Atoms

1. Early atomic physics
2. The Schrödinger equation as a wave equation
3. Quantum mechanics
4. Atoms with many electrons

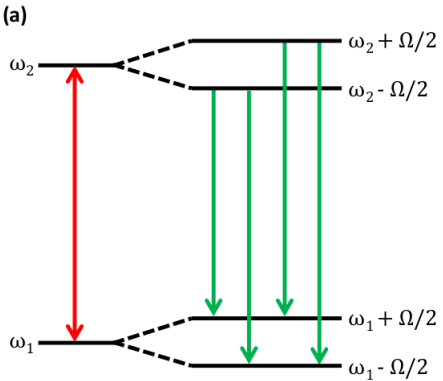
Autler-Townes

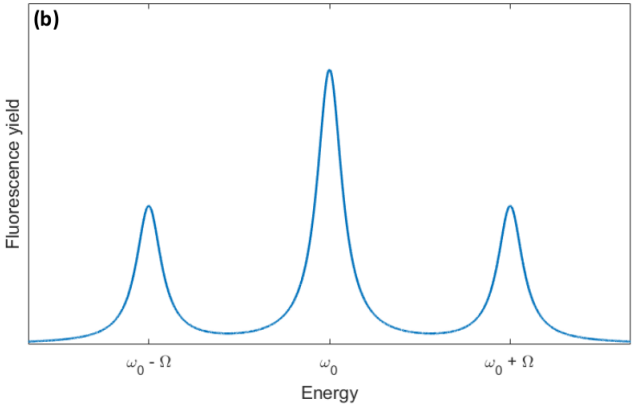
Quantum mechanics

- 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: $\Omega = \langle f | e\vec{r} | i \rangle \cdot \vec{E}/\hbar$





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

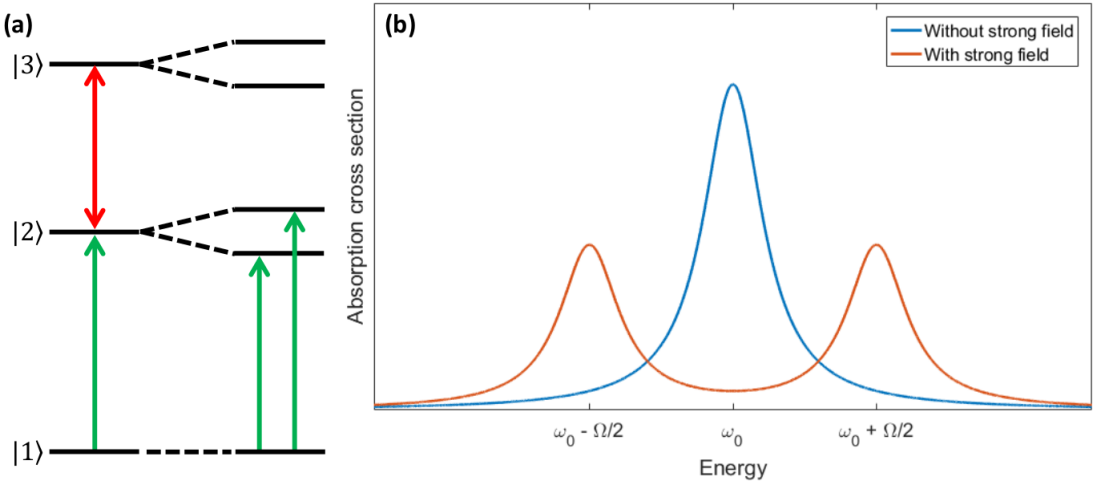
Comment 2

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

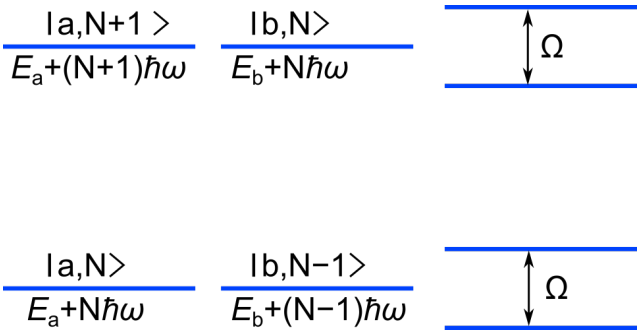
There is a fundamental difference between the level splitting observed in a magnetic field (Zeeman effect) and the level splitting in the strong field of an electromagnetic wave.

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



(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.

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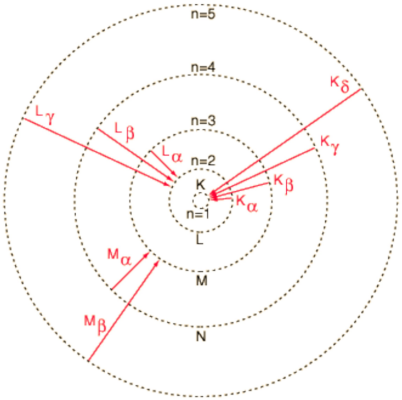
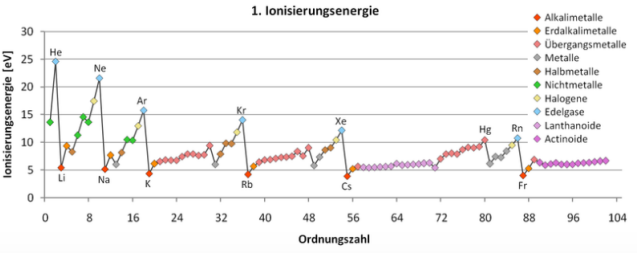
Periodic table

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, Wolfgang Pauli 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

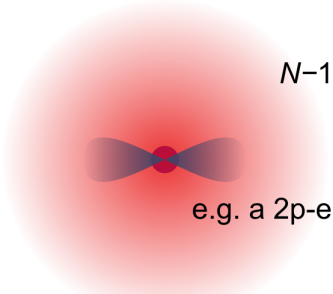
Fermions are called after the Italian physicist Enrico Fermi.

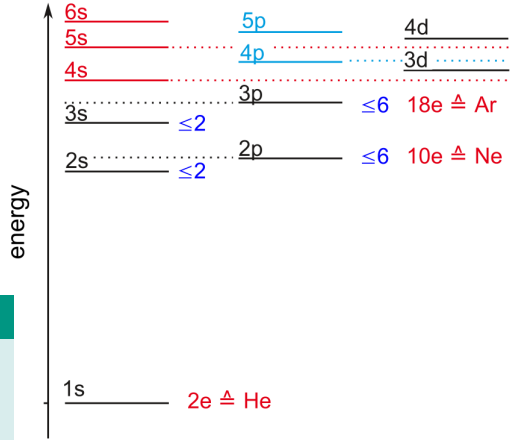
Bosons are called after the Indian physicist Satyendra Nath Bose.

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

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

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 $E_{1s} = 13.6\,\text{eV} \cdot 2^2 = 54.4\,\text{eV}$.

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 Comment 7

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 $[\mathrm{Ar}]4s^1 3d^5$ and there is only one electron in the 4s orbital.

Periodic table of elements 2

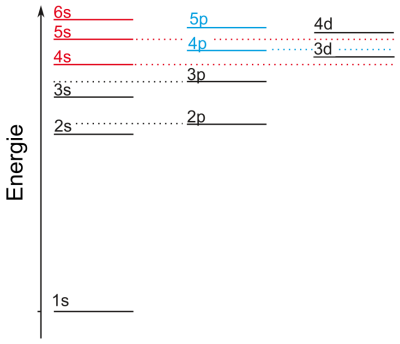
Comment 11

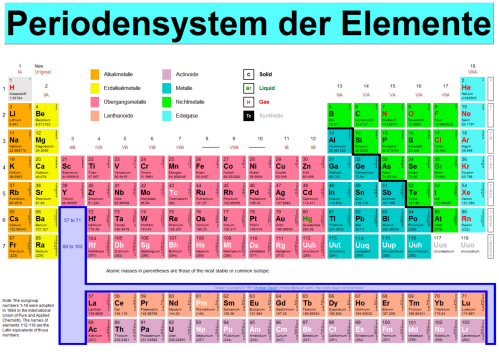
The electron configuration of manganese (atomic number $Z = 25$) is $[Ar]4s^2 3d^5$ and the 4s orbital is again occupied with two electrons.

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





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.

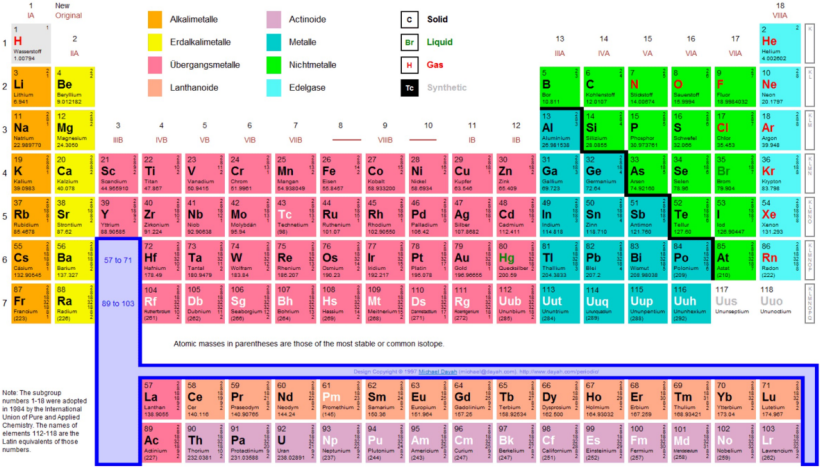
Periodic table of elements 3

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



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.

Revision

Summary in Questions

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 orbitals are occupied. Give the reason.