties.

Bohr's model of the hydrogen atom 2

Bohr's famous assumptions about the atom in 1913



It will now be attempted to show that the difficulties in question disappear if we consider the problems from the point of view taken in this paper. Before proceeding it may be useful to restate briefly the ideas characterizing the calculations on p. 5. The principal assumptions used are:

(1) That the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary mechanics, while the passing of the systems between different stationary states cannot be treated on that basis.

(2) That the latter process is followed by the emission of a *homogeneous* radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.

Bohr’s model of the hydrogen atom 2 Comment

Bohr’s model of the atom is based on some assumptions commonly known as Bohr’s postulates.

Since Bohr’s postulates are formulated in very different ways, I will simply show what he himself writes in his essay published in July 1913.

Stationary states can be described by ordinary mechanics, while the transition between stationary states is only possible through the emission or absorption of the energy quanta of Planck’s theory.

Bohr's model of the hydrogen atom 3

Summary of Bohr's model of the hydrogen atom

1. electrons move in circular orbits around the nucleus.
2. Stable orbits are only possible when the angular momentum $L = rmv$ is quantized according to

$$\boxed{L = n\hbar} \qquad \text{and} \qquad n = 1, 2, \ldots$$

3. Photons are emitted or absorbed in a transition between the stable orbits. The energy of the photons equals

$$\boxed{E = h\nu = |E_n - E_m|} \qquad \text{and} \qquad E_n \neq E_m$$

Bohr’s model of the hydrogen atom 3 Comment 1

Since the wave-particle dualism was not yet established in 1913, Bohr assumes that the electrons behave similarly to planets orbiting the atomic nucleus.

For simplicity, circular orbits are assumed. This restriction was relaxed in Arnold Sommerfeld’s atomic model in 1915 which included elliptical orbits.

Since the energy of the electrons is quantized, there must be special circular orbits for which the angular momentum assumes the value $n\hbar$.

Since electrons moving in circular orbits normally emit electromagnetic waves, radiation must be forbidden for the special circular orbits for some reason.

Bohr’s model of the hydrogen atom 3 Comment 2

Electromagnetic waves are only emitted or absorbed when the electron changes stable orbits. In accordance with Max Planck’s ideas, energy quanta $\hbar\omega$ are emitted or absorbed.

Bohr's model of the hydrogen atom 4

circular orbit:

Coulomb force = centrifugal force

i.e.

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\frac{v^2}{r}$$

small calculation

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\frac{v^2}{r} \quad \rightarrow \quad \frac{e^2}{4\pi\varepsilon_0} = \frac{r^2 m \cdot mv^2}{mr} \quad \rightarrow \quad r = \frac{4\pi\varepsilon_0}{e^2 m} r^2 m^2 v^2$$

radius of the circular orbit

$$\boxed{r = \frac{4\pi\varepsilon_0}{e^2 m} L^2}$$ with the angular momentum $L = r\,mv$

Bohr’s model of the hydrogen atom 4 Comment

On the circular orbit, the centripetal force is caused by the Coulomb force between the atomic nucleus and the electron or in other words: the centrifugal force of the circular motion is compensated by the Coulomb force.

After a little calculation, the equation outlined in red results.

The radius of the circular path is proportional to the square of the orbital angular momentum.

Bohr’s model of the hydrogen atom 5

energy of the electron

$$\underline{E = E_{kin} + E_{pot}}$$

kinetic energy

$$E_{kin} = \frac{1}{2} m v^2$$

potential energy between two charges Q_1 and Q_2

$$\boxed{E_{pot} = \frac{1}{4\pi\varepsilon_0} \frac{Q_1 Q_2}{r}}$$

with the charge of the proton $Q_1 = e$ and the charge of the electron $Q_2 = -e$

$$\boxed{E_{pot} = -\frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}}$$

Bohr’s model of the hydrogen atom 5 Comment 1

The energy of the electron results from the sum of kinetic energy and potential energy.

The formula outlined in red gives the potential energy of two point charges Q_1 and Q_2.

If both charges have the same sign, then the potential energy increases when the distance between the charges is reduced.

This corresponds to a spring that is compressed.

If the compressed spring is released, the potential energy of the spring leads to an accelerated movement.

Bohr’s model of the hydrogen atom 5 Comment 2

In the case of the two point charges, the stored potential energy is converted into kinetic energy of the two charges.

The charge of the atomic nucleus and the electron have opposite signs.

The potential energy increases when the distance between the atomic nucleus and the electron is increased.

If the electron is pulled away from the atomic nucleus and then released, it rushes towards the atomic nucleus.

If the electron has a momentum at right angles to this movement, the electron generally follows an elliptical trajectory around the atomic nucleus.

Bohr's model of the hydrogen atom 5 Comment 3

The electron rushes towards the nucleus and misses it because it is deflected to the side by the transverse momentum.

In the further course of the movement, the kinetic energy of the electron is reduced and the potential energy increases again, etc.

The second formula outlined in red gives the potential energy of an electron in the Coulomb field of a proton.

Bohr's model of the hydrogen atom 6

with the balance between

Coulomb force = centrifugal force

i.e.

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\frac{v^2}{r} \quad \Big| \times r$$

results

$$\underline{-E_{pot} = 2E_{kin}}$$

energy of the electron

$$E = E_{kin} + E_{pot} = -\frac{1}{2}E_{pot} + E_{pot} = \frac{1}{2}E_{pot} \propto \frac{1}{r} \propto \frac{1}{n^2}$$

Bohr’s model of the hydrogen atom 6 Comment

In the case of circular motion, the equilibrium between Coulomb force and centrifugal force shows that the kinetic energy is proportional to the potential energy.

This results in the equation underlined in red and the total energy of the electron is proportional to the potential energy.

The total energy of the electron is therefore inversely proportional to the radius of the circular path.

From the experimental results of Balmer, Lyman and Paschen it is known that the binding energy of the electron is proportional to the inverse square of the quantum number n.

Bohr's model of the hydrogen atom 7

With $r = \frac{4\pi\varepsilon_0}{e^2 m} L^2$ is the energy

$$E = \frac{1}{2} E_{pot} = -\frac{1}{8\pi\varepsilon_0} \frac{e^2}{r} = \underline{-\frac{1}{(8\pi\varepsilon_0)(4\pi\varepsilon_0)} \frac{e^4 m}{L^2}} = E_n = -13.6\,\mathrm{eV} \frac{1}{n^2}$$

therefore

$$\underline{L \propto n}$$

or

$$L = n \cdot \sqrt{\frac{e^4 m}{32\varepsilon_0^2 \pi^2 13.6\,\mathrm{eV}}} = n \cdot \frac{4.1 \cdot 10^{-15}\,\mathrm{eVs}}{2\pi} = n\hbar$$

and

$$\boxed{L = n\hbar} \qquad \text{and} \qquad n = 1, 2, \ldots$$

Bohr’s model of the hydrogen atom 7 Comment

With the formula for the radius of the circular orbit, the underlined equation results and it is obvious that the orbital angular momentum must be proportional to the quantum number n.

With the numerical values it follows that the proportionality constant must be $\hbar$.

Bohr's model of the hydrogen atom 8

the radius of the orbit is ($r = \frac{4\pi\varepsilon_0}{e^2 m} L^2$)

$$\underline{r_n = \frac{4\pi\varepsilon_0\hbar^2}{e^2 m} \cdot n^2}$$

Bohr's radius

$$a_B = \frac{4\pi\varepsilon_0\hbar^2}{e^2 m} \quad \rightarrow \quad \boxed{a_B = 0.529 \cdot 10^{-10}\ \mathrm{m}}$$

and

$$\boxed{r_n = a_B \cdot n^2}$$

Bohr’s model of the hydrogen atom 8 Comment

With the quantized orbital angular momentum, the radius of the Bohr orbits result.

The formula underlined in red gives the radius of the Bohr orbits.

The radius of the orbit is proportional to the quantum number n.

The constant of proportionality results from the numerical values.

The constant of proportionality is called the Bohr radius.

The Bohr radius defines the relevant length scale in atomic physics.

The formulas outlined in red give the Bohr radius and the radius of the Bohr orbits.

Bohr's model of the hydrogen atom 9

generalisation for nuclei with the atomic number *Z*:

orbital radius

$$\boxed{r_n = \frac{a_B}{Z} n^2}$$

energy

$$\boxed{E_n = -13.6\,\mathrm{eV}\frac{Z^2}{n^2}}$$

Bohr’s model of the hydrogen atom 9 Comment

The two equations framed in red give the generalization of the radius and the energy if the nuclear charge is Ze.

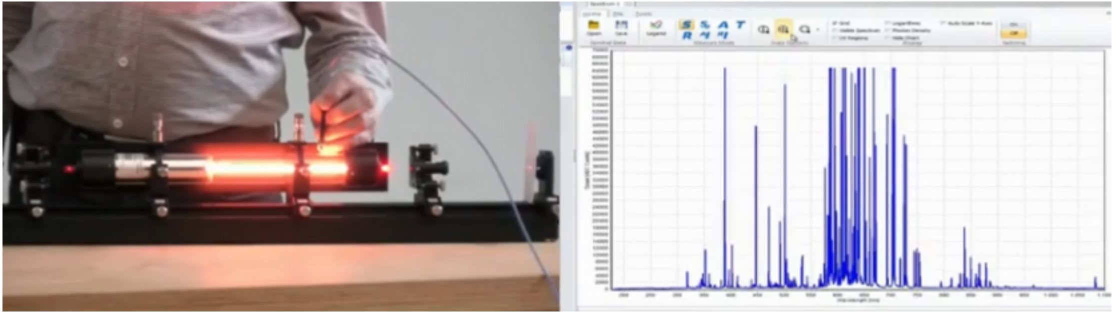
The radius of the orbit decreases with increasing atomic number and the energy $|E_n|$ increases with the square of the atomic number.

Alkali Spectra

Atoms

The spectra of the alkali metals 1

The optical spectrum of the helium and neon atoms



The spectra of the alkali metals 1 Comment 1

As an example, the figure shows the emission spectrum of the helium and neon atoms in the discharge tube of a He-Ne laser.

The spectrum is complicated so that no information about the energy levels of the helium and neon atoms can be obtained.

Bohr’s model of the atom does not help with this spectrum.

For most atoms, the spectra cannot be evaluated without the help of the Schrödinger equation.

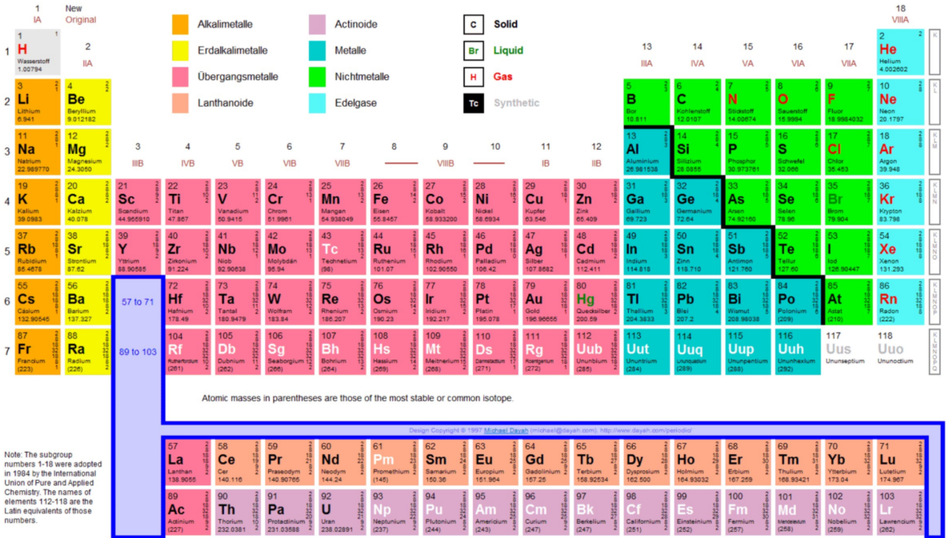
The optical spectra of the alkali metals are an exception.

The spectra of the alkali metals 1 Comment 2

The optical spectra of alkali metals are similar to the spectrum of the hydrogen atom. As with the hydrogen atom, the spectra of alkali metals contain series that are due to the excitation of a valence electron.

Furthermore, the transition energy between the energy levels can be described by the difference between two energy terms that deviate from the hydrogen energy terms only by small modifications.

The spectra of the alkali metals



🟧 Alkalimetalle
🟨 Erdalkalimetalle
🟥 Übergangsmetalle
🟧 Lanthanoide
🟪 Actinoide
🟦 Metalle
🟩 Nichtmetalle
🟦 Edelgase

C Solid
Br Liquid
H Gas
Tc Synthetic

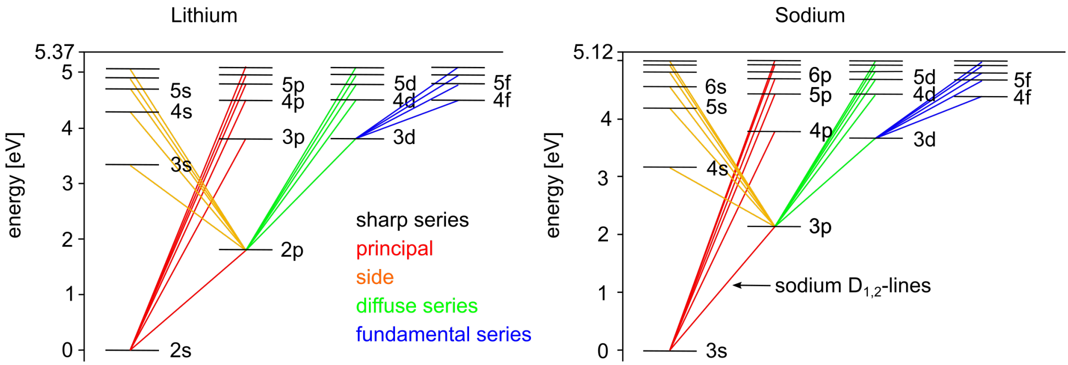
New Original	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 —	9 VIIIB	10 —	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1	1 **H** Wasserstoff 1.00794																	2 **He** Helium 4.002602	K
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Bor 10.811	6 **C** Kohlenstoff 12.0107	7 **N** Stickstoff 14.00674	8 **O** Sauerstoff 15.9994	9 **F** Fluor 18.9984032	10 **Ne** Neon 20.1797	K L
3	11 **Na** Natrium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminium 26.981538	14 **Si** Silizium 28.0855	15 **P** Phosphor 30.973761	16 **S** Schwefel 32.066	17 **Cl** Chlor 35.453	18 **Ar** Argon 39.948	K L M
4	19 **K** Kalium 39.0983	20 **Ca** Kalzium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titan 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chrom 51.9961	25 **Mn** Mangan 54.938049	26 **Fe** Eisen 55.8457	27 **Co** Kobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Kupfer 63.546	30 **Zn** Zink 65.409	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.64	33 **As** Arsen 74.92160	34 **Se** Selen 78.96	35 **Br** Brom 79.904	36 **Kr** Krypton 83.798	K L M N
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirkonium 91.224	41 **Nb** Niob 92.90638	42 **Mo** Molybdän 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silber 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Zinn 118.710	51 **Sb** Antimon 121.760	52 **Te** Tellur 127.60	53 **I** Iod 126.90447	54 **Xe** Xenon 131.293	K L M N O
6	55 **Cs** Cäsium 132.90545	56 **Ba** Barium 137.327	57 to 71	72 **Hf** Hafnium 178.49	73 **Ta** Tantal 180.9479	74 **W** Wolfram 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platin 195.078	79 **Au** Gold 196.96655	80 **Hg** Quecksilber 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Blei 207.2	83 **Bi** Wismut 208.98038	84 **Po** Polonium (209)	85 **At** Astat (210)	86 **Rn** Radon (222)	K L M N O P
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 to 103	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)	110 **Ds** Darmstadtium (271)	111 **Rg** Roentgenium (272)	112 **Uub** Ununbium (285)	113 **Uut** Ununtrium (284)	114 **Uuq** Ununquadium (289)	115 **Uup** Ununpentium (288)	116 **Uuh** Ununhexium (292)	117 **Uus** Ununseptium	118 **Uuo** Ununoctium	K L M N O P Q

Atomic masses in parentheses are those of the most stable or common isotope.

57 **La** Lanthan 138.9055	58 **Ce** Cer 140.116	59 **Pr** Praseodym 140.90765	60 **Nd** Neodym 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
89 **Ac** Actinium (227)	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uran 238.02891	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

The spectra of the alkali metals 2



The spectra of the alkali metals 2 Comment 1

The figure shows the energy level schemes of lithium and sodium as an example.

First there are the sharp series (George Liveing and James Dewar 1890), which are characterized by sharp spectral lines.

There is one principal series that can be observed in absorption and a there are side series that can only be observed in emission.

The principal series is marked in red. The side series with the greatest transition energies is marked in orange.

Similar to the hydrogen atom, an energy level scheme can be set up using the spectral lines.

The spectra of the alkali metals 2 Comment 2

In absorption, the transitions of the principal series start from a level which is marked with the letter ‘s’.

The transitions lead to energy levels marked with the letter ‘p’ (for principal series).

The spectral lines of the side series, which can only be observed in emission, start at the energy levels marked with the letter ‘s’ (for side series) and end at the energy levels marked with the letter ’p’.

Similar to the hydrogen atom, the energy levels can be assigned a quantum number and the transition energy results from the formula $\Delta E = E(n) - E(m)$ (Rydberg Schuster law 1896).

The functions $E(n)$ are called energy terms. The energy terms of the alkali metals are generalizations of the energy terms of the hydrogen atom.

The spectra of the alkali metals 2 Comment 3

In addition, the diffuse series was discovered together with the sharp series.

In the figures, the transitions of the diffuse series with the largest transition energies are marked in green.

On emission, the transitions start at energy levels marked with the letter ‘d’ (for diffuse series).

In 1907 Arno Bergmann discovered a fourth series. The corresponding energy levels are marked with the letter ‘f’.

X-rays

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- The Frank-Hertz experiment

X-ray spectra 1

Wilhelm Conrad Röntgen took an X-ray of the hand of his wife Anna Berta Röntgen in 1895.

X-ray spectra 1 Comment

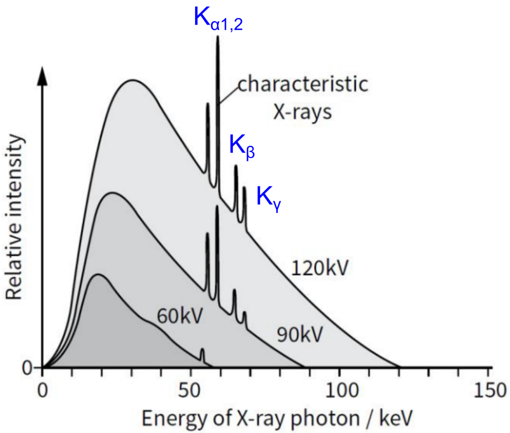
X-rays are generated in cathode ray tubes.

Wilhelm Conrad Röntgen was not the first to experiment with X-rays. But he was the first to see the great potential of X-rays.

In 1901 he was awarded the first Nobel prize in physics "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him."

In Germany X-rays are still called "Röntgenstrahlen".

X-ray spectra 2



Characteristic X-rays were discovered by Charles Glover Barkla in 1909

X-ray spectra 2

Comment 1

The figure shows the X-ray spectrum of a cathode made of tungsten.

The electrons are accelerated with voltages of 60, 90 and 120 kV.

The figure shows the broad spectrum of bremsstrahlung, which is caused by the deceleration of electrons in the cathode.

The sharp spectral lines of the characteristic radiation protrude from the broad spectrum of bremsstrahlung.

Similar to the optical spectra of the alkali metals, the characteristic lines of the X-rays form series.

X-ray spectra 2

Comment 2

When Barkla discovered the characteristic lines, the reason for the characteristic X-rays was not known.

Therefore Barkla named the series of characteristic lines with the letters K, L, M, ...

Since Barkla wasn’t sure whether there were series with higher energies, he started the lettering with letter ‘K’ to leave room for future discoveries.

The lines in a series are designated with increasing energy with the Greek letters α, β etc.

The figure shows only the lines of the K-series.

X-ray spectra 2

Comment 3

It turns out that the characteristic lines are usually split into many components.

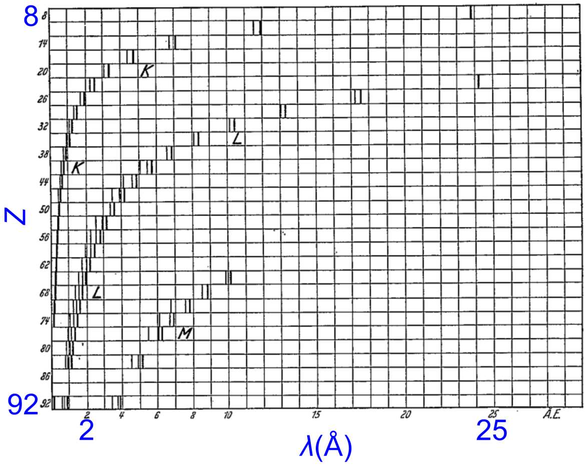
The characteristic lines were explored in great detail by Karl Manne Georg Siegbahn.

He introduced the notation of characteristic X-ray lines, which is still in use - also it is inconsistent due to the lack of understanding at that time.

Charles Glover Barkla was awarded the Nobel prize in 1917 “for his discovery of the characteristic Röntgen radiation of the elements’, another important step in the development of X-ray spectroscopy”.

Karl Manne Georg Siegbahn was awarded the Nobel prize in 1924 “for his discoveries and research in the field of X-ray spectroscopy”

X-ray spectra 3



The strongest lines of the K-, L-, and M-series of every third element from 8 (oxygen) to 92 (uranium)

X-ray spectra 3 Comment

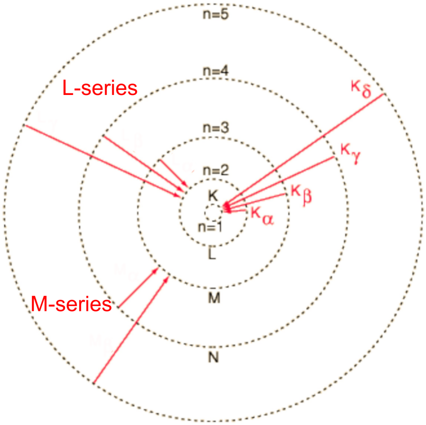
The figure gives an overview of the strongest spectral lines of the K-, L-, and M-series.

In contrast to the optical spectra of the elements, the X-ray spectra are comparatively simple.

Each element can be identified by the small number of its characteristic X-ray lines.

In 1912 Max von Laue showed experimentally that X-rays are electromagnetic waves with a very short wavelength.

X-ray spectra 4



Walther Kossel 1913:

characteristic X-rays lines are emitted when atoms are ionized

Simplified scheme of characteristic X-rays based on Bohr's model of the atom

X-ray spectra 4

Comment 1

The emission of characteristic X-ray radiation is always related to the emission of electrons.

Based on this experimental observation, Walther Kossel recognized in 1913 that the characteristic X-ray radiation can be traced back to the ionization of the atoms.

In analogy to the spectra of the alkali metals, one can try to describe the characteristic radiation by the difference in the energy terms.

Based on Bohr’s model of the atom Walther Kossel assumed that the electrons of an atom are arranged in shells that are determined by the quantum number n.

The K-series results when an electron is knocked out of the shell with the quantum number $n = 1$.

X-ray spectra 4

Comment 2

The L-series results when an electron is knocked out of the shell with the quantum number $n = 2$, and the M-series accordingly when an electron is knocked out of the shell with the quantum number $n = 3$.

The figure illustrates this idea.

It turns out that the reality is a bit more complicated.

More details are shown when atoms with many electrons are discussed.

X-ray spectra 5

Henry G. J. Moseley (1913)

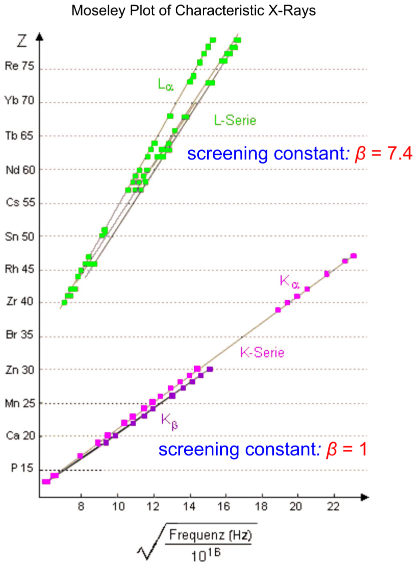
$$h\nu_{nm} = 13.6\,\text{eV}\left|\frac{1}{n^2}-\frac{1}{m^2}\right| \times (Z-\beta)^2$$

β: screening of the nuclear charge

Moseley plot of characteristic X-rays

$$Z \propto \sqrt{\nu_{nm}}$$

for certain elements in a certain frequency range



screening constant: $\beta = 7.4$

screening constant: $\beta = 1$

X-ray spectra 5 Comment 1

Moseley tested the idea that the characteristic X-rays can be described by the difference between two energy terms.

He found out that this approach is particularly simple of many elements.

Straight lines result when the atomic number is plotted against the root of the transition frequency of the characteristic X-ray radiation.

The illustration shows the Moseley plot.

Bohr's formula can be used, when the atomic number Z is reduced by a shielding constant β.

The figure shows all elements with the associated frequencies for which the approach works.

X-ray spectra 5

Comment 2

The approach only works for a relatively small selection of the characteristic X-ray lines.

Many characteristic X-ray lines are determined by interactions that are not contained in Bohr’s atomic model and can only be captured with the Schrödinger equation.

Finally, one can ask why the characteristic X-ray radiation can be described by the difference between two energy terms, while this approach only works for the hydrogen atom and the atoms of the alkali metals in the optical spectra.

The reason is the transition energy of the characteristic X-ray radiation.

X-ray spectra 5 Comment 3

The transition energy of the optical radiation is in the range between 1 eV and 3 eV.

The transition energy of the characteristic X-ray radiation is at least three to four orders of magnitude larger.

The large transition energy of the characteristic X-ray radiation means that interaction between the electrons of the atom are nearly negligible.

This roughly corresponds to the situation of a single valence electron.

In contrast, in optical transitions, the interaction between the electrons cannot be neglected at all.

Therefore, the entire electron configuration must be considered.

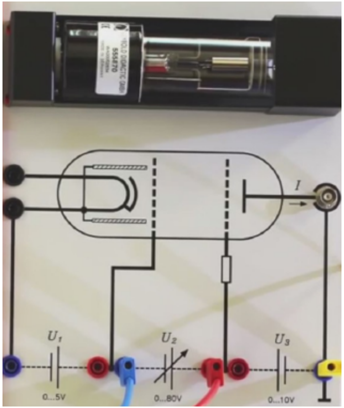
Frank-Hertz experiment

Early atomic physics

- The electron and the elementary charge
- The nucleus
- The spectrum of the hydrogen atom
- Bohr's model of the hydrogen atom
- The spectra of the alkali metals
- X-ray spectra
- The Frank-Hertz experiment

The Frank-Hertz experiment 1

With the Frank-Hertz experiment (1911-14) the energy loss of accelerated electrons is measured



- U_1 voltage between the cathode and the collecting electrode
- U_2 acceleration voltage
- U_3 retarding potential

The Frank-Hertz experiment 1 Comment 1

The experiments by James Frank and Gustav Hertz observe the loss of energy that electrons experience when they collide with an atom.

These experiments were conducted between 1911 and 1914 and were of some importance in the early days of atomic physics.

In addition to optical spectroscopy, they provided another clue to the quantization of atomic energy levels.

The figure shows a sketch of the experiment.

The electrons are vaporized at a cathode, collected with a first grid electrode and accelerated with a second grid electrode.

After the second grid electrode, the electrons are captured by an electrode to which a negative voltage is applied, which decelerates the electrons.

The Frank-Hertz experiment 1 Comment 2

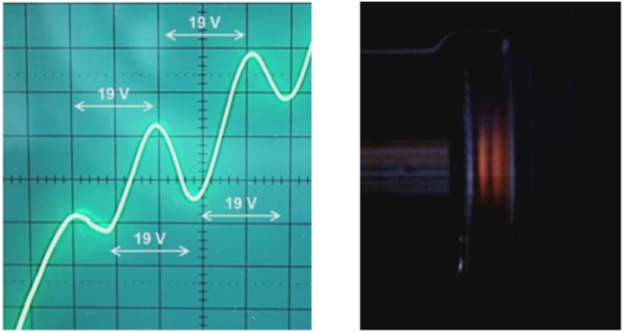
The electrons therefore need a certain minimum energy in order to be able to get to this collecting electrode.

The tube is filled with a gas.

On the way from the cathode to the anode, the electrons can collide with the atoms of the gas and transfer part of their kinetic energy to the atoms.

The Frank-Hertz experiment 2

The Frank-Hertz experiment with Neon



anode current and light emission of excited Neon atoms

(FrankHertzVersuch.mp4)

The Frank-Hertz experiment 2

Comment

The first figure shows the current through the anode.

The current shows minima when the electron can excite the Neon atoms efficiently.

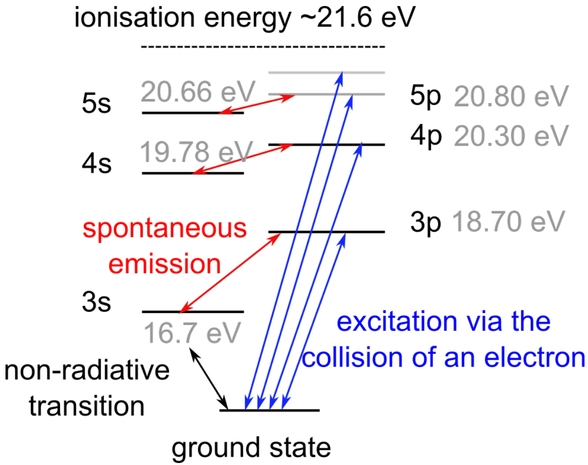
A fraction of the excitation energy is emitted by radiation.

The luminous clouds show the regions where the excitation of the Neon atoms is efficient.

The video explains the experiment in more detail.

The Frank-Hertz experiment 3

simplified energy level scheme of Neon



The Frank-Hertz experiment 3 Comment 1

The figure shows a simplified energy level scheme of the neon atom.

The broad minima of the anode current at a distance of approx. 19 V show that the neon atoms can be excited by the collision with electrons.

However, the collision with the electron does not excite a certain energy level, but rather all levels between the first excited state at 16.7 eV and the ionization energy of 21.6 eV.

If a neon atom is excited, it can spontaneously emit a photon. This explains the reddish glowing clouds that are visible in the tube.

Note that the energy level scheme is highly simplified and there are many more levels and transitions not included in the sketch.

The Frank-Hertz experiment 3 Comment 2

With a small modification of the experiment, the ionization energy of the neon atoms can also be measured.

To do this, the negative voltage U_3 at the anode must be increased to such an extent that no more electrons can overcome the potential barrier.

If the acceleration voltage U_2 exceeds 21.6 V, the neon atoms can be ionized by the electron impact.

If the ionized neon atoms get into the range of the voltage U_3 due to their thermal motion, they are accelerated towards the anode and a current begins to flow.

Schrödinger equation

Atoms

The Schrödinger equation as a wave equation

- Schrödinger equation
- Box potential
- Harmonic oscillator
- Orbital angular momentum
- Rotation of a diatomic molecule
- Schrödinger equation of the H-atom
- normal Zeeman-effect
- Dia- and paramagnetism

Schrödinger equation 1

de Broglie: the action S is proportional to the phase of a matter wave

$$\boxed{\varphi = \frac{S}{\hbar}}$$

with

$$\underline{dS = \vec{p}d\vec{r} - Hdt}$$

and the phase of a plane wave

$$\varphi = \vec{k}\vec{r} - \omega t \quad \rightarrow \quad d\varphi = \vec{k}d\vec{r} - \omega dt$$

follows Planck's law (at least when energy is conserved $H = E$)

$$\underline{E = \hbar\omega}$$

and the de Broglie wavelength

$$\underline{\vec{p} = \hbar\vec{k}} \quad \rightarrow \quad \lambda = \frac{h}{p}$$

Schrödinger equation Comment 1

Louis de Broglie discovered that the phase of a matter wave is proportional to the action S of a particle.

The equation outlined in red shows the relationship between the phase and the action.

Even if the function of the action differs from case to case, classical mechanics shows that the action changes according to the formula underlined in red when the end point of the path is varied in space and time.

The differential dS results from the differential $d\vec{r}$ of the end point of the path multiplied by the momentum of the particle and the differential of the time dt multiplied by the Hamilton function.

Schrödinger equation Comment 2

The Hamilton function results from the energy of the particle when the velocity is expressed by the momentum $p = mv$, i.e. $\frac{1}{2}mv^2 \to \frac{p^2}{2m}$.

The comparison between the differential of the action and the differential of a plane wave gives Planck's law and the de Broglie wavelength.

Schrödinger equation 2

Schrödinger: simplest matter wave

$$\psi(\vec{r},t) = \psi_0 e^{i\frac{S}{\hbar}}$$

with differential of the action $dS = \vec{p}d\vec{r} - Hdt$ are the partial derivatives of the action

$$\frac{\partial S}{\partial x} = p_x, \quad \frac{\partial S}{\partial y} = p_y, \quad \frac{\partial S}{\partial z} = p_z \quad \text{und} \quad \frac{\partial S}{\partial t} = -H$$

partial derivatives of the wave function

$$\frac{\partial \psi}{\partial x} = \psi_0 \frac{i}{\hbar}\frac{\partial S}{\partial x} e^{i\frac{S}{\hbar}} = \frac{i}{\hbar} p_x \psi$$

$$\frac{\partial \psi}{\partial t} = \psi_0 \frac{i}{\hbar}\frac{\partial S}{\partial t} e^{i\frac{S}{\hbar}} = -\frac{i}{\hbar} H \psi$$

Schrödinger equation 2 Comment

In 1926 Erwin Schrödinger was looking for a differential equation with which the wave function of a matter wave can be calculated.

It starts with the simplest version of a wave function i.e. a constant amplitude multiplied by the complex exponential function of the phase of a matter wave.

With the formula underlined in red for the change in the action if the end point and the end time are shifted, one finds the partial derivatives of the action.

The partial derivative of the action according to the coordinates *x*, *y*, *z* gives the corresponding components of the momentum.

The partial derivative of the action with respect to time gives the Hamilton function multiplied by -1.

With the partial derivatives of the action, the partial derivatives of the wave function can be written down.

Schrödinger equation 3

relativistic energy-momentum relation

$$\boxed{E^2 - c^2\vec{p}^{\,2} = m_0^2 c^4}$$

$$-i\hbar\frac{\partial\psi}{\partial x} = p_x\psi \quad \text{und} \quad i\hbar\frac{\partial\psi}{\partial t} = E\psi$$

and

$$E^2 - c^2\vec{p}^{\,2} = m_0^2 c^4 \quad \rightarrow \quad (E^2 - c^2\vec{p}^{\,2})\psi = m_0^2 c^4\psi$$

Klein-Gordon equation

$$\underline{-\hbar^2\frac{\partial^2\psi}{\partial t^2} + c^2\hbar^2\nabla^2\psi = m_0^2 c^4\psi}$$

Schrödinger equation 3 Comment

In a first attempt to find a wave equation, one can begin with the relativistic energy-momentum relation.

With the partial derivatives of the wave function, the energy-momentum relation can be converted into a differential equation.

The underlined equation is nowadays called the Klein-Gordon equation.

Schrödinger ruled out this equation because in 1926 it was not yet known that particles can transform into other particles.

He assumed that the probability of finding a particle must obey a conservation law.

However, this requirement cannot be met with the solutions of the Klein-Gorden equation.

Schrödinger equation 4

Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \quad \rightarrow \quad \boxed{i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\,\psi}$$

momentum operator

$$\boxed{\hat{p}_x = -i\hbar\frac{\partial}{\partial x}} \quad \rightarrow \quad \hat{\vec{p}} = -i\hbar\nabla$$

Hamilton function → Hamilton operator

$$\underline{H = \frac{\vec{p}^{\,2}}{2m} + E_{pot}} \quad \rightarrow \quad \boxed{\hat{H} = \left(-\frac{\hbar^2\nabla^2}{2m} + E_{pot}\right)}$$

Schrödinger equation 4 Comment 1

A look into electrodynamics shows how the problem of particle conservation can be solved.

The following equation describes charge conservation

$$\partial_t \rho = -\nabla \vec{j}.$$

Here ρ denotes the charge density and $\vec{j}$ the current density.

From a mathematical point of view, first-order time differentiation is decisive for charge conservation.

Therefore Schrödinger starts with the time derivation of the wave function, i.e. $i\hbar \frac{\partial \psi}{\partial t} = H\psi$.

To get a differential equation, he transforms the Hamilton function into a differential operator: the Hamilton operator or Hamiltonian.

Schrödinger equation 4

Comment 2

For this purpose, Schrödinger defines the momentum operator with the spatial derivatives of the wave function.

With the momentum operator he converts the Hamilton function into the Hamilton operator by replacing the momentum with the momentum operator.

The equation underlined in red is the Hamilton function of a classical particle with kinetic and potential energy and the equation in the box is the associated Hamilton operator.

Schrödinger equation 4 Comment 3

It soon became apparent that the Schrödinger equation is the fundamental equation of quantum physics.

Paul Dirac derived the relativistic wave equation for the electron in 1927.

In 1933 Erwin Schrödinger and Paul Dirac were awarded the Nobel Prize “for the discovery of new productive forms of atomic theory”.

Schrödinger equation 5

Summary:

- The general Schrödinger equation

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\,\psi}$$

- The Schrödinger equation of a classical particle with potential energy

$$\boxed{i\hbar\frac{\partial\psi}{\partial t} = \left(-\frac{\hbar^2\nabla^2}{2m} + E_{pot}\right)\psi}$$

Schrödinger equation 5 Comment

The slide summarizes the general Schrödinger equation and the Schrödinger equation for a non-relativistic particle with potential energy.

Only this Schrödinger equation is used in this lecture.

Schrödinger equation 6

inspired by electromagnetic waves one defines the probability density

$$\underline{\psi\psi^* = |\psi|^2}$$

the probability of finding a particle in the volume *dV* is

$$\boxed{|\psi|^2 dV}$$

if the particle is located in the volume *V*, the normalization condition reads

$$\underline{\int_V |\psi|^2 d^3 r = 1}$$

Schrödinger equation 6

Comment

In electromagnetic waves, the energy density is proportional to the square of the wave function. This corresponds to the photon density.

Similarly, the square of the magnitude of the wave function of a matter wave determines the probability density that particles can be found.

With a particle beam, the underlined equation can be normalized to the particle density of the beam.

The equation outlined in red then gives the number of particles in the volume element dV.

If the particles are restricted to the volume V, the underlined equation gives the normalization condition of the wave function.

Schrödinger equation 7

1st example: The eigenvalue equation of the momentum operator $\hat{\vec{p}} = -i\hbar\nabla$

With a plane matter wave

$$\psi = \psi_0 e^{i(\vec{k}\vec{r}-\omega t)} = \psi_0 e^{i(\vec{p}\vec{r}-Et)/\hbar}$$

one gets

$$\hat{\vec{p}}\,\psi = -i\hbar\nabla\psi = -i\hbar\begin{pmatrix}\frac{\partial}{\partial x}\\ \frac{\partial}{\partial y}\\ \frac{\partial}{\partial z}\end{pmatrix}\psi = \vec{p}\,\psi$$

eigenvalue equation of the momentum operator

$$\boxed{\hat{\vec{p}}\,\psi = \vec{p}\,\psi}$$

the eigenvalue of the momentum operator is the momentum $\vec{p}$

Schrödinger equation 7 Comment

The momentum operator is considered as a first example for the application of Schrödinger’s theory.

If the momentum operator is applied to a plane wave, then e.g. the derivation according to the x-coordinate brings the x-component of the momentum in front of the wave function.

Overall, the eigenvalue equation outlined in red results for the momentum.

The eigenvalue of the momentum operator $\hat{\vec{p}}$ gives the numerical value for the momentum that can be determined in a measurement.

Schrödinger equation 8

uncertainty relations

$$\boxed{\Delta x \Delta p_x \geq \frac{\hbar}{2}, \quad \text{etc.}}$$

a plane wave is infinite: because of $\Delta x \to \pm\infty$ the position of a particle is completely indetermined

Due to the uncertainty relation, the momentum uncertainty Δp_x is zero, i.e. the momentum has a defined numerical value.

the mathematical formulation of this fact is the eigenvalue equation

$$\boxed{\hat{\vec{p}}\,\psi = \vec{p}\,\psi}$$

Schrödinger equation 8 Comment

The statement of the eigenvalue equation can be compared with the space-momentum uncertainty relation.

Plane waves are defined throughout space without any limitations.

Plane waves are therefore an abstraction that can never be realized in nature.

Nevertheless, plane waves are often used because the mathematical description is so simple.

If a particle is described by a plane wave, it cannot be localized.

Its position is not determined and the momentum uncertainty is zero, i.e. the momentum is exactly defined.

This fact is expressed by the eigenvalue equation of the momentum operator.

Schrödinger equation 9

2nd example: the eigenvalue equation of the Hamilton operator

uncertainty relation for time and energy

$$\boxed{\Delta t \Delta E \geq \frac{\hbar}{2}, \quad \text{etc.}}$$

the energy is exactly defined, i.e. $\Delta E \to 0$ when the time is not at all defined, i.e. $\Delta t \to \infty$

ansatz for wave function when energy is conserved

$$\boxed{\psi(\vec{r}, t) = \varphi(\vec{r}) e^{-iEt/\hbar}}$$

Schrödinger equation 9 Comment 1

The first equation outlined in red gives the time-energy uncertainty relation.

The energy uncertainty decreases as the time uncertainty increases.

If the energy uncertainty is zero, then the time uncertainty is infinitely large.

This means that the energy will never change in all times.

In other words: the energy is preserved.

The second equation outlined in red gives the solution of the Schrödinger equation when the energy is conserved.

Schrödinger equation 9 Comment 2

The solution is a standing wave.

The wave function is the product of a function that describes the spatial variation and a function that only depends on time.

The time dependency is described by a harmonic oscillation that never stops.

Schrödinger equation 10

application of the Schrödinger equation on the wave function $\psi(\vec{r},t) = \varphi(\vec{r})e^{-iEt/\hbar}$

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi \quad \rightarrow \quad i\hbar\frac{\partial}{\partial t}\varphi(\vec{r})e^{-iEt/\hbar} = E\varphi(\vec{r})e^{-iEt/\hbar} = \hat{H}\varphi(\vec{r})e^{-iEt/\hbar}$$

If the Hamilton operator does not depend on time, then the exponential functions can be canceled and an eigenvalue equation for the energy results

time independent Schrödinger equation

$$\boxed{\hat{H}\varphi(\vec{r}) = E\varphi(\vec{r})}$$

Schrödinger equation 10 Comment 1

If this ansatz is used for the wave function in the Schrödinger equation, then the calculation of the first line results

The equation is only valid if the Hamilton operator is not an explicit function of time. Then the exponential functions can be canceled.

The remaining equation is the eigenvalue equation for the time-independent Hamilton operator.

This equation is called the time-independent Schrödinger equation.

The energy is the eigenvalue of the time-independent Hamilton operator and the energy does not depend on time.

Schrödinger equation 10 Comment 2

This result corresponds to the assumption made by de Broglie.

He assumed that the frequency does not depend on the time and that the Hamilton function can be replaced by the energy.

This result also corresponds to the classical mechanics.

In Hamiltonian mechanics it is shown that the energy is conserved if the Hamilton function is not an explicit function of time.

The time-independent Schrödinger equation formulates this result of classical mechanics in the language of quantum mechanics.

Schrödinger equation 11

Generally applies in quantum mechanics:

There is an eigenvalue equation for physical quantities that have a fixed value.

$$\text{operator} \times \text{eigenfunction} = \text{eigenvalue} \times \text{eigenfunction}$$

Schrödinger equation 11 Comment

In general, the following applies in quantum mechanics:

If a physical quantity has a fixed value, there is also an eigenvalue equation.

The wave function for an eigenvalue is called an eigenfunction.

For every eigenvalue there is at least one eigenfunction.

If an operator is applied to one of its eigenfunctions, the result is the eigenvalue multiplied by the eigenfunction.

Revision

Summary in questions 1

1. Calculate the shortest wavelength of the Lyman-, the Balmer, and the Paschen series.
2. Give Bohr's postulates.
3. Give the numerical value of Bohr's radius and the general formula for the radius of Bohr's orbits.
4. Write down Moseley's formula for the energy of the characteristic X-rays.
5. What does the K_α-line mean?
6. Calculate the energy of the K_α- and K_β-line of manganese.

Summary in questions 2

7. Give the eigenvalue equation of the x-component of the momentum.
8. Write down the eigenfunctions of the momentum operator.
9. Write down the general Schrödinger equation.
10. Give the Hamilton operator of a classical particle with potential energy.
11. Write down the time-independent Schrödinger equation.