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# BASICS OF MEDICAL PHYSICS

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Published by Charles University

Karolinum Press

Prague 2017

Edited by Alena Jirsova

Setting and layout by Studio Lacerta ([www.sazba.cz](http://www.sazba.cz))

First English edition

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ISBN 978-80-246-3810-2

ISBN 978-80-246-3884-3 (pdf)



Charles University  
Karolinum Press 2018

[www.karolinum.cz](http://www.karolinum.cz)  
[ebooks@karolinum.cz](mailto:ebooks@karolinum.cz)



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# 1. STRUCTURE OF MATTER

## 1.1 PARTICLES AND FORCE INTERACTIONS

There are two forms of matter: particles and fields. Under physical conditions, particle forms of matter exist in four states: solid, liquid, gas and plasma. Force interactions are characteristic of individual field types, of which there are four: gravitational and electromagnetic fields (existing as part of the environment) and strong and weak nuclear fields (existing at the atomic level).

Individual forms of matter can mutually transform, e.g. the formation of an electromagnetic wave due to the annihilation of particles and antiparticles. The creation of an electron-positron pair during the absorption of  $\gamma$ -radiation is an example of the opposite transformation of a field into particles.

The corpuscular form of matter consists of two groups of fundamental particles: *leptons* and *quarks*. Leptons do not interact with strong nuclear forces. Both groups consist of three generations. The first generation of leptons contains an electron and an electron neutrino, the second contains a muon and a muon neutrino and the third contains particle  $\tau$  and its neutrino (See Table 1.1).

**Table 1.1** Fundamental particles

Leptons		Quarks	
		Flavour	Charge
electron	electron neutrino	u (up)	+2/3
e	$\nu_e$	d (down)	-1/3
muon	muon neutrino	c (charm)	+2/3
$\mu$	$\nu_m$	s (strange)	-1/3
tau	tau neutrino	t (top)	+2/3
$\tau$	$\nu_t$	b (bottom)	-1/3

The three generations of quarks differ according to a property called *flavour*. Each generation has two flavour quarks: *u* quarks (up) and *d* quarks (down) in the first, *c* quarks (charm) and *s* quarks (strange) in the second and *t* quarks (top) and *b* quarks (bottom) in the third. As

well as flavour, each quark is characterised by a non-integer electric charge that equals  $+2/3$  of the elementary charge for the first quark of each pair and  $-1/3$  for the second quark of the corresponding generation (Table 1.1). Quarks also differ according to another property known as *colour*. Each quark possesses a red, green or blue colour. All fundamental particles, leptons and quarks are also distinguished by a spin quantum number equalling  $\pm 1/2$ . Each particle has its own antiparticle. When charged, the antiparticle possesses an opposite electric charge. In the case of flavour and colour, these properties are denoted by the prefix anti-, i.e. the flavours (quarks) *antiu* and *antid* and the colours *antired*, *antigreen* and *antiblue*. Although the antiparticle has the same mass as the particle and the same value of spin (integer or half-value), it has opposite rotation (clockwise or counter-clockwise) and opposite magnetic moment (see Table 1.2). If a particle and antiparticle are in the appropriate quantum states, then they can annihilate each other and produce other particles.

**Table 1.2** Selected basic characteristics of antiparticles

Same mass
Identical value of spin (integer, non-integer) but opposite rotation (clockwise, counter-clockwise)
Opposite magnetic moment (positive, negative) – if half-value
Opposite charge – if not without charge
Opposite colour (anticolour)

Quarks also form composite particles called *hadrons*. Hadrons must possess an integer electric charge and have a colour combination that is colourless or white. These conditions are achieved in two different ways. Hadrons of the first group are composed of two quarks called *mesons* (a quark and an antiquark). Mesons have an integer value of spin. A typical example is the pion particle,  $\pi$ . It is formed by a *u* quark and an *antiu* in the case of meson  $\pi^0$ , by a *u* quark and an *antid* in the case of meson  $\pi^+$  and by a *d* quark and an *antiu* in the case of meson  $\pi^-$ .

Baryons are another group of hadrons. Baryons are composed of three quarks of different colours (red, green and blue). Baryons have half-value spin. For example, a proton consists of two *u* quarks and one *d* quark, while a neutron consists of two *d* quarks and one *u* quark.

Elementary particles (fundamental hadrons and quanta of fields) consist of two large groups according to spin value. The first are *fermions*, which are characterised by a half-value spin quantum number. Their behaviour can be explained using Fermi-Dirac statistics. They also function in accordance with Pauli's exclusion principle, i.e. no two fermions of identical energies can exist in one system. The particles of the second group are called *bosons*, which possess an integer spin quantum number value. Their behaviour can be explained using Einstein-Bose statistics. In the case of bosons, the number of particles at the same energy level is not limited.

**Table 1.3** Hadrons

Particles composed of quarks	– have an integer value of electric charge
	– are white (colourless)
Mesons	– 2 quarks: quark + antiquark (integer spin)
Baryons	– 3 quarks: (half-value spin)

As previously mentioned, there are four types of force interactions: strong, electromagnetic, weak and gravitational. The force interactions of all field types contain non-contact and exchange characters, i.e. they occur due to the exchange of the quanta of these fields. Basic Bose particles represent the excitations of these fields. Thus, the *photon* corresponds to the electromagnetic field, *gluons* (of three different colours) to strong nuclear force, the particles  $W^\pm$  and  $Z^0$  to weak interaction and the hypothetical *graviton* to gravitational interaction. The ranges of the gravitational field (source is mass) and electromagnetic field (source is electric charge) are not limited, whereas the range of the strong interaction (source is colour) is approximately  $10^{-15}$  m and the range of the weak interaction (enabling the change of flavour) is approximately  $10^{-18}$  m. These last two are called saturated fields. At distances corresponding to the sizes of the respective atomic nuclei, i.e. approximately  $10^{-15}$  m, the relative ratios of the strong, electromagnetic, weak and gravitational interactions are  $1 : 10^{-3} : 10^{-15} : 10^{-40}$ . These ratios indicate that gravitation is negligible in particle physics but very important for macroscopic objects. Gravitational interaction occurs only in particles with mass; it cannot be absorbed, transformed or shielded against and it always attracts and never repels. The electromagnetic force acts between electrically charged particles and can be cancelled out; it can also attract and repel. The weak interaction is responsible for changing one quark to another. The strong interaction binds protons and neutrons together to form the nucleus of an atom.

Of the particles with a mass other than zero, only electrons and protons are stable; other particles are unstable. For example, a free neutron decays after approximately  $10^3$  s due to  $\beta$ -decay into a proton, electron and electron antineutrino,  $n \rightarrow pe^-\bar{\nu}_e$ . This decay corresponds to the transmutation of a  $d$  quark into a  $u$  quark.

Of the particles with non-zero mass, muon  $\mu^-$  possesses the longest life span ( $2.10^{-6}$  s). Most hadrons decay immediately after formation since they exist no longer than  $10^{-12}$  s.

## 1.2 ENERGY

Energy is a scalar physical quantity and represents the ability to work. The law of conservation of energy states that the total amount of energy in an isolated system remains constant over time. This means that energy cannot be created or destroyed and that it is capable of being transformed from one form to another or transferred from one place to another. For example, the result of the annihilation of an electron and a positron (with a weight equal to the energy equivalent of 0.51 MeV) is two light quanta (photons) of the same energy. Total energy  $E$  of a particle (or system of particles) in a force field is given by the sum of its resting energy  $E_0$ , kinetic energy  $E_k$  and potential energy  $E_p$

$$E = E_0 + E_k + E_p \quad (1.1)$$

where  $E_0$  is the energy related to the particle mass according to Einstein's relationship

$$E_0 = m_0c^2, \quad (1.2)$$

where  $m_0$  is the mass at rest and  $c$  is the velocity of light in a vacuum (the highest velocity of propagation of energy). A photon, which possesses zero mass and a rest energy of zero, does not exist at rest and moves throughout a system of coordinates at velocity  $c$ .

The mass  $m$  of a particle moving with relativistic velocity  $v$  (almost at the velocity of light in a vacuum) increases according to the relation

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}, \quad (1.3)$$

where  $v$  is the velocity related to the observer.

Particles with non-zero mass  $m_0 > 0$ , energy  $E$ , velocity of movement  $v$  and momentum  $p = mv$  are related by the equation

$$E^2 = m_0^2 c^4 + p^2 c^2 \quad (1.4)$$

Kinetic energy  $E_k$  is defined by the following equation

$$E_k = \frac{mv^2}{2} = \frac{p^2}{2m} \quad (1.5)$$

Kinetic energy is energy due to motion. It is also independent of direction and can only possess positive or zero values,  $E_k \geq 0$ . Generally, potential energy may be positive or negative according to the zero level chosen. In central fields of Newton-type forces where the force of interaction is inversely proportional to the squared distance, (e.g. Coulomb's law, Newton's law of gravitation), the zero level is set where there is no interaction, i.e. at "infinity"; therefore, potential energy  $E_p$  is negative ( $E_p < 0$ ). It must be negative because positive force is required to remove the particle (body, electric charge), which is attracted to the distance. Here, the force of interaction is negligible and energy equals zero. In the mechanics of a mass point, the equation for potential energy is as follows:  $E_p = mgh$ , where  $m$  is mass,  $g$  is gravity acceleration and  $h$  is height. In this case, if the zero energy level is defined at the surface of the earth and  $h > 0$ , then the potential energy will be positive and will equal the product,  $mgh$ .

Energy is expressed in joules. However, in atomic physics and radiation physics, this unit is not suitable. In these cases, energy is mostly expressed in *electronvolts* (eV). 1 eV is the energy obtained by an electron accelerated by the potential difference of 1 volt. Since 1 J = 1 C.1 V and charge 1 C equals a total charge of approximately  $6 \times 10^{18}$  electrons, 1 eV =  $1.6 \times 10^{-19}$  J. The relation of 1 eV to 1 J is the same as that for the charge of 1 electron to 1 C. In the physics of elementary particles, the unit eV is also applied as a unit of mass according to equation (1.2). Based on this relationship, the rest mass of electron  $m_e = 0.51 \text{ MeV}/c^2$ . The  $c^2$  unit is usually omitted. Thus, similarly, the mass of proton  $m_p = 938.28 \text{ MeV}$  and the mass of neutron  $m_n = 939.57 \text{ MeV}$ .

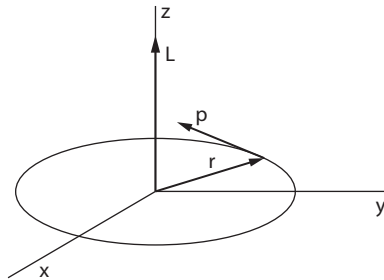
### 1.3 QUANTUM EFFECTS

The laws of classical physics are not sufficient to describe the physical processes that occur at the atomic level. Within the region of very small distances, there are processes that exist separate to the macro-level and that have other physical quantities. One of them is an effect related to *Planck's constant*  $h$  or *Dirac's constant*,  $\hbar = 1.05 \times 10^{-34}$  J.s. These constants are related by  $\hbar = h/2\pi$ . Planck's constant in circular motion with radius  $r$  represents the smallest amount of radiated energy.

One of the effects of quantum properties is the discrete value of angular momentum. Angular momentum  $\mathbf{L}$  is defined as a vector product (cross-product) of position vector  $\mathbf{r}$  and the vector of momentum,  $\mathbf{p} = m\mathbf{v}$ .

$$\mathbf{L} = [\mathbf{r} \times \mathbf{p}] \tag{1.6}$$

In general, the cross-product of two vectors is the vector perpendicular to the plane determined by the vectors multiplied. Its magnitude equals the product of their magnitudes multiplied by the sine of their angle. In the case of regular circular motion, the directions of momentum of vector  $\mathbf{p}$  and position vector  $\mathbf{r}$  change at every moment, whereas the magnitude and direction of the cross-product remain constant (see Fig. 1.1). The two vectors  $\mathbf{r}$  and  $\mathbf{v}$  are perpendicular to each other. Therefore, angular momentum  $L = rmv$ , since  $\sin(\pi/2) = 1$ .



**Figure 1.1:** Orbital angular momentum  $L$  of a particle with momentum  $p$  at circular motion with the radius  $r$ .

According to quantum mechanics, the angular momentum of the orbital motion of a particle can possess only certain discrete values, which are multiples of Dirac's constant. Similarly, the projections of angular momentum of an atom in the direction of the coordinate axes can only possess well-defined values (see later).

As well as orbital angular momentum, elementary particles possess their own angular momentum, *spin* and *magnetic moment* due to rotation. Particles with half-value spin are called *Fermi particles (fermions)* and those with integer-value spin are called *Bose particles (bosons)*. For example, the spin of an electron or of a nucleon equals  $\frac{1}{2}$  and the spin of a photon equals 1 (in multiples of  $\hbar$ ). The spin value determines the behaviour of the particle. Thus, Fermi particles with identical spin cannot exist at the same energy level. This explains why all of the electrons in heavy atoms occupy the higher energy levels more distanced from the nucleus instead of the lowest energy levels. On the other hand, Bose particles tend to occupy the same energy state.

Elementary particles and their system (atom, molecule) possess both corpuscular and wave properties – a finding originally resulting from experimentation into the properties of light. Interference or diffraction of light demonstrates that light is represented by waves, while the photoelectric effect demonstrates that light is a flux of quanta of energy in the form of photons. Energy  $E$  of a photon (J) is related to frequency  $f$  ( $\text{s}^{-1}$ ) of the wave and to its wavelength  $\lambda$  (m) by the equation

$$E = hf = hc/\lambda, \tag{1.7}$$

where  $c$  is the velocity of light in a vacuum and  $h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s} = 4.13 \times 10^{-15} \text{ eV}\cdot\text{s}$  is Planck's constant. Therefore, Planck's constant reflects the sizes of energy quanta in quantum mechanics.

The motion of each particle with mass  $m$ , momentum  $p$  and energy  $E$  is related to wavelengths  $\lambda$  of the de Broglie wave given by the equation

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \tag{1.8}$$

and to frequency  $f$  given by the equation

$$f = \frac{E}{h} \tag{1.9}$$

Equation (1.8) reveals that the wavelengths of elementary particles are very short. In the case of a wavelength of an electron in an electron microscope accelerated by a voltage of 1 kV, its energy (expressed in eV) will be  $1 \text{ keV} = 10^3 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV} = 1.6 \times 10^{-16} \text{ J}$ .

Using equation (1.8) we get

$$\lambda = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s}}{\sqrt{(2 \times 9.11 \times 10^{-31} \text{ kg}) \cdot (1.6 \times 10^{-16} \text{ J})}} = 3.88 \times 10^{-11} \text{ m} = 0.039 \text{ nm}$$

Therefore, the wavelength of this electron is four orders shorter than that of visible light. That is why the resolving power of an electron microscope is more accurate than that of an optical microscope (see later in Chapter 6).

The corpuscular-wave dualism of a subatomic particle has consequences. For example, it is not possible to *simultaneously* estimate position vector  $\mathbf{r}$  of a particle (or its coordinates) or its momentum  $p$  with an arbitrary accuracy. *Heisenberg's uncertainty principle* holds for the uncertainty of position vector  $\Delta r$  and momentum  $\Delta p$

$$\Delta r \cdot \Delta p \geq \hbar \tag{1.10}$$

Thus, the smaller region of motion results in a higher uncertainty of momentum. A similar relation also holds for the simultaneous determination of an energy level and its duration. If the uncertainty of an energy level is  $\Delta E$  and the time interval in which the measurement is performed is  $\Delta t$ , then

$$\Delta E \cdot \Delta t \geq \hbar \quad (1.11)$$

Therefore, if the given energy state lasts for a long time, its energy may be established with a high degree of certainty. For example, the mean time between atom excitation and photon emission during de-excitation is approximately  $10^{-8}$  s. With respect to the above equation, the uncertainty of estimating the energy level is

$$\Delta E = \frac{\hbar}{\Delta t} = \frac{1.05 \times 10^{-34} \text{ Js}}{10^{-8} \text{ s}} \cong 1.1 \times 10^{-26} \text{ J} \cong 7 \times 10^{-6} \text{ eV}$$

Quantum effects can be quantitatively described by quantum mechanics.

### 1.3.1 Quantum numbers

From a quantum-mechanical perspective, the motion of an electron in the force field of the atomic nucleus is not represented by a certain trajectory but by a “cloud”. Its form and distance from the nucleus is determined by other parameters such as orbital angular momentum, magnetic moment and spin. The region of space in which the electron moves is called the *orbital*. The electron state is described by the wave function, which involves a number of dimensionless parameters that equal the number of degrees of freedom. With regard to the rotation of the electron, the number of degrees of freedom is 4. Therefore, the state of the electron can be completely expressed by four *quantum numbers*. These numbers are natural integers (with the exception of spin) that determine the geometry and symmetry of the electron cloud. No two electrons in the same atom can have the same four quantum numbers.

*Principal quantum number*  $n$  determines the total electron energy. In accordance with the quantum theory of the hydrogen atom, an electron may exist at various energy levels  $E_n$  given by the equation

$$E_0 = -\frac{me^4}{8\varepsilon_0^2 h^2} \cdot \left(\frac{1}{n^2}\right), \quad (1.12)$$

where  $m = 9.11 \times 10^{-31}$  kg is the rest mass of the electron,  $\varepsilon_0 = 8.854 \times 10^{-12}$  F.m<sup>-1</sup> is the permittivity of the vacuum and  $e = 1.6 \times 10^{-19}$  C is the electron charge. The principal quantum number is a natural number, which can possess values of  $n = 1, 2, 3$  and so on. Moreover, its value estimates the shell in which the electron appears. The shells K, L, M, N, O, P and Q correspond to the values  $n = 1, 2, 3, 4, 5, 6$  and  $7$ , respectively. As  $n$  increases, the orbital becomes larger and the electron spends more time farther from the nucleus. The electron also moves at a higher potential energy and is, therefore, less tightly bound to the nucleus.  $n$  also expresses the maximal number of electrons in the shells according to the relation  $2n^2$  (for more detail, see paragraph 1.5).

*Orbital quantum number*  $\ell$  of an electron in a shell expressed by  $n$  may possess the values  $\ell = 0, 1, 2, \dots, (n-1)$  and determines the form and symmetry of the electron cloud, which is in turn determined by angular momentum  $L$ . The magnitude of  $L$  is given by equation

$$L = \hbar \sqrt{\ell(\ell+1)} \quad (1.13)$$

The orbital quantum number is used for notating states in spectroscopy. Values of  $\ell$  are denoted by letters so that the values of  $\ell = 0, 1, 2, 3, 4$  and  $5$  correspond to the letters  $s, p, d, f, g$  and  $h$ , respectively. According to equation (1.13), the value of orbital angular momentum corresponding to state  $s$  equals zero and the value corresponding to state  $p$  is  $\sqrt{2}\hbar$ , etc. The notation of states is a combination of the principal quantum number and letter. Thus, a state with  $n = 2$  and  $\ell = 0$  is  $2s$ , a state with  $n = 4$  and  $\ell = 2$  is  $4d$ , etc.

If an arbitrary direction (axis  $z$ ) is chosen in the space, then the values of projection of the angular momentum in this direction,  $L_z$ , are discrete values given by the product  $m_l\hbar$  where  $m_l$  is the *magnetic quantum number*.

Magnetic quantum number  $m_l$  can possess the values  $m_l = \pm 0, \pm 1, \pm 2, \dots, \pm \ell$  for a given  $\ell$ , which determines the spatial position of the orbital. The magnitudes of the orbital angular momentum can only have discrete values given by equation (1.13). Moreover, the direction of angular momentum is not arbitrary and is limited with respect to the orientation of the external magnetic field. The magnetic quantum number estimates the direction of vector  $\vec{L}$  by determining its component in the direction of the external magnetic field.

*Orbital magnetic moment*  $\vec{\mu}_{orb}$  is related to angular momentum  $\vec{L}$  (see Fig. 1.1) and given by the equation

$$\vec{\mu}_{orb} = -\left(\frac{e}{2m_e}\right)\vec{L}, \quad (1.14)$$

where  $m_e$  is the mass of the electron.

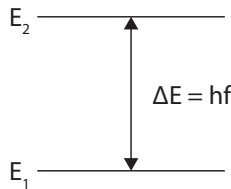
The unit used to express the orbital magnetic moment of the electron is the *Bohr magneton*,  $u_B = e\hbar/2m_e = 9.28 \times 10^{-24} \text{ A}\cdot\text{m}^2$  (or  $\text{J}\cdot\text{T}^{-1}$ , since  $\text{J}/\text{T} = \text{J}/(\text{Wb}\cdot\text{m}^{-2}) = \text{J}\cdot\text{m}^2/\text{Wb} = \text{J}\cdot\text{m}^2/(\text{V}\cdot\text{s}) = \text{C}\cdot\text{V}\cdot\text{m}^2/(\text{V}\cdot\text{s}) = \text{A}\cdot\text{m}^2$ ). For a given  $\ell$ , the number of possible orientations of the orbital angular momentum in the external magnetic field equals  $2\ell+1$  since the values of  $m$  may vary within a range from  $-\ell$  through  $0$  to  $+\ell$ . Thus, the magnetic quantum number estimates the magnitude of the projection of mechanical angular momentum  $\vec{L}$  and of magnetic moment  $\vec{\mu}_{orb,z}$  in a certain direction. For the  $z$ -component of orbital magnetic moment  $\vec{\mu}_{orb,z}$ , it holds that  $\mu_{orb,z} = m_l \cdot u_B$ . Orbital magnetic dipole moments are multiples of  $u_B$ .

*Spin quantum number*  $s$  is a value that describes the angular momentum of an electron. An electron possesses its own, internal angular momentum, which does not depend on its orbital angular momentum. However, it also possesses its own magnetic moment, which is related to its internal angular momentum. The magnitude of angular momentum  $S$  due to the spin of the electron is given for any electron, bound or free, by  $S = \hbar\sqrt{s(s+1)}$  where  $s = \frac{1}{2}$  is the spin quantum number of the electron. In an external magnetic field, the vector of the spin angular momentum can have two orientations. Component  $S_z$  of the spin angular momentum of an electron along the external magnetic field in direction  $z$  is determined by spin magnetic quantum number  $m_s$ , which has two values,  $\pm \frac{1}{2}$ , and thus the value of this component is  $\pm \frac{1}{2}\hbar$ . Similar to orbital angular momentum, spin dipole magnetic momentum  $\mu_s$  is also related to spin angular momentum  $S$  by  $\mu_s = -\frac{e}{m}S$ , where  $e$  is the charge and  $m$  is the mass of the electron. Spin dipole moments of electrons (and of other elementary particles) are multiples of  $u_B$ .



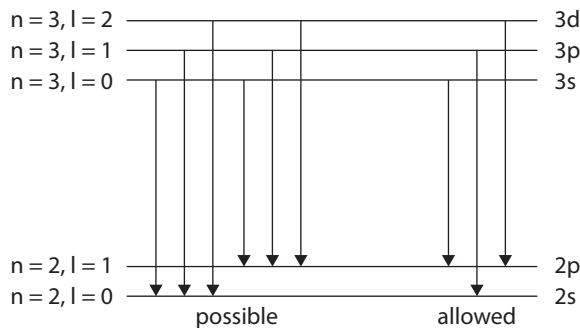
Thus, the state of an electron in an atom is completely determined by a set of 4 quantum numbers:  $n$ ,  $\ell$ ,  $m$  and  $s$ . Electron configurations of atoms with more electrons are governed by the *Pauli exclusion principle*, which states that any two electrons in an atom cannot exist in an identical quantum state. There is a different set of quantum numbers for each electron in a given atom.

An electron can transit from one state to another due to the absorption or emission of energy. Transitions between quantised states occur as a result of two photon processes: emission and excitation. Absorption of energy is connected with the transition of electrons from lower to higher energy levels. A downward transition involves the emission of energy (photons). All of these processes require that the photon energy given by the Planck relationship defined in equation 1.7 is equal to the energy separation of the participating pair of quantum energy states (see Fig. 1.2).



**Figure 1.2:** Energy separation between energy states.

During electron transitions from one state to another due to the absorption or emission of energy, only these transitions occur. By means of this process, the principal quantum number can vary arbitrarily, whereas the orbital quantum number varies only by  $\pm 1$ . These transitions are called *allowed* while other transitions are called *forbidden*. Thus, of the  $3 \times 2 = 6$  possible transitions from shell  $M$  ( $n = 3$ ,  $\ell = 0, 1, 2$ ) to shell  $L$  ( $n = 2$ ,  $\ell = 0, 1$ ), only those from  $3d$  to  $2p$ , from  $3p$  to  $2s$  and from  $3s$  to  $2p$  are allowed (see Fig. 1.3).



**Figure 1.3:** Transitions from orbital  $n = 3$  to orbital  $n = 2$ .

## 1.4 HYDROGEN ATOM

The simplest system composed of nucleons and electrons is the hydrogen atom. In this system, one electron moves in the central electric field of one proton. The distance from the nucleus, at which the electron appears with the highest probability, can be estimated from the relationship of uncertainty (see equation 1.10).

If the electron moves at distance  $r$  from the nucleus then the uncertainty only equals  $r$ . From equation (1.10), the uncertainty of momentum  $p$  is

$$\Delta p = \frac{\hbar}{r} \quad (1.15)$$

The total energy of the electron in the field of the atom is given by the sum of its kinetic and potential energies. According to equation (1.5) via equation (1.15), *kinetic energy*  $E_k$  is

$$E_k = \frac{p^2}{2m_e} = \frac{\hbar^2}{2m_e r^2}, \quad (1.16)$$

where  $m_e$  is the mass of the electron. *Potential energy*  $E_p$  of an electron with charge  $-e$  in the force field of a proton with charge  $+e$  at distance  $r$  is given by

$$E_p = -\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r} \quad (1.17)$$

where  $\epsilon_0$  is the permittivity of the vacuum. The potential energy of an electron in the field of the nucleus is negative. It reaches the highest (zero) value at “infinite” distance from the nucleus, where the force action of charges of the electron and nucleus is negligible. Thus, total energy  $E$  of an electron in the field of one proton is

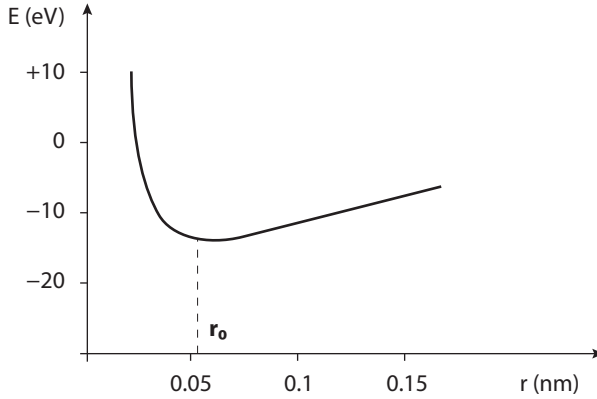
$$E = E_k + E_p = \frac{\hbar^2}{2m_e r^2} - \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r} \quad (1.18)$$

Values of total electron energy can be calculated and plotted as a function of distance  $r$  from the nucleus (see Fig. 1.4). This curve of total energy manifests in a minimum value for a certain distance,  $r_0$ . It holds generally in physics that each system is stable at the minimum value of its energy. Therefore, the highest probability of the appearance of an electron is only at this distance. An electron in its stable state does not emit energy.

Distance  $r_0$  calculated from equation (1.18) using  $dE/dr = 0$  (the extreme of the function can be calculated on the condition that its first derivative equals zero) is given by

$$r_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \quad (1.19)$$

If numerical values are substituted for electron mass  $m_e = 9.1 \times 10^{-31}$  kg, permittivity of vacuum  $\epsilon_0 = 8.8 \times 10^{-12}$  F.m<sup>-1</sup>, electron charge  $e = 1.6 \times 10^{-19}$  C and  $\hbar = 1.05 \times 10^{-34}$  Js, then  $r_0 = 5.29 \times 10^{-11}$  m. This distance is called the *Bohr radius*. After substituting  $r_0$  back into



**Figure 1.4:** Total electron energy  $E$  as a function of its distance  $r_0$  from the nucleus.

equation (1.18) for the total electron energy, the energy of the hydrogen atom in its basic state is given by the equation

$$E = -\frac{1}{32\pi^2\epsilon_0^2} \cdot \frac{m_e e^4}{\hbar^2} \quad (1.20)$$

Equation (1.20) corresponds to the solution provided by Schrödinger's equation for an electron in the field of a proton where  $n = 1$ . A state  $n = 1$  is the basic state, while states  $n = 2, 3, \dots$  are excited states to which an electron may transit after the absorption of energy. If numerical values are substituted for the quantities in equation (1.12), subsequently  $n = 1, 2, 3, \dots$  up to infinity according to the following energy values:  $E_1 = -13.6$  eV,  $E_2 = -3.38$  eV,  $E_3 = -1.5$  eV, etc. up to  $E_\infty = 0$ , respectively.

It can be demonstrated that for each energy level, value  $E_n$  corresponds to the most probable distance  $r_n$  from the nucleus, given by the following equation

$$r_n = n^2 r_0 \quad (1.21)$$

The most probable distance from the nucleus increases with  $n^2$ .

Based on the wave theory of matter, the wavelength of an electron depends on its momentum as defined by equation (1.8). It can be shown that it equals the value of path  $2\pi r_0 = 3.3 \times 10^{-10}$  m. In simplistic terms, an electron can move around the nucleus for an infinitely long period without emitting energy if its path is an integer multiple of the de Broglie wavelength, i.e. if

$$n\lambda = 2\pi r_n, \quad (1.22)$$

where  $n$  is the principal quantum number. During transitions from higher to lower energy levels, the hydrogen atom emits photons that possess a discrete (line) spectrum.

## 1.4.1 Spectrum of the hydrogen atom

An electron at a higher energy level than its ground state is not stable. A fast transition to either a lower or ground state occurs with the simultaneous emission of a photon. If the state changes from energy  $E_k$  to energy  $E_n$ ,  $k > n$ , then according to equation (1.12) a quantum of radiation is emitted with the following energy

$$E = E_k - E_n = \frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \left( \frac{1}{n^2} - \frac{1}{k^2} \right) \quad (1.23)$$

The frequency or wavelength of this radiation is given by equation (1.7) when the energy value is substituted into the above equation. Since there are discrete values of electron energies, only certain energies (frequencies, wavelengths) may be emitted by the atom. Therefore, a *line spectrum* of radiation is observed.

The set of spectral lines observed during transitions from all higher levels to a certain energy level (corresponding to a given  $n$ ) is called a *series* (see Fig. 1.5). The spectral emission lines of the hydrogen atom correspond to a transition to the basic energy level (with  $n = 1$ ). They can be observed in the ultraviolet region of light, forming the *Lyman series*. The *Balmer series* corresponds to a transition to a level of  $n = 2$  and only this series can be observed within the region of visible light. The series corresponding to  $n = 3$  (*Paschen series*) and to higher values of  $n$  are within the region of infrared light. Thus, the highest energy emitted due to a transition from  $n$  equal to infinity to a basic state of  $n = 1$  will correspond to equation (1.23)

$$E = \frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} = \frac{0.91 \times 10^{-30} \times (1.6 \times 10^{-19})^4}{32 \times (3.14)^2 \times (8.86 \times 10^{-12})^2 \times (1.05 \times 10^{-34})^2} = 2.16 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$$

It corresponds to the wavelength

$$\lambda = \frac{hc}{E} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{2.16 \times 10^{-18}} = 9.2 \times 10^{-8} \text{ m} = 92 \text{ nm}$$

Analogously, the highest energy in the Balmer series ( $n = 2$ ) is

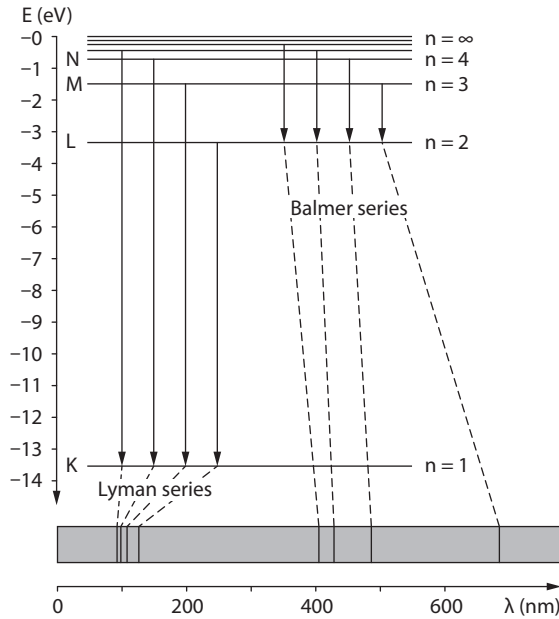
$$E_{n=2} = \frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \cdot \frac{1}{2^2} = 0.54 \times 10^{-18} \text{ J} = 3.38 \text{ eV}$$

Its wavelength is 368 nm, which reaches the region of visible light.

## 1.5 ELECTRON STRUCTURE OF HEAVY ATOMS

The electron structure of atoms with multiple electrons is mainly determined by two rules:

1. *The system of particles is stable at a minimum total energy.*
2. *Only one electron exists in each individual quantum state of the atom.*



**Figure 1.5:** Series of spectral lines for the hydrogen atom.

Like the hydrogen atom, the state of each electron in a heavy atom is determined by four quantum numbers. Each electron moves in the central force field of the nucleus with charge  $Ze$  (where  $Z$  is the atomic number) and is shielded by the presence of other electrons at a lesser distance from the nucleus. All electrons with an identical principal quantum number are at an approximately equal distance from the nucleus. Therefore, they interact with the same field intensity and possess approximately the same energies. According to this arrangement, the same shell – denoted by letters  $K, L, M$ , etc. – is occupied. Since the  $(2\ell + 1)$  values of the magnetic quantum number correspond to each orbital quantum number  $\ell$  and given that the spin number has two possible values, the highest number of electrons present in each shell is given by

$$2 \sum_{\ell=0}^{n-1} (2\ell + 1) = 2n^2 \quad (1.24)$$

However, the electron energy also depends on the orbital quantum number, which rises with increasing  $\ell$ . Its dependence on  $\ell$  also increases in tandem with the increasing number of electrons in the atom.

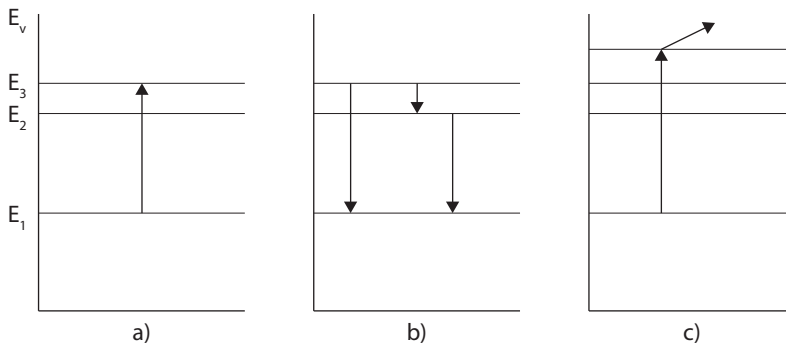
The shell (given by  $n$ ) or subshell (given by  $\ell$ ), which is completely occupied by electrons, is *closed*. Closed subshell  $s$  ( $\ell = 0$ ) contains two electrons, closed subshell  $p$  ( $\ell = 1$ ) six electrons and subshell  $d$  ( $\ell = 2$ ) ten electrons, etc. The total orbital and spin angular momentum of the electrons in a closed subshell equals zero and the distribution of their effective charge is completely symmetrical.

The periodicity of the physical and chemical properties of the elements corresponds to the order in which electron shells are filled. In the case of heavy atoms, higher shells are filled before the lower shells are completely filled (with respect to the potential number of electrons given by the value  $2n^2$ ). This scenario occurs when a minimum total energy is needed for the system to achieve stability. The order in which shells are filled in heavy atoms is as follows:  $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 6d$ . For example, since the energy of state  $3d$  exceeds that of state  $4s$ , level  $4s$  is filled beforehand. However, states  $s$  and  $p$  in the previous shell must be completely filled before filling the states in shells with higher  $n$ .

In addition to the Pauli principle, *Hund's rule* plays an important role in filling shells with electrons. Where possible, electrons in shells generally remain unpaired, i.e. they possess parallel spins. This results from the mutual repulsion of electrons. Electrons with parallel spin are more separated in space compared with paired electrons and thus this arrangement allows for lower energy and higher stability.

## 1.6 EXCITATION AND IONISATION OF ATOMS

The quantum state of a bound electron with a minimum energy is called the ground state. States with higher energies are called excited states. An excited state is reached through the absorption of energy. An electron can absorb only energy that corresponds to the difference between the ground level and one of the excited energy levels (see Fig. 1.6).



**Figure 1.6:** (a) Excitation, (b) emission of fluorescence radiation, (c) ionisation.

One of the ways an electron gains the energy necessary for the transition to a higher energy level is through the absorption of a photon. Absorption and quantum transitions occur provided the bound electron can absorb a photon whose energy  $hf$  equals the energy difference between the initial state and the final state (higher energy). If the energy absorbed exceeds the given potential, then the electron is emitted as a free electron. This process is called (positive) ionisation. In general, ionisation is the physical process of converting an atom or molecule to an ion by adding or removing charged particles, such as electrons or other ions. An ionised atom is not stable and tends to return to a ground state of minimum energy. However, if the electron does not absorb enough energy to leave the atom, then the electron briefly enters an excited state until the energy absorbed is radiated out. The electron does not exist in an excited