Atoms

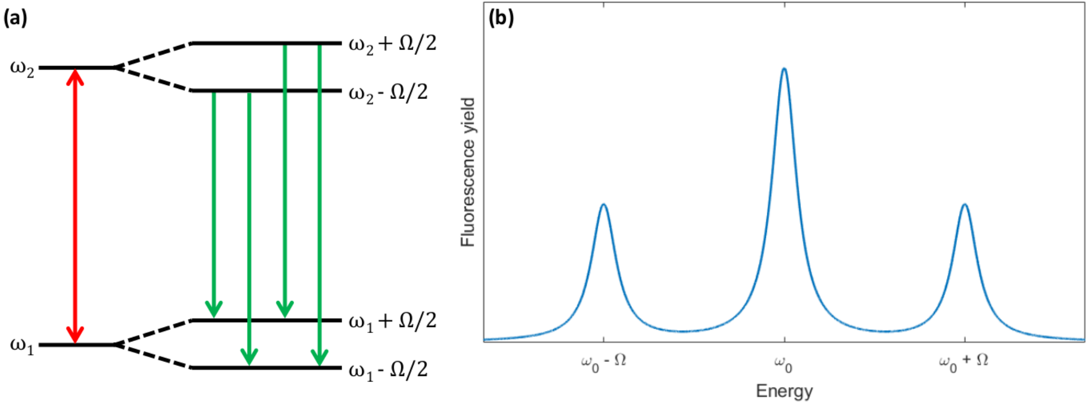
Autler-Townes

Quantum mechanics

- Stern-Gerlach experiment
- Spin of the electron
- Dirac notation
- Spin-orbit coupling
- Addition of angular momenta
- Anomalous Zeeman effect
- Hyperfine interaction
- Selection rules for elm. dipole transitions
- Autler-Townes splitting

Autler-Townes splitting 1: Mollow triplet

Rabi frequency: $\boxed{\Omega = \langle f|\, e\vec{r}\, |i\rangle \cdot \vec{E}/\hbar}$



Autler-Townes splitting 1

Comment 1

In modern physics, powerful laser pulses are often used.

The energy of the electric dipole interaction due to the electromagnetic wave is no longer small compared to the spectral width of the transition.

The energy of the electric dipole interaction divided by $\hbar$ is called the Rabi frequency.

Due to the interaction with the electromagnetic wave, the energy levels are shifted.

The energy level diagram in figure (a) depicts the splitting of states $|1\rangle$ and $|2\rangle$ due to a strong resonant laser field (red arrows). The green arrows show transitions where spontaneous emission can occur.

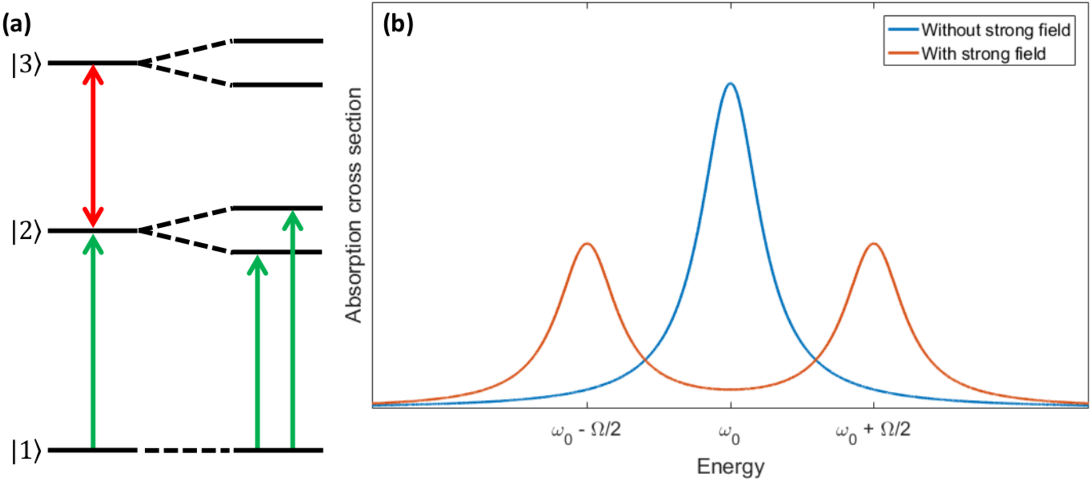
Autler-Townes splitting 1 Comment 2

The figure (b) shows a sketch of a fluorescence spectrum from as resonantly coupled two-level system, showing the Mollow triplet structure.

The four possible transitions would lead to spectral features at frequencies ω_0, $\omega_0 - \Omega$, and $\omega_0 + \Omega$.

(Figure 5.2 in the PhD thesis by Nathan Harkema (The University of Arizona 2020))

Autler-Townes splitting 2



Autler-Townes splitting 2 Comment 1

Figure (a) shows an energy level diagram for a three-level system that interacts with two laser fields.

A strong laser field (red arrow) couples states $|2\rangle$ and $|3\rangle$ while a weak laser (green arrow) field probes near the $|1\rangle \rightarrow |2\rangle$ transition.

Figure (b) shows a sketch of an absorption spectrum for the weak field in figure (a) with (red curve) and without (blue curve) the strong laser field.

When the strong laser field is present, the absorption line for the $|1\rangle \rightarrow |2\rangle$ transition splits into two components.

This kind of splitting was discovered by Stanley Autler and Charles Townes in 1955 by using a strong and a weak radio frequency light source.

Autler-Townes splitting 2 Comment 2

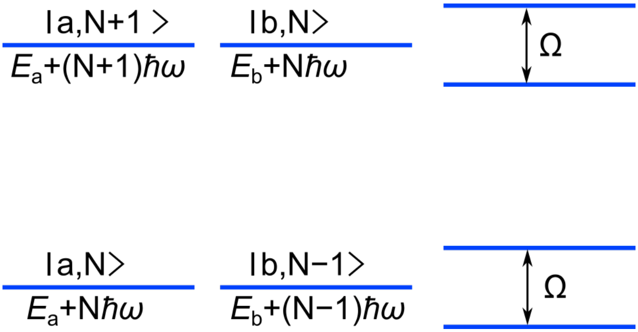
There is a fundamental difference between the level splitting observed in a magnetic field (Zeeman effect) and the level splitting in the strong field of an electromagnetic wave.

More than one quantum state is involved in a splitting in a magnetic field, e.g. a p-orbital splits into three components according to the magnetic quantum numbers $m = 0, \pm 1$.

The splitting shown in the previous figures is due to the fact that the quantum states $|1\rangle$, $|2\rangle$ etc. are so-called dressed states in the field of a strong electromagnetic wave.

The quantum states are composed of the atomic quantum states $|n\rangle$ and the quantum states of the photons, i.e. $|n, N\gamma\rangle$. (N denotes the number of photons involved.)

Autler-Townes splitting 3: dressed states



$|a,N+1\rangle$ $|b,N\rangle$

$E_a+(N+1)\hbar\omega$ $E_b+N\hbar\omega$

Ω

$|a,N\rangle$ $|b,N-1\rangle$

$E_a+N\hbar\omega$ $E_b+(N-1)\hbar\omega$

Ω

(see also the nice article of Cohen-Tannoudji, C.N. (1996). The Autler-Townes Effect Revisited. In: Chiao, R.Y. (eds) Amazing Light. Springer, New York, NY.)

Autler-Townes splitting 3 Comment

The figure shows the energy level diagram in more detail.

For the dressed states, the energy of the atomic quantum state, e.g. E_a of $|a\rangle$ must be considered together with the energy of the photons, i.e. $N\hbar\omega$ if N photons are coupled to the state $|a\rangle$.

The figure shows the case that $E_b - E_a = \hbar\omega$.

Therefore $E_a + (N+1)\hbar\omega = E_b + N\hbar\omega$ and $E_a + N\hbar\omega = E_b + (N-1)\hbar\omega$.

The electric dipole interaction $\vec{d}\vec{E}$ shifts the energy levels as shown on the right side of the figure.

Due to the electric dipole interaction, the quantum states are given by a linear combination of $|a, N+1\rangle$ and $|b, N\rangle$ for the upper levels and $|a, N\rangle$ and $|b, N-1\rangle$ for the lower levels.

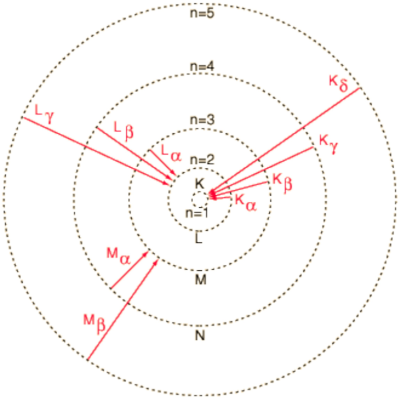
Atoms

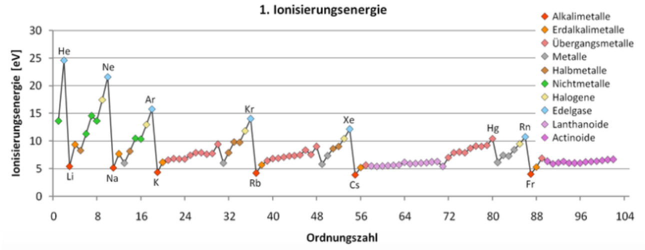
Periodic table

Atoms with many electrons

- Periodic table of elements
- Coupling schemes
- Entanglement
- Exchange interaction
- Hund’s rules
- Crystal-field, Ligand-field and the quench of the orbital angular momentum

Periodic table of elements 1





Wolfgang Pauli (1925): Electrons must differ in at least one quantum number

Periodic table of elements 1 Comment 1

The pictures show that the electrons in atoms are arranged in shells.

The spectra of the characteristic X-rays and the measurement of the ionization energy of the atoms give a strong indication that the electrons in the atom are bound in shells that can hold a certain number of electrons.

In 1925, based on all available experimental data, Niels Bohr came to the conclusion that electrons must differ in at least one quantum.

This discovery is known as the Pauli Exclusion Principle or short Pauli Principle.

Two electrons cannot occupy one quantum state together.

Periodic table of elements 1 Comment 2

With the Schrödinger equation it became clear that the periodic table of the elements can be explained with the Pauli principle.

The Pauli principle is very general.

In nature, particles can be divided into two groups.

Particles that obey the Pauli principle like electrons are called fermions.

Particles that do not obey the Pauli principle are called bosons.

In contrast to fermions, any number of bosons can occupy a quantum state.

Periodic table of elements 1 Comment 3

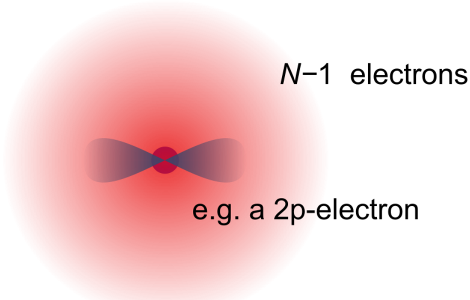
Fermions are called after the Italian physicist Enrico Fermi.

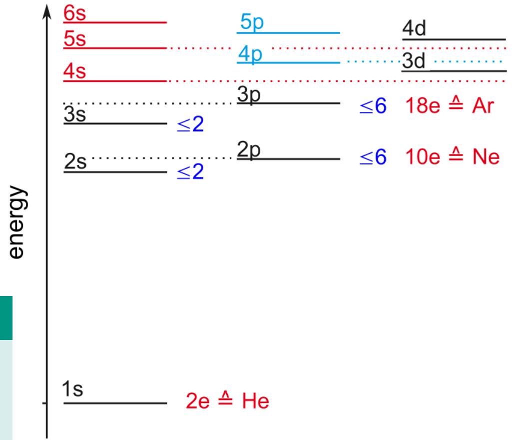
Bosons are called after the Indian physicist Satyendra Nath Bose.

Electrons, protons, and neutrons are fermions, while photons are bosons.

It turns out that all particles with integer spin are bosons, while particles with half-integer spin are fermions.

Periodic table of elements 2





Schrödinger equation for each electron

$$E_{n,\ell}\,\varphi_{n,\ell}(\vec{r}) = \left\{-\frac{\hbar^2\nabla^2}{2m} + \underline{E^{pot}_{n,\ell}(r)}\right\}\varphi_{n,\ell}(\vec{r})$$

Periodic table of elements 2 Comment 1

The electron - electron repulsion is the most important additional interaction when considering atoms with two or more electrons.

The potential energy of an electron results from the attraction of the nucleus and the repulsive forces between the electrons.

The electron - electron repulsion reduces the binding energy of the electrons.

The most important effects are due to the fact that each electron moves in a negatively charged spherical cloud which is formed by the orbitals of all other electrons.

The negatively charged cloud screens the nuclear charge and thereby reduces the binding energy of the electrons.

Periodic table of elements 2 Comment 2

The picture illustrates the situation.

The spherical electron cloud is formed by the orbitals of the $N-1$ electrons.

The negative charge density is only a function of the radius r.

In the illustration, the orbital of a 2p electron is embedded in the electron cloud as an example.

The resulting Schrödinger equation is very similar to the Schrödinger equation of the hydrogen atom.

The potential energy is now composed of the Coulomb energy of the atomic nucleus and the potential energy of the electron cloud.

Periodic table of elements 2 Comment 3

The total potential energy only depends on the distance r to the nucleus.

The wave function $\varphi_{n,\ell}(\vec{r})$ is formed by the product of the radial wave function $R_{n,\ell}(r)$ and the spherical harmonic $Y_{\ell,\mathrm{m}}(\theta, \varphi)$.

Therefore, the orbitals of the various electrons can still be described with the notation that was introduced for the hydrogen atom.

In contrast to the solution of the Schrödinger equation for the hydrogen atom, the energy eigenvalues depend not only on the principal quantum number n but also on the orbital angular momentum quantum ℓ, i.e. $E_{n,\ell}$.

The reason for this is that the shielding of the atomic nucleus has different effects depending on the principal quantum number n and the angular momentum quantum number ℓ.

Periodic table of elements 2

Comment 4

The numerical procedure is as follows.

The calculation starts with a reasonable assumption for the radial wave functions of the electrons.

With these wave functions the effective potential of each electron can be calculated.

Functionals that have been optimized over time are used for this calculation.

Solving the Schrödinger equation leads to improved wave functions that are used to calculate an improved potential energy.

The calculations are repeated in iterative steps until the minimum energy is reached.

Periodic table of elements 2

Comment 5

The energy level diagram on the right shows a sketch of the main effects.

The ground state is formed by the 1s orbital.

This orbital can be occupied with two electrons according to the Pauli principle.

The two electrons differ in the quantum number m_s of the spin.

The configuration with two electrons in the 1s orbital is found in the helium atom, which has the atomic number $Z = 2$.

The ionisation energy of Helium is 24.6 eV.

This is larger than the 13.6 eV of the hydrogen atom, but significantly smaller than $E_{1\mathrm{s}} = 13.6\,\mathrm{eV} \cdot 2^2 = 54.4\,\mathrm{eV}$.

Periodic table of elements 2 Comment 6

This binding energy would be expected if the nuclear charge is not shielded.

After the 1s orbital is occupied, the 2s and 2p orbitals will be occupied if the atomic number is increased up to 10.

The 2s orbital can be occupied with two electrons and the 2p orbital with up to six electrons.

The main quantum number $n = 2$ denotes the L shell, which can be occupied with up to 8 electrons

The binding energy of the 2s orbital is larger than the binding energy of the 2p orbital.

Periodic table of elements 2

The reason for this is that the shielding of the nuclear charge is more effective with a 2p orbital than with a 2s orbital.

s electrons can reach the nucleus, while the centrifugal force prevents p electrons from approaching the nucleus.

In the case of neon with the atomic number $Z = 10$, the 1s, 2s and 2p orbitals are fully occupied.

The ionization energy is 21.6 eV and only slightly smaller than the 24.6 eV of the helium atom.

This result shows that the shielding of the nuclear charge is very effective.

Periodic table of elements 2

Comment 8

For the sodium atom is the atomic number $Z = 11$.

The additional electron occupies the 3s orbital.

The ionization energy is 5.1 eV.

The small ionization energy shows that the nuclear charge is effectively shielded through the fully occupied L-shell.

The sodium D-lines (yellow sodium line) are caused by the excitation of the valence electron in the 3p orbital

The excitation energy is 2.1 eV.

Periodic table of elements 2

Comment 9

For the Argon atom with the atomic number $Z = 18$, the 3s and 3p orbitals are completely occupied by electrons.

Argon, like helium and neon, is a noble gas and the ionization energy is comparatively large at 15.8 eV.

The shell model based on Bohr’s atomic model only works for the principal quantum numbers $n = 1$ and $n = 2$.

In the case of potassium with the atomic number $Z = 19$, the valence electron occupies the 4s orbital and not, as expected, the 3d orbital.

The ionization energy of potassium is 4.34 eV.

Periodic table of elements 2

Comment 10

The binding energy of the 4s orbital is larger than the binding energy of the 3d orbital.

The energy difference between the binding energy of the 4s electrons and the 3d electrons is so small that even tiny changes in the number of electrons can change the order in which the orbitals are occupied.

For magnesium with the atomic number $Z = 20$ the 4s orbital is occupied with two electrons.

Then the 3d orbitals up to vanadium with the atomic number $Z = 23$ are occupied with electrons.

The electron configuration of chromium with the atomic number $Z = 24$ is $[\mathrm{Ar}]4\mathrm{s}^1 3\mathrm{d}^5$ and there is only one electron in the 4s orbital.

Periodic table of elements 2

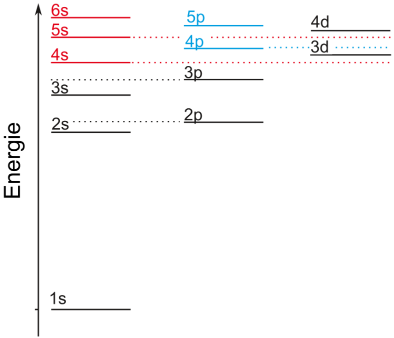
Comment 11

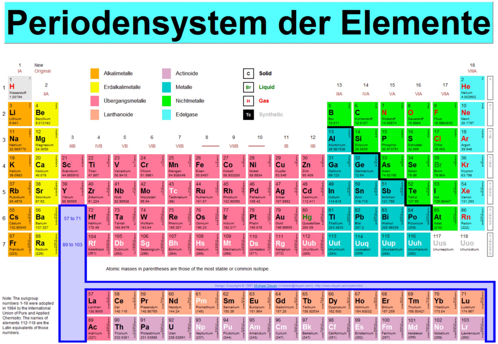
The electron configuration of manganese (atomic number $Z = 25$) is [Ar]$4s^2 3d^5$ and the 4s orbital is again occupied with two electrons.

The electron configuration of copper (atomic number $Z = 29$) is [Ar]$4s^1 3d^{10}$ and the 4s orbital is again occupied only with one electron.

The binding energy is obviously particularly high when either an orbital is completely or only half occupied by electrons.

Periodic table of elements 3





Periodensystem der Elemente

- 🟧 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																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 to 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 to 103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

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

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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.

Periodic table of elements 3

Comment 1

Despite these subtleties, the periodic table of the elements shows the successive occupation of the atomic orbitals.

When the 3d orbital is fully occupied, the 4p orbital is occupied.

These are the elements from gallium to krypton.

A fully occupied p orbital is always a noble gas configuration.

The ionization energy of noble gas configurations is particularly large.

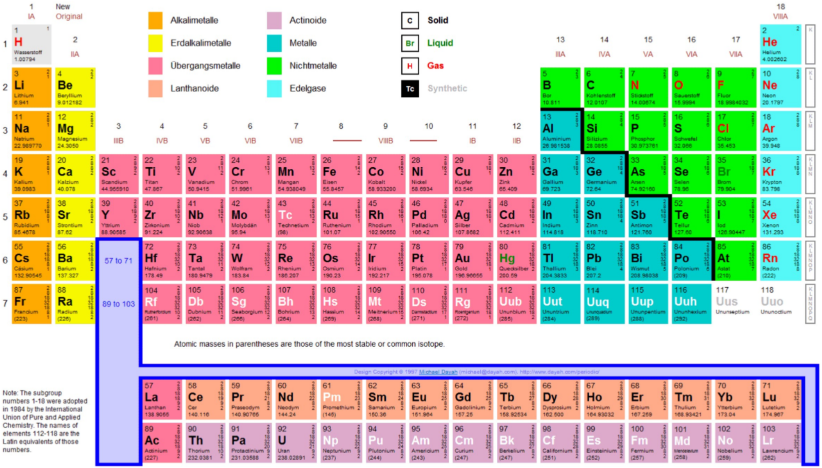
Noble gases do not form covalent bonds and are insulators when they crystallize at low temperatures.

Periodic table of elements 3 Comment 2

Following the noble gas configuration of krypton, the occupation of the 5s, 4d and 5p orbitals follows with increasing atomic numbers.

These orbitals are completely occupied for the noble gas xenon.

Periodic table of elements 4



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

C Solid
Br Liquid
H Gas
Tc Synthetic

	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
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
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
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
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
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)
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

New
Original

K / KL / KLM / KLMN / KLMNO / KLMNOP / KLMNOPQ

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

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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)

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Periodic table of elements 4 Comment 1

Since the differences in ionization energy are very small, the periodic table shows another interesting effect.

When the noble gas configuration of xenon is complete, the 6s orbital is occupied by electrons.

The occupation of the 5d orbital begins with lanthanum.

If the atomic number is increased from $Z = 57$ to $Z = 58$, the 5d orbital will not be any more occupied, but the 4f orbital.

These are the rare earth elements from cerium to lutetium.

The diameter of the 4f orbital is smaller than the diameter of the 6s and 5p orbitals, i.e. the 4f orbital is shielded from the environment of the atom by these orbitals.

Periodic table of elements 4

Comment 2

Therefore, electrons of the 4f orbital are hardly affected by the environment when the atom is part of a molecule or solid.

Due to this fact, the excited states of the 4f orbital have long lifetimes and therefore narrow spectral lines, which is the reason for many interesting optical and magnetic properties of these elements.

Coupling schemes

Atoms with many electrons

- Periodic table of elements
- Coupling schemes
- Entanglement
- Exchange interaction
- Hund’s rules
- Crystal-field, Ligand-field and the quench of the orbital angular momentum

Coupling schemes 1

electron-electron repulsion

$$\hat{H}_C = \sum_{i<j} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

LS-scheme when spin-orbit coupling is negligible

$$\boxed{\hat{\vec{L}} = \sum_i \hat{\vec{L}}_i}$$

and

$$\boxed{\hat{\vec{S}} = \sum_i \hat{\vec{S}}_i}$$

Coupling schemes 1 Comment

The repulsive force between the electrons is an important interaction.

The equation underlined in red indicates the potential energy due to electron-electron repulsion.

Since the Coulomb repulsion does not affect the spin of the electrons, spins and orbital angular momenta are independent of one another as long as the spin-orbit coupling is negligibly small.

Therefore the orbital angular momentum of the electrons add up to a total orbital angular momentum and the spins add up to a total spin of the electron configuration.

This regime is known as the LS coupling scheme.

Coupling schemes 2

Notation of an electron configuration

$$\boxed{{}^{2S+1}L_J}$$

and

$$\underline{\hat{\vec{J}} = \hat{\vec{S}} + \hat{\vec{L}}}$$

completely occupied orbitals

$$\boxed{L = 0 \quad \text{and} \quad S = 0 \quad \text{and} \quad J = 0}$$

Coupling schemes 2

Comment

In terms of angular momentum, the notation of electron configurations is similar to the notation of a single orbital.

The symbol framed in red shows the notation.

The total orbital angular momentum is indicated by the capital letters S, P, D, F, etc.

The total angular momentum results from the sum of the total spin and the total orbital angular momentum.

When an orbital is completely occupied by electrons, the total angular momentum adds up to zero.

Therefore only the incompletely occupied orbitals contribute to the total angular momentum of the electron configuration.

Coupling schemes 3

spin orbit coupling

$$\hat{H}_{SL} = \sum_i \xi \frac{\hat{\vec{S}}_i \hat{\vec{L}}_i}{\hbar^2}$$

- for $Z \lesssim 50$ the LS-scheme works, i.e. $\vec{J} = \vec{L} + \vec{S}$
- for $Z \gtrsim 50$ only J and M_J are good quantum numbers

  remark: nevertheless the LS notation scheme is always used to denote electron configurations

but selection rules for ΔS and ΔL break down

Coupling schemes 3

Comment 1

The spin-orbit coupling is always present.

The total orbital angular momentum and the total spin form the total angular momentum J due to the spin-orbit coupling, as long as the electron-electron repulsion dominates for atomic numbers less than $Z \approx 50$.

If the atomic number becomes large, i.e. greater than $Z \approx 50$, only the total angular momentum is strictly defined.

The selection rules $\Delta S = 0$ and $\Delta L = 0, \pm 1$ are no longer valid.

Coupling schemes 3

Comment 2

Interestingly, the LS notation is still used to describe the quantum states.

The reason for this lies in the mathematics of quantum states.

The quantum states are developed into a sum of pure LS states.

The LS quantum numbers of the largest contribution are then used to denote the overall quantum state.

Entanglement

Atoms with many electrons

- Periodic table of elements
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- Exchange interaction
- Hund’s rules
- Crystal-field, Ligand-field and the quench of the orbital angular momentum

Entanglement 1

Elementary particles are identical

but different from what would be expected

$$\underline{|a\rangle_1 \, |b\rangle_2}$$

and

$$\underline{|a\rangle_2 \, |b\rangle_1}$$

are not identical

Entanglement 1

Comment

Elementary particles are identical.

It is not possible to put a label on an elementary particle.

Therefore it is not possible to distinguish elementary particles.

The underlined formulas show two quantum states $|a\rangle$ and $|b\rangle$, which are e.g. occupied by an electron 1 and an electron 2.

Since the electrons cannot be distinguished, one might expect that the two formulas describe the same quantum state.

But that’s not true! Because if one could write down the quantum state of the two elementary particles in one way or another, then one could assign the number 1 or 2 to the particles. But that is not possible.

Entanglement 2

Quantum state of two electrons which occupy quantum states $|a\rangle$ and $|b\rangle$

$$\boxed{|a,b\rangle_{1,2} = |a\rangle_1\,|b\rangle_2 - |a\rangle_2\,|b\rangle_1}$$

Quantum state of two photons which occupy quantum states $|a\rangle$ and $|b\rangle$

$$\boxed{|a,b\rangle_{1,2} = |a\rangle_1\,|b\rangle_2 + |a\rangle_2\,|b\rangle_1}$$

General rule for the quantum states of N electrons

$$\boxed{|\psi\rangle_{1,2\ldots i,\ldots j,\ldots.N} = -\,|\psi\rangle_{1,2\ldots j,\ldots i,\ldots.N}}$$

General rule for the quantum states of N photons

$$\boxed{|\psi\rangle_{1,2\ldots i,\ldots j,\ldots.N} = +\,|\psi\rangle_{1,2\ldots j,\ldots i,\ldots.N}}$$

Entanglement 2

Comment 1

It turns out that the common quantum state of the two elementary particles is a linear combination of $|a\rangle_1 |b\rangle_2$ and $|a\rangle_2 |b\rangle_1$.

The first equation outlined in red gives the linear combination for two electrons.

The quantum state is not identical to zero because $|a\rangle_1 |b\rangle_2$ is not identical to $|a\rangle_2 |b\rangle_1$.

The quantum state is only zero (i.e. $|a, b\rangle_{1,2} = |0\rangle$) when $|a\rangle = |b\rangle$.

This corresponds to the Pauli exclusion principle.

Two electrons must differ in at least one quantum number.

Entanglement 2

Comment 2

The second equation framed in red gives the linear combination for two photons.

The occupation number of a quantum state is not restricted for photons. Therefore $|a\rangle = |b\rangle$ is possible.

The third equation framed in red gives the general rule for a quantum state of N electrons.

The quantum state is antisymmetric when two electrons are exchanged, i.e. the quantum state changes sign.

The last equation framed in red gives the general rule for a quantum state of N photons.

Entanglement 2

Comment 3

The quantum state is symmetric when two photons are exchanged, i.e. the quantum state does not change the sign.

These properties of the quantum states of *N* elementary particles are called entanglement.

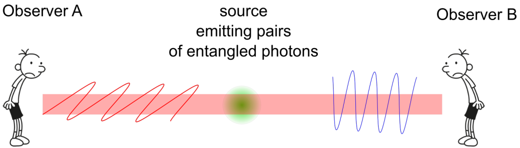
Entanglement is a general feature of quantum mechanics and occurs in both fermions and bosons, i.e. one can experiment with both entangled electrons and entangled photons.

Entanglement 3

Einstein Podolsky Rosen paradox: realization in optics

- a photon source emits entangled photons $|a, b\rangle_{1,2} = |a\rangle_1 |b\rangle_2 + |a\rangle_2 |b\rangle_1$

- the polarisation of the two quantum states $|a\rangle$ and $|b\rangle$ is perpendicular
- and the photons propagate in opposite direction towards an observer A and B



When one of the observers measures the polarization of his photon, the polarization of the other photon is immediately established.

Entanglement 3

Comment

Let us now look again at the Einstein-Podolsky-Rosen paradox.

To realize the paradox in optics, a light source is required that emits entangled photon pairs.

The formula underlined in red describes the quantum state of the two entangled photons.

The quantum states $|a\rangle$ and $|b\rangle$ differ in polarization and in the direction of propagation.

Therefore the probability that an observer will observe a certain polarization of his photon is 50 %.

With the measurement, the entangled quantum state collapses and the polarization of the other photon is instantly established.

Exchange interaction

Atoms with many electrons

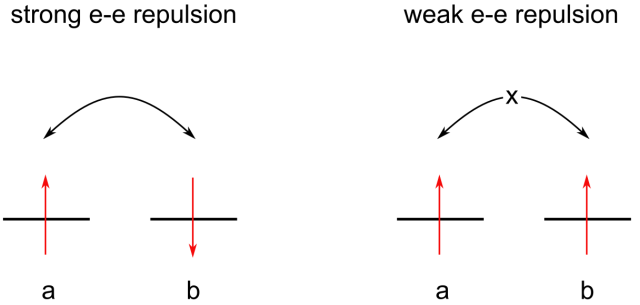
- Periodic table of elements
- Coupling schemes
- Entanglement
- Exchange interaction
- Hund’s rules
- Crystal-field, Ligand-field and the quench of the orbital angular momentum

Exchange interaction 1

electron-electron repulsion

$$\boxed{\hat{H}_{12} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}$$

is sensitive to entanglement



Exchange interaction 1 Comment 1

The electron-electron repulsion reacts very sensitively to the entanglement of electron states.

The potential energy of electron-electron repulsion depends on the orientation of the electron spins due to the entanglement.

The influence of the entanglement on the energy of the quantum states is called the exchange interaction.

The exchange interaction is a real quantum effect and has no analogue in classical physics.

Exchange interaction 1

Comment 2

The illustration shows what is happening.

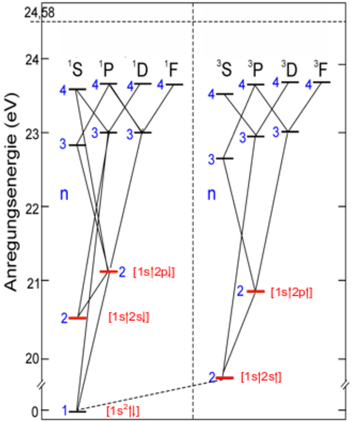
When electron spins are anti-parallel, they can jump into the same orbital and the electron repulsion energy is large, i.e. the binding energy of the electrons is greatly reduced.

When the electron spins are parallel, they cannot occupy the same orbital due to the Pauli principle and the electron repulsion is weaker since they have to stay in different orbitals.

These considerations explain many experimental observations, which can also be calculated at least numerically by solving the Schrödinger equation.

Exchange interaction 2

excited states of the helium atom



Exchange interaction 2 Comment 1

The figure shows the energy level scheme of the helium atom.

The ionisation energy is 24.58 eV above the ground state with two electrons in the 1s orbital.

The notation of the electron configuration is [$1s^2$].

The spins of the electrons are antiparallel, or more precisely the m_s quantum number has the values $\pm 1/2$.

In the figure this is indicated by two anti-parallel vectors in the notation of the electron configuration.

Four excited states are marked by red bars.

Exchange interaction 2 Comment 2

The notation of the electron configuration shows that one electron remains in the 1s orbital while the other is excited into either the 2s or 2p orbital.

The total orbital angular momentum of the electron configuration is either $L = 0$ or $L = 1$ and the total spin is either $S = 0$ or $S = 1$.

The notation of the energy levels is given at the top of the figure, i.e. ^{1}S,^{1}P, and ^{3}S,^{3}P.

The energy level diagram shows that the binding energy of the singlet states $E(^1\mathrm{S})$ is smaller than the binding energy of the triplet states $E(^3\mathrm{S})$.

Likewise is the binding energy $E(^1\mathrm{P})$ smaller than the binding energy $E(^3\mathrm{P})$.

That is the effect of the exchange interaction.

Exchange interaction 2 Comment 3

The level diagram also shows the electric dipole transitions.

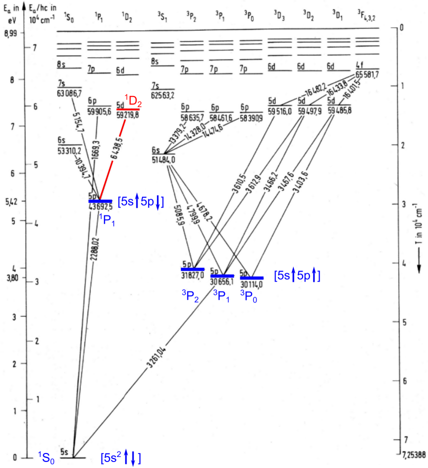
The selection rules are $\Delta\ell = \pm 1$ and consequently $\Delta L = \pm 1$ and $\Delta S = 0$.

The electromagnetic spectrum of the helium atom breaks down into the transitions between the singlet states with $S = 0$ and the triplet states with $S = 1$.

The effect of the spin-orbit coupling is small and cannot be resolved in the figure.

Exchange interaction 3

energy level scheme of cadmium (electron configuration [Kr]$5s^2$, $4d^{10}$)



Exchange interaction 3

Comment 1

The figure shows the excitation spectrum of the cadmium atom.

The ground state of the valence electrons is given by the 5s orbital, which is occupied by two electrons.

All other orbitals with lower energy are completely occupied with electrons.

The fully occupied orbitals realize the noble gas configuration of krypton.

The atomic number of Cadmium is $Z = 48$.

The periodic table of the elements shows that the 5s orbital is occupied by electrons before the 4d orbital.

However, if the 4d orbital is completely occupied by 10 electrons, then its binding energy is larger than that of the 5s orbital.

Exchange interaction 3

Comment 2

Consequently, in the case of the cadmium atom, the 5s electrons are the valence electrons.

Similar to helium, one electron is excited into an orbital with higher energy.

The first excited energy levels are indicated by blue bars.

One electron is excited from the 5s orbital to the 5p orbital.

These excited states are either the singlet state $^1P_1$ or the triplet states $^3P_{2,1,0}$.

The binding energy of the singlet state is reduced due to the exchange interaction compared to the binding energy of the triplet states.

For the triplet states, the splitting due to the spin-orbit coupling is visible.

Exchange interaction 3 Comment 3

The energy of the state $^3P_0$ is less than the energy of the states $^3P_1$ and $^3P_2$.

As expected, spin and orbit are preferably aligned antiparallel.

The energy level scheme also shows the electric dipole transitions.

The selection rule is $\Delta\ell = \pm 1$ and consequently $\Delta L = \pm 1$.

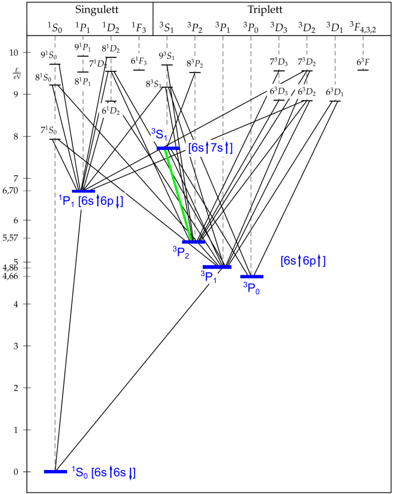
The influence of the spin-orbit coupling is small and the additional selection rule $\Delta S = 0$ is also fulfilled for cadmium .

The Zeeman effect of cadmium was discussed for the transition $^1P_1 \leftrightarrow {}^1D_2$.

The normal Zeeman effect can be observed since the total spin is zero.

Exchange interaction 4

energy level scheme of mercury (electron configuration $[\mathrm{Xe}]6s^2$, $4f^{14}$, $5d^{10}$)



Übergang	λ / nm
$6^1S_0 \leftrightarrow 6^1P_1$	184,95
$6^1S_0 \leftrightarrow 6^3P_1$	253,65
$6^3P_1 \leftrightarrow 7^3D_2$	265,20
$6^3P_1 \leftrightarrow 7^1D_2$	265,51
$6^3P_0 \leftrightarrow 8^3S_1$	275,28
$6^3P_1 \leftrightarrow 8^1S_0$	285,69
$6^3P_1 \leftrightarrow 8^3S_1$	289,36
$6^3P_2 \leftrightarrow 9^3S_1$	292,54
$6^3P_0 \leftrightarrow 6^3D_1$	296,72
$6^3P_2 \leftrightarrow 7^3D_3$	302,15
$6^3P_2 \leftrightarrow 7^3D_2$	302,35
$6^3P_2 \leftrightarrow 7^1D_2$	302,75
$6^3P_1 \leftrightarrow 6^3D_2$	312,57
$6^3P_1 \leftrightarrow 6^3D_1$	313,16
$6^1D_2 \leftrightarrow 6^3P_1$	313,18
$6^3P_2 \leftrightarrow 8^3S_1$	334,15
$6^3P_2 \leftrightarrow 6^3D_3$	365,02
$6^3P_2 \leftrightarrow 6^3D_2$	365,48
$6^1P_1 \leftrightarrow 8^1D_2$	390,64
$6^3P_0 \leftrightarrow 7^3S_1$	404,66
$6^3P_1 \leftrightarrow 7^1S_0$	407,78
$6^1P_1 \leftrightarrow 9^1S_0$	410,81
$6^1P_1 \leftrightarrow 7^3D_2$	433,92
$6^1P_1 \leftrightarrow 7^1D_2$	434,75
$6^3P_1 \leftrightarrow 7^3S_1$	435,83
$6^1P_1 \leftrightarrow 8^1S_0$	491,61
$6^1P_1 \leftrightarrow 8^3S_1$	502,56
$6^3P_2 \leftrightarrow 7^3S_1$	546,08
$6^1P_1 \leftrightarrow 6^3D_2$	576,96
$6^1P_1 \leftrightarrow 6^1D_1$	579,07
$8^3P_2 \leftrightarrow 7^3S_1$	690,75
$6^1P_1 \leftrightarrow 7^1S_0$	1013,98

Datenquelle:
NIST Atomic Spectra Database
v3.1.3

Exchange interaction 4

Comment 1

The figure shows the energy level scheme of mercury.

The two valence electrons occupy the 6s orbital.

As before, we can observe the effect that although the 6s, 4f and then 5d orbitals are occupied by electrons according to the periodic table of elements, it is the 6s orbital that has the smallest binding energy when all other orbitals are fully occupied.

One valence electron is excited into an orbital with higher energy.

The energy levels with the lowest excitation energy are indicated by blue bars.

One 6s electron is excited in the 6p orbital.

Exchange interaction 4 Comment 2

The singlet state $^1P_1$ results for antiparallel spin orientation and the triplet states $^3P_0$, $^3P_1$, and $^3P_2$ for parallel spin orientation.

Due to the exchange interaction, the binding energy of the singlet state is reduced compared to the binding energy of the triplet states.

The atomic number of mercury is $Z = 80$ and the spin orbit coupling is no longer negligible.

The energy level diagram shows that the level splitting due to the spin-orbit coupling is noticeable for the first excited triplet states.

The energy level scheme also shows the electric dipole transitions.

Exchange interaction 4

Comment 3

The selection rule $\Delta L = \pm 1$ still applies due to the fundamental selection rule for a single electron $\Delta \ell = \pm 1$.

Due to the strong spin-orbit coupling, the selection rule $\Delta S = 0$ is no longer valid.

The heuristic interpretation of this effect is that the motion of the electron spin is very fast due to the spin-orbit coupling, so that the orientation of the spin can change during the electric dipole transition.

The $^3\mathrm{P}_2 \leftrightarrow {}^3\mathrm{S}_1$ transition of the green mercury line is marked green in the energy level diagram.

This transition shows the anomalous Zeeman effect previously discussed.

Revision

Summary in Questions 1

1. As a first approximation, each electron in an atom moves in a spherical cloud of charge that is formed by the other electrons. Write down the Schrödinger equation of an electron.
2. Describe the resulting wave function of the electron.
3. What does the Pauli principle mean?
4. How many electrons can occupy an s, p, d, and f orbital?
5. With increasing atomic number, s orbitals are occupied by electrons before the p orbital is occupied. Give the reason.
6. Describe the characteristic properties of fermions and bosons.

Summary in Questions 2

7. Give the entangled quantum state of two fermions.
8. Give the entangled quantum state of two bosons.
9. Entanglement affects the energy of atomic eigenstates. Why?
10. The spins of electrons prefer to align parallel in an atom due to exchange interaction. Why?