

Modeling and simulation methods in nanotechnology

Short description:

This series of lectures contains introduction to computational methods used in physics and biophysics for modeling and simulations of nanostructures. The selected examples are the following: tunneling through a potential barrier, modeling of the energy structure of graphene systems, optimisation of strain effects in nanoscale, and molecular dynamics of nano-size biological systems. Description of the problems, is preceded by a short introduction to quantum mechanics. The presented methods are related to the numerical techniques studied during the course of numerical methods at the second grade. Here, students create (write) their own numerical codes, which solve the problems presented at the lectures or learn how to operate ready-to-use numerical packages.

Course 1. 3 hours

Introduction to elementary quantum mechanics

Short history of quantum physics

Classical physics describes macroscopic systems. The term “macro” concerns usually sizes above 1 micrometer. As classical systems we can consider individual objects having macroscopic masses and sizes (usually modeled as material points) or sets of such objects (e.g. planetary systems). The aim of theory is the description of the *state of a physical system*. In classical mechanics the state of a system built of many material points is uniquely determined by positions and momenta of all the elements of the system in any instant of time. The values of positions and momenta are found by solving equations of Newton’s mechanics and dynamics, which in fact are second order differential equations. Classical state of a systems built of a very large number of weakly interacting particles is described within the framework of statistical physics (forgetting about their internal structure) using some macroscopic quantities as temperature, volume and pressure.

At the end of the XIX century there was a growth of experimental techniques both in the spectroscopy and in the electric research. The results of several experiments couldn’t be explained on the basis of classical physics without introducing new theory describing microscopic nature of matter, i.e., nature of atoms and molecules. Some of these experiments and phenomena were the following: *black-body radiation, photoelectric effect and Franck-Hertz experiment*.

Black-body radiation.

A black body is a physical object that absorbs all incident electromagnetic radiation, to which it is exposed. Within the framework of classical physics the radiation of a black-body was described and governed by the Rayleigh-Jeans law, which says that the radiated energy should be proportional to the fourth power of radiation frequency, independently on temperature. However, the experiments proved that there is a maximum of radiation and it depends on temperature. This was known as

Wien's displacement law (Fig. 1). For example, radiation maximum from the Sun surface appears at 480 nm. Moreover, summing the Rayleigh-Jeans formula over all the frequencies we would get infinite energy. This is called *ultraviolet catastrophe* and it was the main reason for looking for a new physics describing micro world.

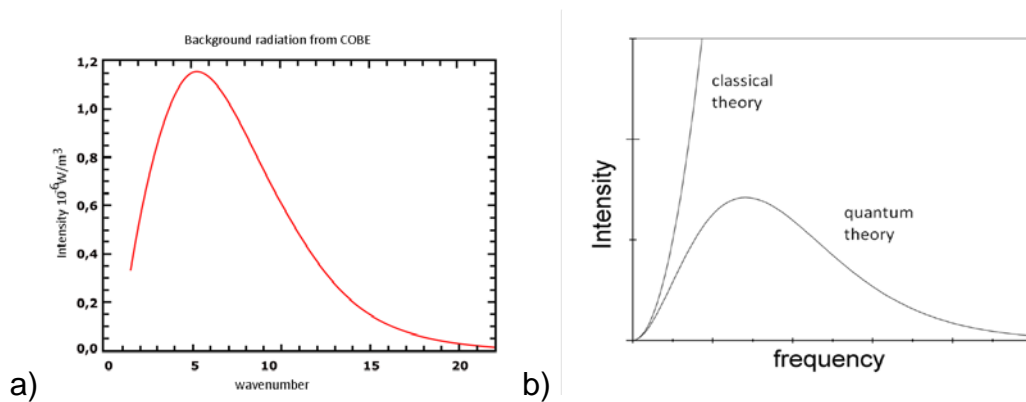


Fig.1 a) Background radiation as the rest from the Big-Bang. From Wikipedia http://pl.wikipedia.org/wiki/Cia%C5%82o_doskonale_czarne. b) Comparison of intensity of radiation of a black-body well described by Planck theory (curve with maximum) with classical prediction (monotonic curve).

Oscillating charged particles are the source of radiation in classical physics (e.g., electrons in atoms). To explain discrepancies between the observations and Rayleigh-Jeans formula, Max Planck assumed in 1900 that the oscillating particles can emit radiation only in portions of energy called *quanta*, $E=h\nu$, where ν – radiation frequency ($\nu=c/\lambda$, λ - wavelengths, c – speed of light), and h is a constant having value $4,135\ 667\ 516 \cdot 10^{-15}$ eV. This totally revolutionized our view on the structure of matter, since it meant that the energy structure of atoms (of the elementary pieces of matter) is discrete, i.e. quantized, what means that only some definite values of the energy are admitted at this level.

Photoelectric effect.

Photoelectric effect was discovered by Heinrich Hertz in 1887. Later, it was studied in detail by Philipp von Lenard and finally in 1905 explained by Albert Einstein based on quantum theory proposed by Planck.

In a vacuum tube containing two electrodes (Fig.2a), light beam (electromagnetic waves) is directed to a target metallic electrode (T). The electrons are ejected from metal and the applied potential (voltage) can accelerate or slow down the electrons on their way to cathode (K). For a given voltage V the electrons can be even turn back to the emitter (T). The energy of the turned back electrons equals $E=eVh$ (h being a path of electrons) and doesn't depend on the light intensity (Fig. 2b). The energy E depends linearly on frequency ν with some threshold Φ called *work function*. Einstein thus concluded that

$$h\nu = E + \Phi,$$

Φ is the energy needed to eject electrons from metal (is different for different materials).

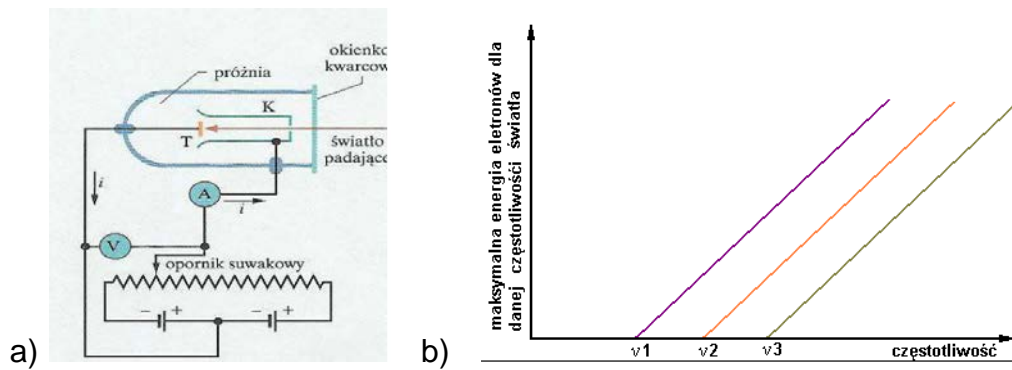


Fig.2 a) Scheme of a set-up to observe photoelectric effect. b) Energies of emitted electrons vs. frequency of radiation for different metals of target (T). From http://library.thinkquest.org/28383/nowe_teksty/html/2_8.html

Franck-Hertz experiment.

The experiment involves a tube containing low pressure mercury vapor and three electrodes (Fig.3). The electrons emitted from cathode are accelerated by a mesh-grid electrode situated between cathode and anode. One measures the current between the electrodes vs. potential difference applied to a mesh-grid electrode. The electrons collide with the mercury atoms, for low voltage their kinetic energies are small and the collisions are elastic, while for higher voltages the scattering is inelastic and the electrons give part of their energy to excite mercury atoms. Every 4.88 eV the current drops dramatically down, what means that the energy needed to excite mercury atoms from the ground to the first excited state is just 4.88 eV; the conclusion: the energy structure of atom is discrete (quantized)

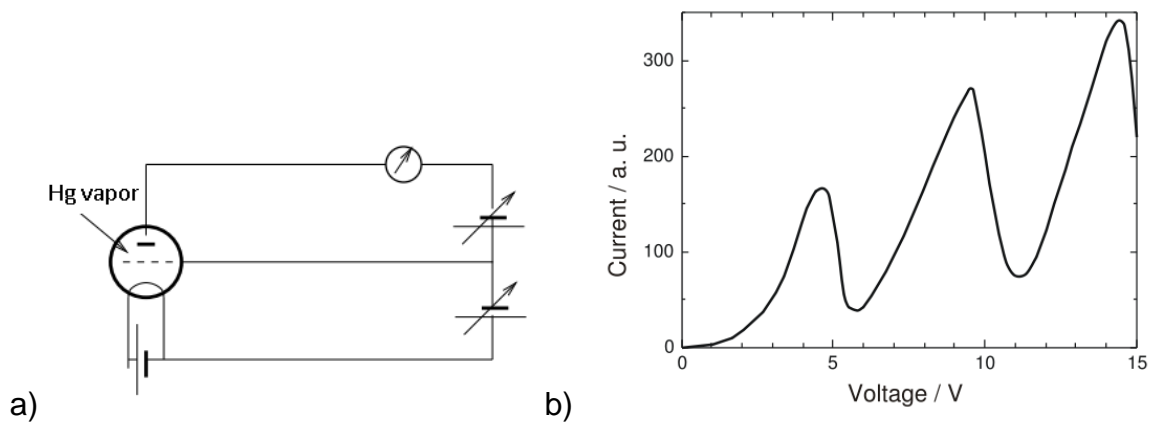


Fig.3 a) Scheme of a setup to observe Franck-Hertz experiment. b) Anode current versus voltage ad mesh-grid electrode. From http://en.wikipedia.org/wiki/Franck%E2%80%93Hertz_experiment

Diffraction of waves and electrons. Waves of matter.

The experiments described above reveal quantum nature of matter, at least as we speak about the energy structure of atoms and radiation processes (absorption and emission). However, another experiments show yet another striking property of matter: elementary pieces of matter, like e.g. electrons behave sometimes as waves.

The most fundamental feature of waves is their diffraction (and interference) on slits and edges. A typical picture of the intensity of light (observed at screen) after passing by two closely spaced slits (the width of slits compared with the wavelengths) is shown in Fig. 4. After constructive interference of spherical waves generated at slits we can observe bright and dark fringes at the screen (if the slits are point-like, the fringes are concentric). The pattern of fringes appears also for diffraction gratings. When the wavelengths is very small and it is difficult to perform a proper gratings (e.g. for X-rays), the waves can be diffracted on crystals, where the role of gratings is played by equally-spaced crystallographic planes built of regular mesh of atoms.

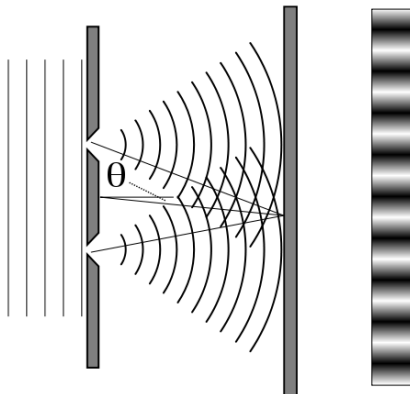


Fig.4 Diffraction of a plane wave on a double slit and appearance of fringes on the screen. From http://en.wikipedia.org/wiki/Double-slit_experiment

However, a very similar picture one gets using electrons instead of X-rays. It is shown in Fig. 5.

DYFRAKCJA ELEKTRONÓW I PROMIENI X

Rys. 39.9. a) Układ doświadczalny wykorzystywany do prezentacji falowego charakteru padającej wiązki metodami dyfrakcyjnymi. Obrazy dyfrakcyjne otrzymane dla b) wiązki promieniowania rentgenowskiego i c) wiązki elektronów (fali materii). Zwróć uwagę, że zasadnicza geometria obu obrazów jest identyczna.

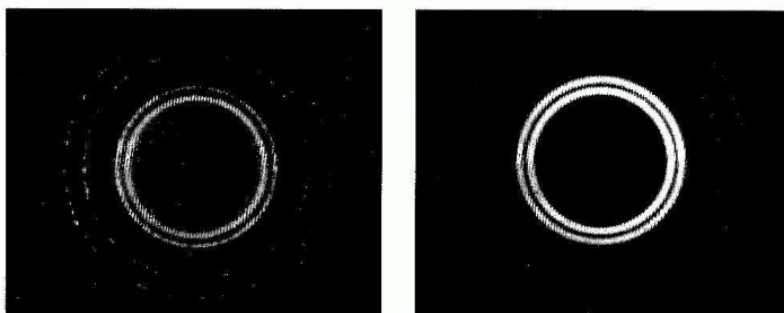
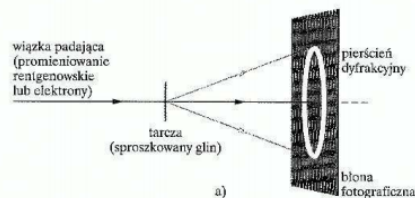


Fig.5 Comparison of diffraction of X-rays and electrons on Al crystal. From "Podstawy Fizyki", D. Halliday, R. Resnick, and J. Walker, PWN Warszawa 2007.

In the experiment with electrons, classical physics suggests that the particles should pass through one or another slit yielding for a dense beam of electrons a direct picture (a kind of reflection) of two slits (each electron "switches on" one pixel at the scintillating screen). However, the result of

experiment is completely different (see Fig. 6). Although each electron reaches some place at screen, the picture obtain after many, many electrons passes through the double-slit, is the same as for the waves!

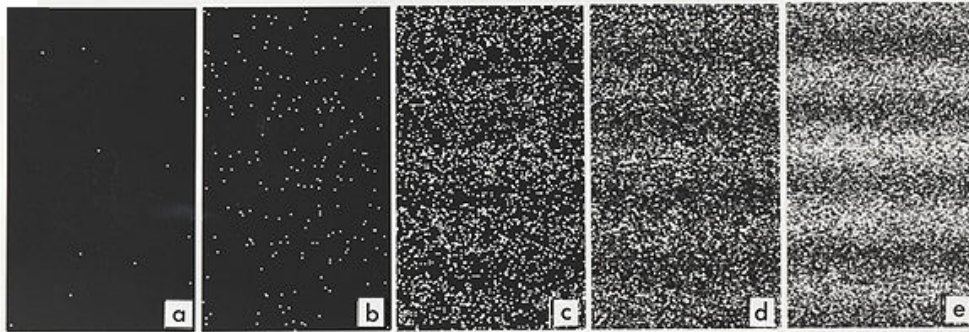


Fig.6 Interference pattern obtained on luminescence screen in the experiment of electron beam passing by double slit. Pictures from a to d correspond to growing number of diffracted electrons. From http://en.wikipedia.org/wiki/Double-slit_experiment

In result, it means that we are not able to trace the electron on its way from the slit to the screen, i.e. we cannot know its trajectory – we cannot know its position and momentum in a given instant of time. It is not our disability, it is a most fundamental property of nature, which appears to be non-deterministic. This property is reflected in quantum mechanics by the so called *uncertainty principle*, discovered by Heisenberg. Bright and dark fringes (areas) at screen shown in Fig. 6, reveal that we can only use probabilistic theory to determine the state of electron. Any new physics, i.e. quantum physics, must therefore be a probabilistic theory.

Some fundamental axioms of quantum mechanics.

Axiom 1.

The state of a physical system is uniquely and fully described in quantum mechanics by a mathematical function called *wave function* (state function or state vector) $\Psi(\mathbf{x},t)$ where, \mathbf{x} represents space-position variables of all the particles contained in the system and t represents time. The wave function provides information about the probability amplitude of position (or momentum). Its physical interpretation is the following:

$$\Psi^* \Psi d\mathbf{x} = |\Psi|^2 d\mathbf{x},$$

gives probability of finding the state in a volume $d\mathbf{x}$, while $|\Psi|^2$ is the probability density.

Therefore, the integral of $|\Psi|^2$ over the entire space gives 1, since a given system is always somewhere in the space. We say that the wave function must be “square-integrable”.

Axiom 2.

Any measurable physical quantity A (that can depend on x and t) is represented by a hermitian operator \mathbf{A} . The operators act on the wave functions, as the result we get another function (in some particular cases the same function) $\mathbf{A}\Psi=\Phi$. For example, taking derivative of a function can be considered as action of some operator on this function, or a constant that multiplies a function is the

simplest example of an operator. If $\mathbf{A}\Psi = a\Psi$, (a – a number), then Ψ is the so called eigenfunction of the operator \mathbf{A} and a is called its eigenvalue.

Axiom 3.

The results of measurements of a quantity A are only eigenvalues of the corresponding operator \mathbf{A} . Note that,

All the eigenfunctions of any operator (let us call them φ_i , $i=1,2,\dots$) span the basis in the functional space of square-integrable functions of a given type (given variables). The corresponding eigenvalues are a_i . Therefore, any function describing a state of a given system can be represented in this basis (as a linear combination)

$$\Psi = \sum_i c_i \varphi_i$$

Please note analogy to vector space. As in a vector space, one can define scalar product of φ_i and φ_j as

$$\langle \varphi_i | \varphi_j \rangle = \int \varphi_i^* \varphi_j d\tau$$

where τ - represents all the space coordinates. The symbol $\langle | \rangle$ is the so called Dirac notation for scalar product.

A function is called normalized if $\langle \varphi_i | \varphi_i \rangle = 1$; two functions are orthogonal if their scalar product vanishes. If $\Phi = H\Psi$, then

$$\langle \varphi | \Phi \rangle = \langle \varphi | H\Psi \rangle = \text{ozn} = \langle \varphi | H | \psi \rangle.$$

Axiom 4.

If a given system is in the state described by the wave function Ψ , the probability of getting value a_i while measuring a quantity A equals:

$$P_i = |\langle \varphi_i | \Psi \rangle|^2 = \left| \int \varphi_i^* \Psi d\tau \right|^2$$

Additionally,

A) average value of A obtained after a large number of measurements equals:

$$\bar{A} = \langle \Psi | A\Psi \rangle = \int \Psi^* A\Psi d\tau$$

and is called *expectation value* of \mathbf{A} (\mathbf{A} being the corresponding operator).

B) operator of momentum $\vec{p} = (p_x, p_y, p_z)$ has also vector character. Its components are

$$p_x = -i\hbar \frac{\partial}{\partial x} \text{ and similarly for } p_y \text{ and } p_z.$$

Therefore, the kinetic energy operator reads:

$$T = \frac{mv^2}{2} = \frac{p^2}{2m} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \quad (1)$$

Axiom 5.

The wave functions are solutions of the Schrödinger equation

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

Where for a system composed of n particles, $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n)$ and each $\mathbf{x}_i = (x_i, y_i, z_i)$.

The wave function fulfils also

$$H\Psi(\mathbf{x}, t) = E\Psi(\mathbf{x}, t) \quad (2)$$

known also as Schrödinger equation, where \mathbf{H} is operator of the total energy of the system called also Hamiltonian. $\mathbf{H} = \mathbf{T} + \mathbf{V}$, where \mathbf{V} is the potential energy operator.

If V is time-independent the eigenstates of \mathbf{H} are called *stationary* states. The Schrödinger equation (2) is in fact a second order differential equation, to solve it one has to impose boundary conditions on Ψ , which cause that the solution of (2) exists usually for a discrete set of

$$E_i, \Psi_i$$

Solution of the Schrödinger equation is the main aim of every quantum problem. Solving the equation (2) we find wave functions representing possible states of a given physical system. Therefore we obtain full information about the system. Solving the time-dependent Schrödinger equation we get information on the dynamics of a given system and we can foresee how it will behave in time.

Simple examples of physical systems

Very limited number of model physical systems can be solved exactly. In this lecture we will show only few of them. For all the other cases representing more complex physical systems, the equation (2) must be solved in an approximated way.

Particle in one-dimensional potential well (particle in a box).

Let us consider a particle of mass m , which can freely move in one direction only (let say x-direction) on the limited section (segment) of the lengths L . If independently on the particle energy it cannot leave this segment, in quantum mechanics its potential energy is represented by two infinitely high barriers set at the edges of the segment L (the so called *impenetrable* walls). If the particle could leave this segment for the energy V , we would call such a problem "a particle in a potential well of length L and finite potential barrier V ". Both cases are represented in Fig. 7.

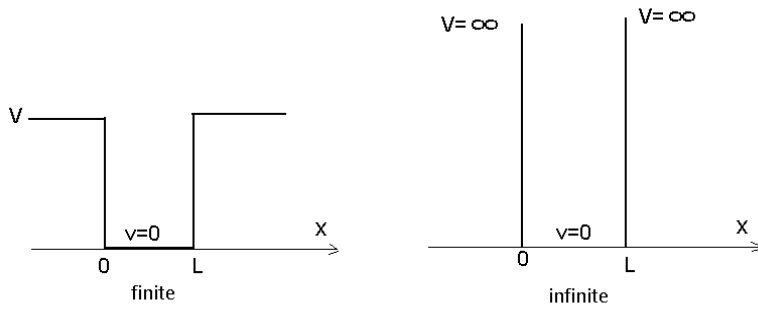


Fig.7 Finite(left) and infinite (right) one-dimensional potential well of width L.

In both cases the Schrödinger equation depends only on one variable x. As differential equation it requires imposition of two boundary conditions to get its unique solution. In case of infinite potential barrier we have to require that the wave function vanishes at $x=0$ and $x=L$ and also beyond the section $[0,L]$ $\Psi(0) = \Psi(L) = 0$. It simply means that the particle cannot leave this segment. These conditions yield following eigenvalues:

$$E_n = \frac{h^2 n^2}{8mL^2}, \tag{3}$$

where n – a quantum number counting (numbering) the consecutive solutions. The corresponding wave functions are:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), \quad n = 1, 2, 3, \dots$$

This is schematically shown in Fig. 8. It is very instructive to have a look at the problem of scale. For large, macroscopic sizes L and macroscopic masses, one gets in (3) a dense spectrum of eigenenergies. For example, for $L=1$ meter and $m=1\text{kG}$, the difference E_2-E_1 is about 10^{-66} J (10^{-47} eV) and is absolutely non-measurable, while for micro world like for electron in the 1nm trap, this energy difference is of the order of 1 eV and is measurable.

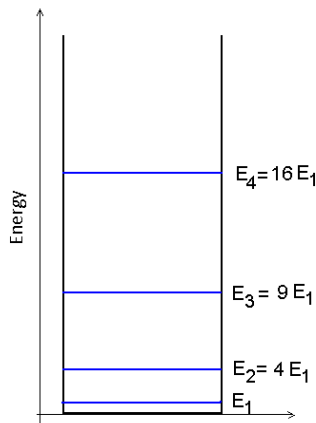


Fig.8 Energy levels in one-dimensional infinite potential well.

Let us note, that transitions between the states, e.g. excitations from the ground state to higher energy levels (via photons) are possible only for photon energies equal:

$$h\nu = E_n - E_m$$

Such process is called absorption, and the reverse process is known as emission. Absorption and emission spectra will have discrete character (see Franck-Hertz experiment, Fig. 3).

Square modulus of ψ_n (probability density) are shown in Fig. 9, they remind “waves”.

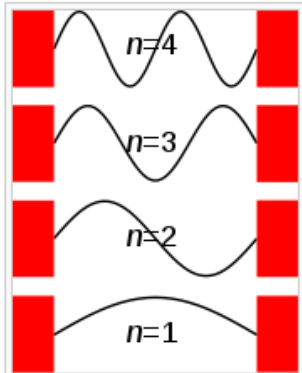


Fig.9 Wave functions for several states in one-dimensional infinite quantum well. From http://en.wikipedia.org/wiki/Particle_in_a_box

Symmetry.

A physical system can be invariant under some symmetry operations (transformations). For example, two-atomic molecule like H_2 remains unchanged if we rotate it around the bond axis or if it is reflected in a plane perpendicular to the bond and placed half-way between both atoms. Infinite crystal, which is periodic system remains unchanged under *translations* by a lattice vector. If a system is invariant under some symmetry operation then the corresponding Hamiltonian is also invariant and there exists an operator representing this symmetry operation, which commutes with the Hamiltonian, $[\mathbf{H}, \mathbf{S}] = 0$, i.e., the order of the product of both operators acting on any wave function is unimportant, $\mathbf{H}\mathbf{S}\psi = \mathbf{S}\mathbf{H}\psi$. It is easy to show that commuting operators have the same eigenfunctions. Therefore, if a physical system is somehow symmetric, the corresponding wave functions will need to reflect all symmetries and should be enumerated with the quantum numbers connected with eigenvalues of \mathbf{S} .

Course 2. 3 hours.

Atoms, molecules and elements of the solid state theory

Hydrogen atom.

Hydrogen atom is the simplest system composed of two interacting charged particles: proton and electron. Since proton is about 1000 times heavier than electron, we can reasonably assume that it is much more inert than the electron, so we can treat proton as fixed in the coordinate system (at position 0). Therefore, hydrogen atom reduces to electron moving in the static Coulomb field of proton. Let us note that in classical physics the electron would simply fall down to proton, so the Hydrogen atom could not exist...

Potential energy of electron in the electrostatic Coulomb field of proton is

$$V(r) = -\frac{e}{r} \quad (4)$$

where e is the electron charge and r is its distance to nucleus. The energy is negative, what means that it can be balanced by the positive kinetic energy of the electron. The Hamiltonian consists of \mathbf{T} (equation 1) and \mathbf{V} (4). The solution of

$$H\Psi(\vec{r},t) = E\Psi(\vec{r},t)$$

leads to a discrete *spectrum* of eigenvalues (possible energies of electron in Hydrogen atom):

$$E_n = -\frac{me^4}{8h^2\varepsilon_0^2} \frac{1}{n^2} \quad (5a)$$

In (5a) n is the principal (main) quantum number, enumerating energy levels of H. These energies are negative, which means that the electron is bound in the proton field. To realize it (to ionize the atom) one have to add (supply) positive energy equal $|E_1|$. These energy equals 13.6 eV and is very well measurable.

Let us note, that it is again a problem of a particle in a potential well, although now the well (4) is three-dimensional, spherical and has a “shape” of infinitely deep “funnel”. Its shape is shown in Fig. 10, where some energy levels are also marked.

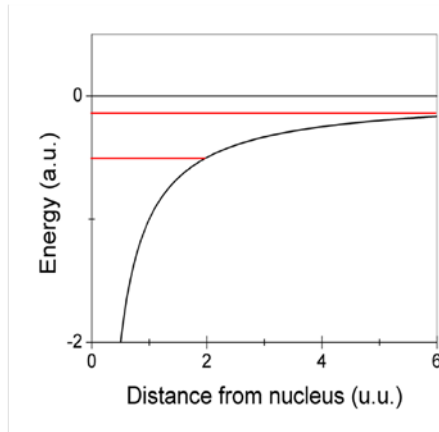


Fig.10 Potential energy (black) and two lowest (red) energy levels in Hydrogen atom (in atomic units, i.e. putting $m=h=e=1$).

In general, when quantum well is two- or three-dimensional, the problem of degeneracy of energy levels occur. Degeneracy of energy levels appears when there are more than one eigenfunction for the same eigenvalue. It occurs also in case of the Hydrogen atom. The lowest energy level is not degenerate (not counting the electron spin). The first excited level is four-time degenerate, the second excited level is nine-times degenerate. Degeneracy appears when the system is invariant under some symmetry operations. Hydrogen atom has extremely high symmetry: it is invariant under any rotation around any axis passing by point-like proton. This is so called spherical symmetry and the resulting degeneracy is called *orbital*. This degeneracy is enumerated by the so called orbital (l) and magnetic(m) quantum numbers. The energy level n and all the corresponding eigenfunctions are called *shell*. In a given shell there are n different types of functions called *orbitals*, each one additionally degenerate $1x, 3x, 5x, \dots$. These different types we labels by letters s, p, d, \dots and call them *subshells*. All the orbitals (wave functions) depend on x,y,z , or on r, θ and ϕ if we work in spherical coordinates (Fig. 10a) are the following

$$\Psi(x, y, z) = \Psi(r, \theta, \varphi) = R_n(r)Y_{l,m}(\theta, \varphi) = \Psi_{n,l,m}, \quad (5b)$$

where $Y_{l,m}$ – the so called spherical harmonics. n is the main quantum number, l – orbital quantum number and m – magnetic one. The energies depend only on n .

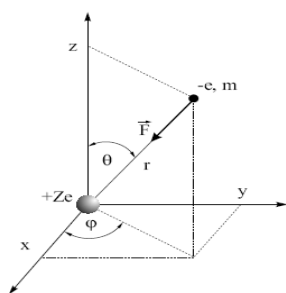


Fig.10b Spherical coordinates.

Radial dependence (on r) of the orbitals is the same in each type. Square modulus of the orbital integrated over angular variables gives *radial distribution of the density* in a given state. For the first three shells they are shown in Fig. 11.a. Maximum of a given distribution marks distance from the nucleus at which the probability of finding electron in a given state is the highest. Surfaces at which total densities have constant values are called *isosurfaces*. For several orbitals they are shown in Fig. 11b. Please note, that due to orbital and magnetic degeneracy, any combination of functions with different l and m for a given n is also a good wave function. Therefore, the shapes shown in Fig. 11.b are “possible” but not “unique”.

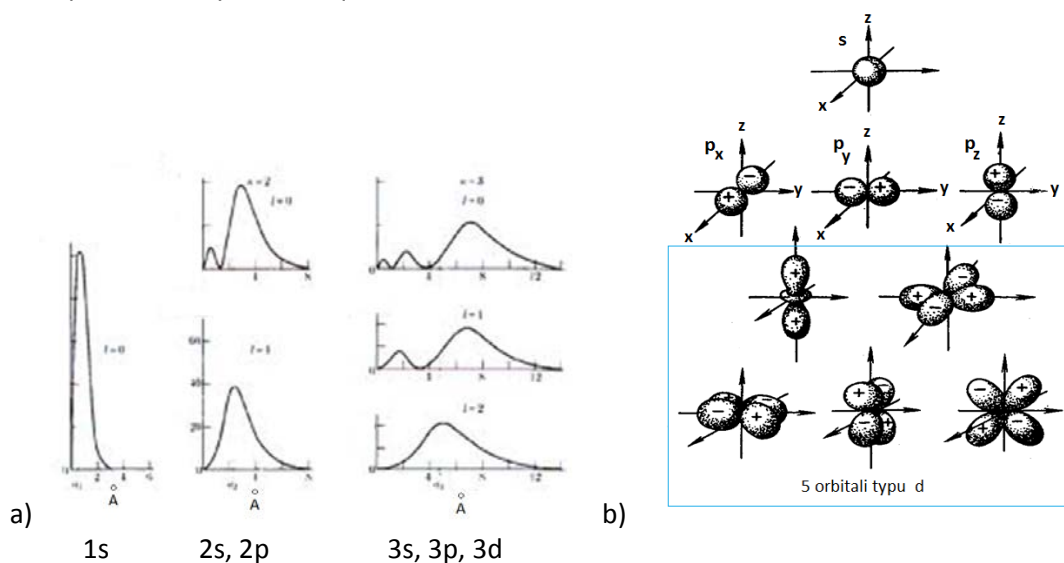


Fig.11 Radial (a) and angular (b) density distributions for several lowest orbitals in Hydrogen atom. From any book of quantum chemistry or quantum mechanics.

In many electron atoms Coulomb interaction lifts the orbital degeneracy, now the energies depend on n and l , but still do not depend on m . Each energy level (given nl) is $2l-1$ times degenerated. The sequence of the energy levels is at the beginning 1s, 2s, 2p, 3s, 3p, 3d, ... but changes for higher n . Due to spin of electron and the Pauli principle each atomic orbital can be occupied by two electrons (only). When several subshells are fully occupied the atoms (or rather the state) is called *closed-shell*. Nobel gasses are the examples. Such atoms are not eager to react with other atoms. Contrary, the *open-shell* systems “prefer” to “give” or to “receive” electrons, trying to close the electronic shells

and subshells, since it is energetically favorable. Such atoms react easily with the others forming molecules and crystals.

Hybridized orbitals and chemical bonds

Chemical bond.

Although atoms are electrically neutral they can bind forming molecules and crystals. A fixed junction between two or more atoms is called a *chemical bond*. There are different types of bonds. When one atom lacks one electron to close the external subshell, e.g. Cl ($1s^2 2s^2 2p^2 3s^2 3p^5$) and the other have only one electron at the outermost subshell, like Na ($1s^2 2s^2 2p^2 3s^1$), sodium will eagerly give one electron to chlorine, which eagerly will receive it. Two charged ions will appear, which will attract electrostaticly each other forming *ionic bond*. Another type of bond appears in metals: quasi-free electrons form negatively charged cloud, which keeps stable lattice of positively charged ions. The molecular or van der Waals bond occur between atoms of noble gases or large molecules (e.g. proteins), but also between layers of graphene in graphite. However, we will be mostly interested in *covalent bond*, which happens when hybridized orbitals of neighboring atoms strongly overlap.

Hybridized orbitals.

As mentioned above, one can create linear combinations of functions belonging to degenerate energy level. Each such combination is also a good wave function, i.e. an orbital having only different density distribution than the constituent functions. For the energy levels that are not exactly degenerated, but are energetically close we can assume they are degenerated and make linear combinations of the corresponding wave functions. Such situation takes place, for example in carbon C ($1s^2 2s^2 2p^4$), where the energies of 2s and 2p levels are close (at least comparing with 1s). Of 2s and $2p_x$ orbitals we can create two new hybridized orbitals sp. One as $2s+2p_x$ and the other as $2s-2p_x$. Since the orbital $2p_x$ has density localized along the 0X axis and the wavefunction is positive for $x>0$ (negative for $x<0$) both hybridized orbitals will be “directed” one along $X+$, the other along $X-$. It is illustrated in Fig. 12.

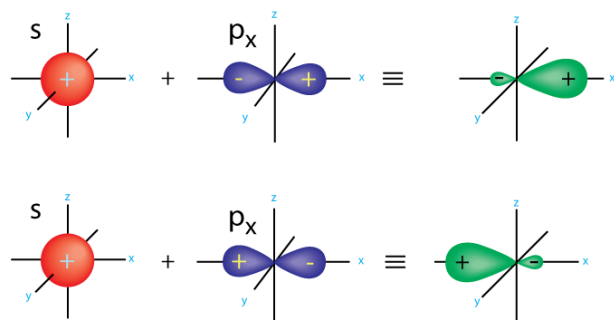


Fig.12. Formation of sp hybridized orbitals. From <http://www.grandinetti.org/comment/18>

Such orbitals explain stability of bond in F₂ molecule, what is shown in Fig. 13. The overlapping sp hybridized orbitals of both atoms correspond to electron cloud “most probably” existing in the space between the atoms, which keeps the repelling F¹⁺ ions. The sum of two overlapping sp orbitals forms the so called σ bonding molecular orbital.

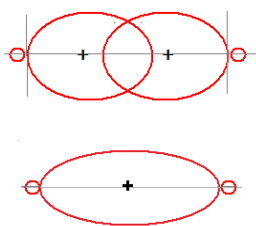


Fig.13. Formation of covalent bond in F_2 molecule. Sum of two sp hybridized orbitals creates bonding molecular orbital σ .

Another hybridization, sp^2 , allows us to explain stability of many bonds, like e.g. these in benzene (and partially in C_2H_4). This hybridization occurs when one s and two p -type orbitals (e.g. p_x and p_y) are used to form three new orbitals (leaving the p_z orbital unchanged):

$$\begin{aligned}\phi_1 &= \frac{1}{\sqrt{3}}(s + \sqrt{2}p_x) \\ \phi_2 &= \frac{1}{\sqrt{6}}(\sqrt{2}s - p_x + \sqrt{3}p_y) \\ \phi_3 &= \frac{1}{\sqrt{6}}(\sqrt{2}s + p_x - \sqrt{3}p_y) \\ \phi_4 &= p_z\end{aligned}$$

These orbitals are also directed into apexes of triangle, as shown in Fig. 14. Formation of covalent bonds in C_2H_4 molecule is presented in Fig. 15.

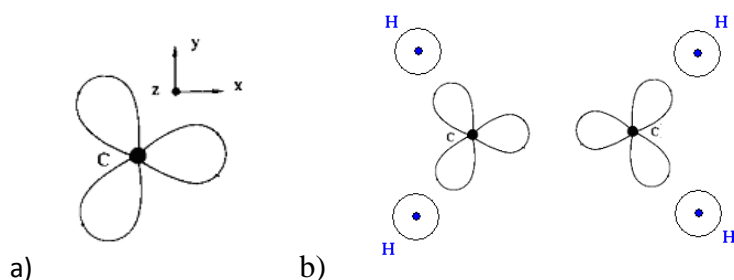


Fig.14. a) Hybridized orbitals sp^2 . b) $1s$ Hydrogen orbital and sp^2 Hybridized orbital of carbon before formation of chemical bond in a molecule C_2H_4 .

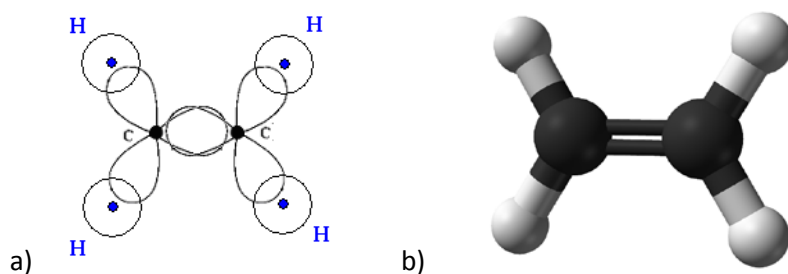


Fig.15. a) Formation of covalent bond in C_2H_4 molecule. b) A model of molecule C_2H_4 . True bond between carbon atoms is not of σ type, but is of a π type formed from two sp^2 hybridized orbitals of carbon. From <http://en.wikipedia.org/wiki/File:Ethylene-CRC-MW-3D-balls.png>

Periodic potentials

Crystals are physical systems with space-periodic structure. This structure is formed by atoms connected *via* chemical bonds. The crystal can be obtained by periodically repeating the so called *unit cell*, which contains one or more atoms forming the lattice. The center of each unit cell can be identified with *lattice nodes*. Fig. 16 shows some models of three-dimensional lattices (crystals) and a model of one-dimensional crystal is shown in Fig. 17. In both cases spheres mean atoms and (different colors for different types of atoms) and bars mean chemical bonds.

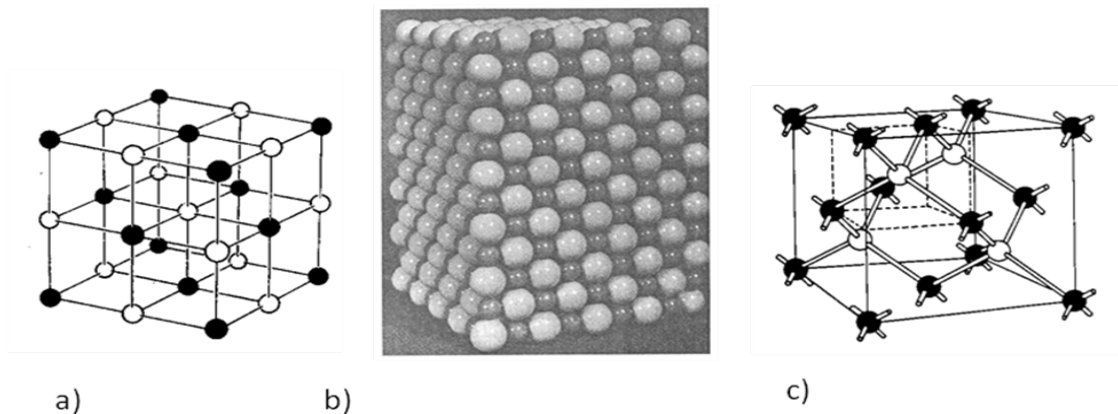


Fig.16. Models of crystal lattices: a) and b) NaCl, c) GaAs. From "Wstęp do fizyki ciała stałego", C.W. Kittel, PWN, Warszawa 1999.

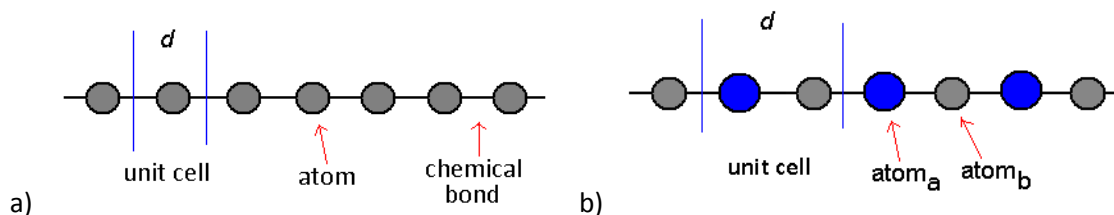


Fig.17. A model of one-dimensional lattice, a) made of the same atoms, b) made of two different atoms. Case b) is so called "lattice with basis"- unit cell contains more than one atom.

Macroscopic crystal is a very complex system. It contains millions of strongly interacting atoms (electrons and protons). The exact quantum-mechanical description of such a system is impossible, not only because of computational complexity, but also due to problems with physical interpretation of functions, which depends on millions of variables. Therefore we usually make several approximations. In the first one we separate electrons from nuclei, similarly as what we did in the case of Hydrogen atom. In the next step, still very complex many-electron Hamiltonian is reduced to a one-particle Hamiltonian. This is called *one electron approximation*. It is assumed that we can describe the state of a single (individual) electron in a molecule or crystal, using one-electron function; further, the function describing the entire system can be approximately composed of one-electron functions. These one-electron functions are called atomic, molecular or crystal *orbitals*. They are solutions of one-electron Schrödinger-like equation; now each electron interacts with the lattice of positive ions and with all the other electrons. For crystals, this interaction potential is approximated by periodic term, which for one-dimensional chain of atoms (Fig. 17) reads: $V(x+d) = V(x)$, where d - period of lattice (the size of unit cell in this case).

Bloch theorem and band structure of energy in crystals

It is easy to understand that since crystal is periodic, the entire information about its properties is embedded in a single unit cell, plus boundary conditions imposed on the wave function. This condition is nothing else, but *translational symmetry*. In turn, translational symmetry means that if we move crystal by any lattice vector (a vector connecting any two lattice nodes) the crystal (lattice) doesn't change. It is obvious that this property can concern only infinite crystals. However, for crystals containing large number of unit cells, translation by a single unit will change almost nothing, except its edge. If we are interested in the properties of crystals originating from its *bulk* character, but not in the surface features, we can reasonably treat such large macroscopic crystal as infinite, We will show latter that this approximation will have some influence on possible values of the wave vector.

Now, let us have a look at the most important theorem concerning periodic systems, namely the Bloch theorem, which says that the wave function describing a state of electron in a periodic potential must fulfill the following condition (here for one-dimension only)

$$\Psi(x + d) = e^{ikd} \Psi(x) \quad (6a)$$

where k is the so called wavevector and d is translation vector. There is another form of this theorem

$$\Psi(x) = e^{ikx} u(x) \quad (6b)$$

where $u(x)$ is a periodic functions, $u(x+d)=u(x)$.

Bloch theorem results from translational invariance of a given system. The Hamiltonian \mathbf{H} commutes with the translation operator \mathbf{T} and both operators have common eigenfunctions. Therefore, the eigenfunctions of \mathbf{H} can be enumerated as eigenfunctions of \mathbf{T} . A quantum number that enumerates eigenvalues of \mathbf{T} is called \mathbf{k} – wave vector, which in one dimension reduces to scalar k . In fact, if the right-hand side of (6b) depends on k , so $\Psi(x)$ must be enumerated by k . The result of action of \mathbf{T} on Ψ is

$$T_d \Psi(x) = \Psi(x + d) = e^{ikd} \Psi(x)$$

Since e^{ikd} is a dimensionless quantity, the dimension of k is reciprocal lengths. e^{ikd} is periodic with periodicity equal 2π , so it is sufficient if k changes only in the interval $(0, 2\pi/d)$ or $(-\pi/d, +\pi/d)$. This interval is called *Brillouin zone (BZ)*. For infinite crystal k takes continuous values, but if the crystal is finite and contains e.g. N unit cells (in one dimension), k takes discrete values $0, \dots, 2\pi n/(dN), \dots$, very closely spaced for a large N (i.e. almost continuous index).

Independently of k , each wave function is also the solution of (2) with periodic potential, which are enumerated using “usual” quantum number, e.g. n . Therefore, for a periodic potential the eigenvalues of \mathbf{H} have to be labeled as $E_n(k)$, where for each n , k changes in $(-\pi/d, +\pi/d)$. The energy

spectrum have a structure of *bands*. Bands are enumerated by n and in each band the energy changes like $E_n(k)$, we call it *dispersion relation*. The number k enumerates N one-electron states belonging to a given band.

Metals and semiconductors

For finite crystals bands contain large numbers of one-electron levels densely located on the energy scale. The number of electrons is also finite. All these electrons occupy one-electron states (energy levels). In fact we usually use only the electrons from the outermost (valence) atomic shells, since the periodic potential in equation (2) concerns only valence electrons. There are several possible situations, which are shown in Fig. 18.

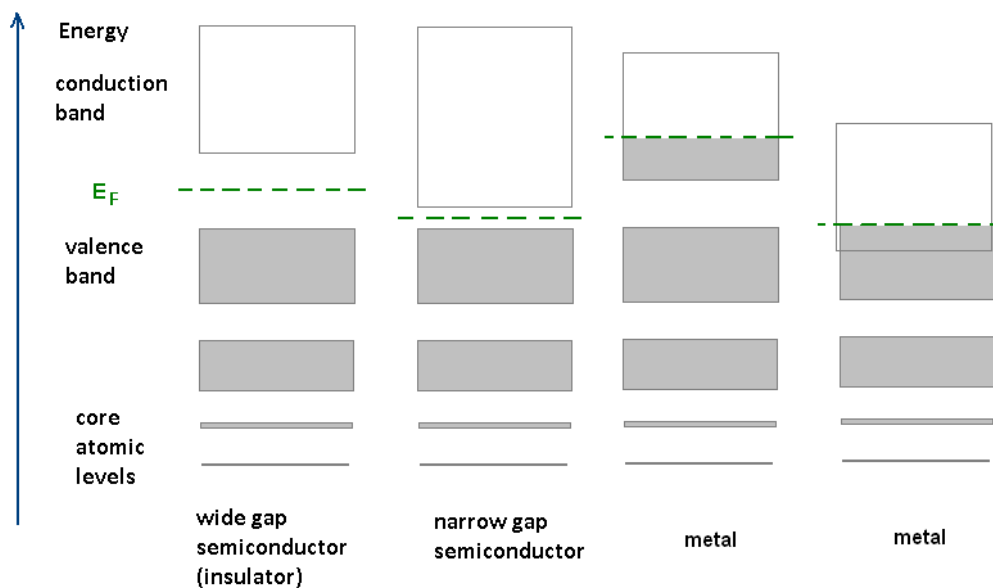


Fig.18. Energy bands in insulators, semiconductors and metals.

Occupancy of bands determine whether a given crystal is metal, semiconductor or insulator. If the bands are separated by *energy gaps*, the number of valence electrons decides on the crystal character. Since due to spin each one-electron level can be occupied by two electrons, so for even number of electrons several bands are completely occupied and the other ones are empty. The highest (energetically) fully occupied band is called *valence band* and the lowest unoccupied – *conduction band*. When the energy band between these two bands is large (several eV) such crystal is an insulator, when the gap is small, we deal with semiconductor. If these two bands overlap or if the number of electrons is odd we get metal and when the bands merely touch each other we deal with *semimetal*. Graphene is such a case of semimetal.

In metals, the highest occupied level (in $T=0K$) marks the so called Fermi level (or Fermi energy) E_F . For semiconductors E_F lies in the middle of the energy gap. Metal can conduct electric current, because just above the Fermi level there is continuum of unoccupied one-electron levels, which can be easily occupied by electrons slowly increasing their energies in the electric field. This is impossible in semiconductors and insulators, since high energy is required to move (energetically) electron from valence to conduction band. Such transitions are usually performed optically.

Course 3. 3 hours.

Methods of calculation of the energy bands. Graphene structures.

Model space.

Instead of solving differential equation (2) one can approximately expand the wave function in a finite orthonormal basis set of N functions φ

$$\Psi = \sum_{i=1}^N c_i \varphi_i \quad (7)$$

and approximate the energy as

$$E = \langle \Psi | H | \Psi \rangle \quad (8)$$

In the basis φ_i , the expression $\langle \Psi | H | \Psi \rangle$, strictly speaking the set of numbers $H_{ij} = \langle \varphi_i | H | \varphi_j \rangle$, takes the form of matrix and the problem $H\Psi(\mathbf{x}) = E\Psi(\mathbf{x})$ (equation 1) is equivalent to the problem of finding eigenspectrum of Hamiltonian matrix H

$$\begin{bmatrix} H_{11} & \dots & H_{1N} \\ \dots & \dots & \dots \\ H_{N1} & \dots & H_{NN} \end{bmatrix} \begin{bmatrix} c_1 \\ \dots \\ c_N \end{bmatrix} = E \begin{bmatrix} c_1 \\ \dots \\ c_N \end{bmatrix} \quad (9)$$

The solutions reduces to diagonalization of matrix H , which is done by unitary transformation S , such, that $SHS^T = D$, where D is diagonal matrix. The eigenvalues of H are situated at the diagonal of D . We get N values E_i (some of them can be the same – degeneracy), which in line with the *variational principle* are interpreted as upper approximations (bounds) to the exact energies of the system represented by the Hamiltonian H . For periodic systems all H_{ij} depend on k , since the wave function depends on k . Therefore, solving (9) for periodic system we get energy bands $E_i = E_i(k)$. However, we have to solve (9) for many values of k from the BZ.

Graphene.

Graphene is a two-dimensional rhombic (hexagonal) lattice with two-atomic basis (see Fig.19).

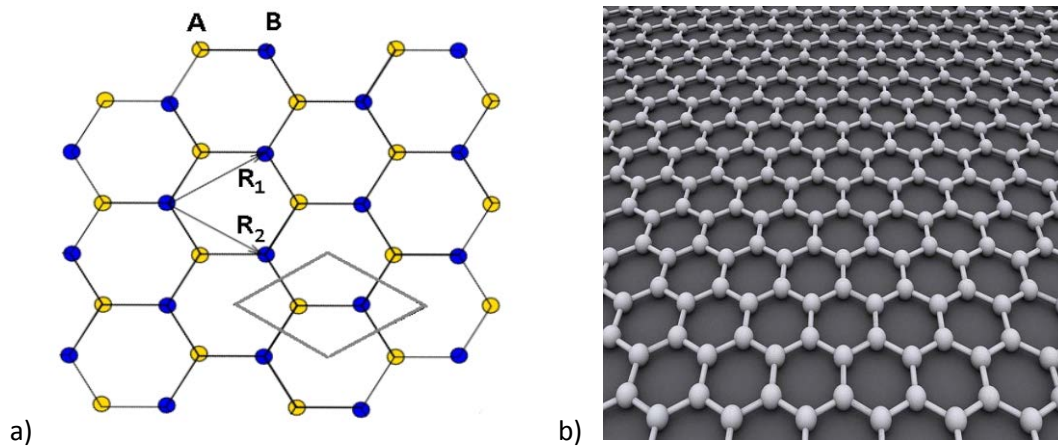
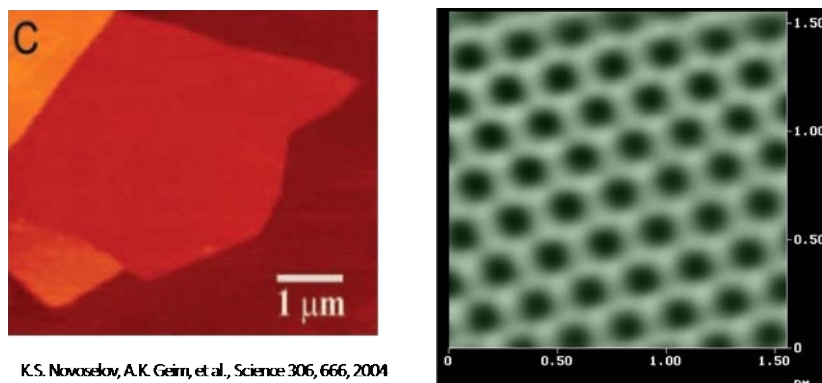


Fig.19. a) Hexagonal lattice of graphene. Unit cell contains two carbon atoms. R_1 and R_2 are two basis vectors of this lattice (any other lattice-translation vector can be built as a linear combination of R_1 and R_2). b) A model of graphene. From <http://en.wikipedia.org/wiki/Graphene>

It was for the first time isolated from graphite in 2005 by Geim and Novoselov, who in 2010 were awarded Nobel Prize for this achievement. They obtained single layers of graphene using a Scotch tape for removing consecutive layers from the “bulk” graphite. It is quite easy to recognize a single layer since, contrary to any other graphite system, it is transparent. Nowadays graphene is obtained also using CVD methods or by evaporation of silicon from layers of SiC. Examples of single layers of graphene obtained using STM techniques are shown in Fig. 20.



K.S. Novoselov, A.K. Geim, et al., Science 306, 666, 2004

Fig.20. Microscopic pictures of graphene. From http://www.polymermicroscopy.com/eng_afm_graphit.htm and <http://www.graphene.manchester.ac.uk/story/image-gallery/>

Stability of graphene is guaranteed by the in-layer covalent σ bonds, formed between neighboring carbon atoms. These bonds are formed by overlapping sp^2 hybridized orbitals. However, each carbon atom supports yet another electron occupying p_z orbital (perpendicular to the graphene layer). These orbitals also form bonds, the so called π bonds (π molecular orbitals), bonding or antibonding, depending on whether we add or subtract p_z orbitals from neighboring atoms. Since graphene is periodic in two dimensions, each energy level corresponding to π -type molecular orbital transforms into a band. Such bands are called π -bands. Both bands $E_i(\mathbf{k})$, $i=1,2$ (π and π^*) depend on the wavevector, which now is a two-dimensional vector (k_x, k_y) , The Fermi level is situated between them and this is the reason why these bands are responsible for electrical properties of graphene.

Tight binding method.

The tight binding method is a practical realization of a model space method. We expand one-electron functions (7) describing valence electrons (π electrons in graphene) onto the basis of p_z atomic orbitals. The unit cell contains only two such orbitals and due to periodicity we first have to construct crystal (delocalized) orbitals of them. They are called the *Bloch sums (orbitals)*, since they fulfill the Bloch theorem. They depend on k . Such two Bloch orbitals simplify the problem: dimension of the Hamiltonian matrix is equal 2 (but each matrix element depends on k). Such a simple matrix one can easily diagonalize analytically. As the result we get two solutions $E(k)$, one is called π -bonding $E_-(k)$ and another antibonding $E_+(k)$.

$$E(k_x, k_y) = \pm t \left\{ 1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right\}^{1/2} \quad (10)$$

Brillouin zone is also two-dimensional and looks like a hexagon. The energies of both bands are shown in Fig. 21.

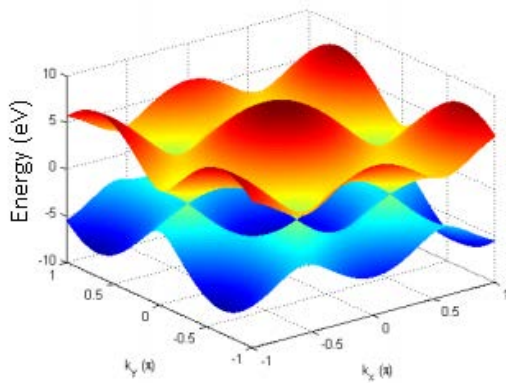


Fig.21. π bands in w graphene. From PhD thesis by M. Pelc, Toruń, 2012.

The Hamiltonian matrix has four elements. The diagonal ones correspond to two p_z orbitals at the same node $H_{ij} = \langle \varphi_i | H | \varphi_j \rangle$. It is the so called *on site* integral. Since both diagonal elements are the same we can assign them arbitrary value, which can be treated as arbitrary choice of the origin at the energy scale. Customarily we assign them value zero. Off-diagonal elements depend on $H_{ij} = \langle \varphi_i | H | \varphi_j \rangle$, where i, j correspond to neighboring atoms. This integral is also treated as an empirical parameter, its value (taken from the experimental data) is about 2.7 eV. After diagonalization we get (10).

Finite graphene structures.

Finite graphene structures are in fact large molecules built of carbon atoms, they are not periodic, so for them we cannot keep the concept of a unit cell. Therefore, a basis in (7) must contain p_z orbitals localized at all atoms. k is no longer a good quantum number (we need not to solve equation 9 for

many k values, but instead we the Hamiltonian matrix may be really big. Since we usually work in the nearest neighbors approximation, which neglects all the integrals connecting non-neighboring atoms, the H matrix is almost empty – non-zero elements appear only close to diagonal. After diagonalization we obtain a set of eigenvalues, which represent energy levels of a given “molecule”.

Periodic graphene structures.

Nanoribbons.

Graphene nanoribbons (GNR) and carbon nanotubes (CN) belong to periodic structures made of graphene. Ribbons are formed by cutting-off a strip from the graphene sheet. When the cut goes along σ bonds we get *armchair* ribbon; when the cut goes in perpendicular direction we obtain *zigzag* ribbon. Examples of such ribbons are shown in Fig. 22.

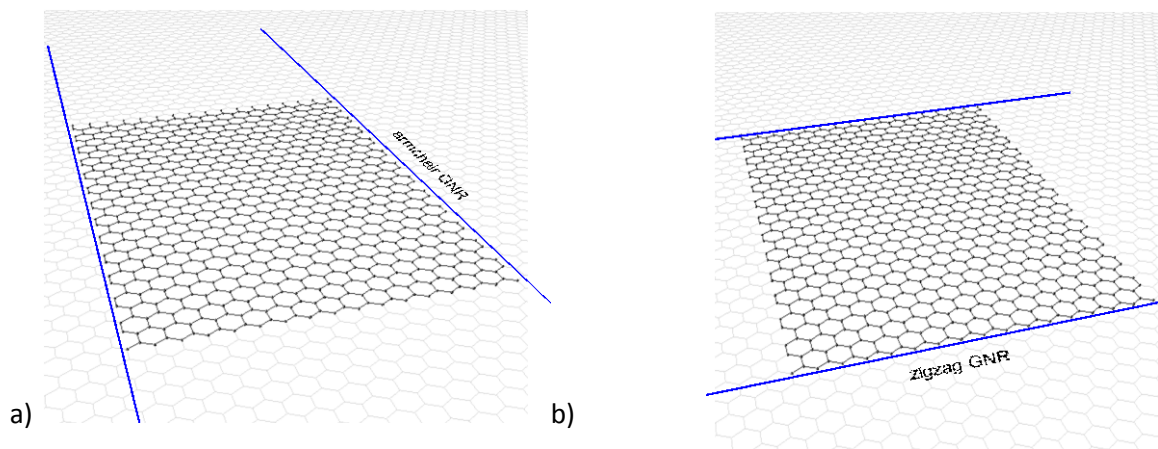


Fig.22. Graphene nanoribbons. a) armchair, and b) zigzag.

Cutting graphene in any other direction we get *chiral* ribbon; two examples are shown in Fig. 23. Such a ribbon may have quite irregular, but periodic, edges.

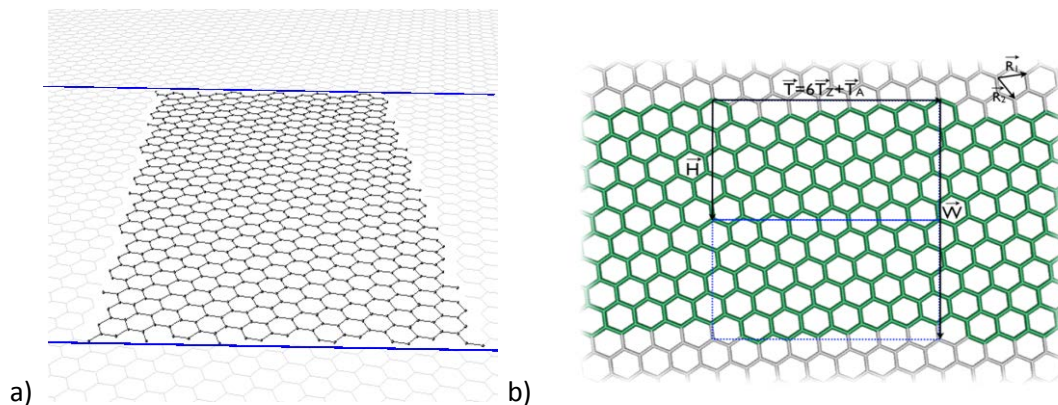


Fig.23. Examples of chiral ribbons. In b) unit cell is marked as space confined by vectors T and W .

Any GNR can be uniquely identified (determined) by three elements: the translation vector T , the width W and details of the edge (edges) in the GNR unit cell. The unit cell of GNR contains all the atoms enclosed in the rectangle made of T and W (see Fig. 23 b).

It is easy to built Hamiltonian matrix for such a system. The procedure is the following:

1. first, enumerate all the nodes in the unit cell and do the same for neighboring unit cells,
2. set all the matrix elements equal to zero,

3. in off-diagonal elements connecting atoms belonging to the same unit cell put value t ,
4. in matrix elements connecting i -th node of a given unit cell with j -th node of the right unit cell put value $t \times \exp(ikd)$, while in elements connecting node " k " of a given unit cell with node " l " of the left unit cell put $t \times \exp(-ikd)$,
5. check whether the entire matrix is hermitian,
6. since k changes in the interval $0-2\pi/d$, the factors $\exp(\pm ikd)$ can be substituted by $\exp(\pm ik)$ and k can vary from 0 to 2π .

Nanotubes.

Graphene nanoribbons can be rolled up to form carbon nanotubes, as it is shown in Fig. 24.

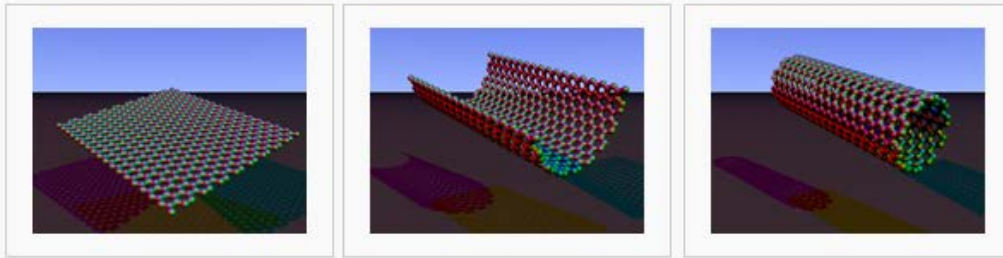


Fig.24. Formation of a nanotube from a graphene nanoribbon.
From http://en.wikipedia.org/wiki/Carbon_nanotube

In case of nanotubes the carbon atoms from one edge of the ribbon must be connected with carbon atoms from the opposite edge. This is shown in Fig. 25. One has to remember about that when the corresponding Hamiltonian matrix is formed.

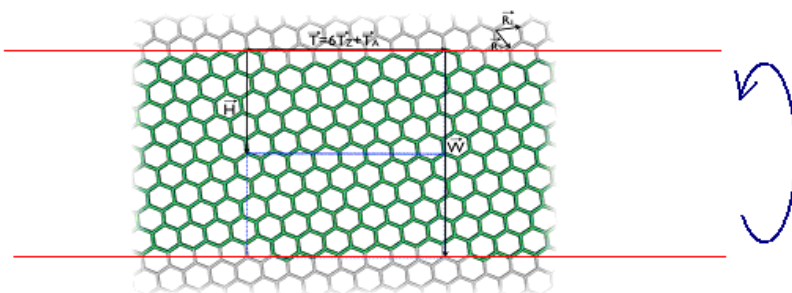


Fig.25. Formation of nanotube from GNR by rolling up and connecting atoms from opposite edges.

Here are three different types of nanotubes, armchair, zigzag and chiral, they are presented in Fig. 26. Now, the type of tube is determined by the shape of edge when the tube is cut perpendicular to its axis.

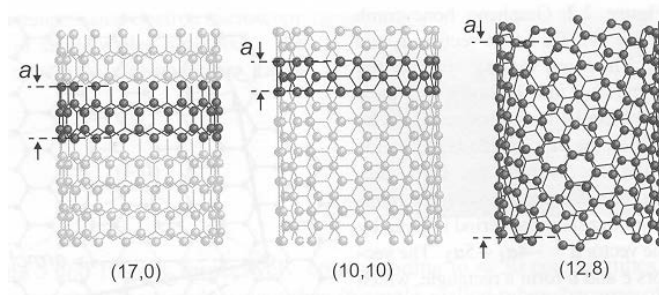


Fig.26. Three types of carbon nanotubes. From the left: zigzag, armchair and chiral. From "Physical Properties of Carbon Nanotubes", M.S. Dresselhouse, G. Dresselhouse, and R. Saito, Imperial College Press, London 1998.

Any carbon tube can be uniquely defined by *chiral vector*, called also a vector of circumference. It is in fact vector W shown in Fig. 25 (usually it is named C_n). Components of chiral vector in the basis defining graphene lattice (vectors R_1 and R_2 in Fig. 19a) reduce to two integer numbers (n,m) . These two numbers uniquely define any carbon nanotube.

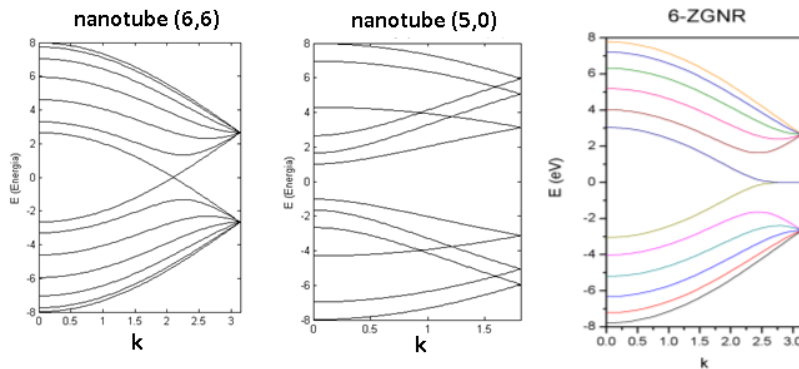
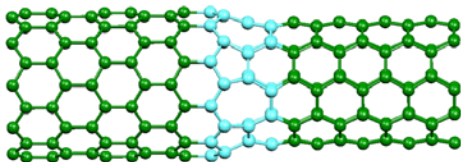


Fig.27. Band structure of three different graphene systems. From the left: armchair tube (6,6), zigzag tube (5,0) and zigzag GNR of width equal 6 graphene unit cells.

Since GNRs and CNs are quasi-one-dimensional systems, their energy structure has a band character $E_i(k)$. Three examples are shown in Fig. 27. Depending on the diameter and chirality of a tube, and in case of GNR – on its widths and edge-shape, these systems can be metallic or semiconducting. We can see in Fig. 27, that CN (6,6) and zigzag GNR are metals – there is no energy gap between the valence and conducting bands (remember that E_F , which is at zero energy, separates both bands). In contrast, the tube (5,0) is a semiconductor with the energy gap as large as ~ 2 eV. Additionally, two different nanotubes can be connected (joined) by the so called *topological defects* 5/7. One example is shown in Fig. 28. Junctions between the tubes can be exploited to built *quantum dots* and *superlattices*.



Ry1s.28. Junction between zigzag $(2n,0)$ and armchair (n,n) tubes. Junction is defined by n pentane/heptagon pairs.

Graphene ribbons and carbon nanotubes may have potential applications in future carbon-based nanoelectronics. Prototype transistors have already been fabricated using both the tubes and the ribbons. They have sizes of several nanometers.