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I. S. CHEKMAN (Kyiv, Ukraine)

WAVE PROPERTIES OF NANOPARTICLES: THE VIEW OF A PROBLEM

Bogomolets National Medical University <chekman_ivan@yahoo.co.uk>

The results of studies on nanopharmacology have made conditions to develop a hypothesis: from the standpoint of quantum mechanics an increase in pharmacological properties of nanoparticle based medications is driven by the preponderance of wave properties over corpuscular ones. According to results obtained the changes of spin states in molecules is one of the essential properties of living matter, which is characterized by self-organization. Self-organization is also common in nanostructures. Therefore, the quantum wave properties of nanoparticles with their high ability to change spin states determine pronounced pharmacological effect of nanoparticle based medications. At this stage of research the scientific facts received do not rise to the possibility to experimentally or mathematically justify the assumptions made, so please take them for granted. I am convinced that this article will be the 'nanomotor' that will attract world's scientists to continue research in order to prove current hypothesis – the wave properties of nanoparticles determine their high activity – experimentally.

Key words: wave properties, nanoparticles, spin states, high activity.

The second half of XX and beginning of XXI century can be called a period of significant growth of interest of world's scientists in conducting research in nanoscience, development of which will enhance an appearance of new technology that deals with synthesis of different nanomaterials, medicines and study of their properties. Research on the mechanical, physical, chemical, biological, and pharmacological properties of nanoscale structures are currently rapidly developing [1, 2, 6, 11, 16].

Nanostructured materials is also the subject of growing interest for basic and applied sciences, because with a decrease in the size of their structures to the nanoscale, they acquire new properties, which may be driven by their quantum wave effects and an increase in vibrational-energetic activity of nanoparticles [4, 12, 13, 25, 28].

Nowadays mechanical, thermodynamic, electrical, optical, magnetic, and biological properties of nanostructured materials are being determined.

On pharmacology department of Bogomolets National Medical University (Kyiv, Ukraine) the studies on pharmacological and toxicological properties of nanosized silica, nanosilver, nanocopper, nanoiron, and nanocarbon have been being carried out for last 15 years. The results of studies have made conditions to develop a hypothesis that from the standpoint of quantum mechanics an increase in pharmacological properties of nanomaterials is driven by the preponderance of wave properties over corpuscular ones [15, 16, 19, 20].

Quantum mechanics is a fundamental physical theory that, from the view on microscopic and nanoscale materials' characteristic, extends, refines, and combines the results of studies in classical mechanics, physics, chemistry, and electrodynamics [5, 7].

Quantum mechanics explains the three major phenomena in surrounding objects: 1. Presence of wave-particle duality of matter, i.e. the existence of wave and particle properties in all surrounding objects. 2. Presence of mixed quantum states in materials. 3. Quantization of certain physical phenomena. Examples of quantum parameter are the angular momentum, the total energy of the limited system and the energy of electromagnetic radiation of a certain frequency. Quantum mechanics is important in understanding how individual atoms combine with each other and form a specific chemical elements, compounds, nanoparticles, micro- and macrostructures.

Properties of nanoparticles that can confirm a significant role of the wave properties of nanomaterials in improving their mechanical, thermodynamic, electrical, magnetic, catalytic properties, and biological and pharmacological activity have been already established today.

Spin is an intrinsic angular and magnetic momentum of an electron and is purely quantum characteristic

A change in the spin state of electrons in a molecule can be caused by either a strong external magnetic field or by spin-orbit coupling (SOC). Spin effects play an important role in biochemical and pharmacological reactions and require further fundamental research [8, 39]. Furthermore it is fundamentally important to take into account the possibility of transitions with a change in spin in metalloclusters that cannot be done using conventional medicines which are diamagnetic molecules in singlet ground state. These drugs are also able to influence the course of biochemical processes in the cell by chemical reactions that are typical of traditional bioorganic chemistry [18].

Chemical reactions can be regarded as occurring with spin adjustment. If a nanoparticle is able to easily change the spin state, then great opportunities for so-called spin catalysis open up, i. e. effect of nanoparticle on biochemical reactions is greatly enhanced. As an example, this phenomenon can be explained by the reaction of molecular oxygen binding to hemoglobin. Ferriporphyrin surrounded by protein molecules is an active center of hemoglobin and has 4 unpaired electron spins (quintet state). A molecule of oxygen is known to be paramagnetic and to have a triplet ground state. After molecular oxygen binding to hemoglobin the ground state of the whole complex (oxyhemoglobin) is singlet, i. e. during such kind of binding a change in spin state definitely takes place [31].

Cytochrome P450 is a part of horseradish peroxidase, found in the roots of plant horseradish, and a number of other important enzymes that carry out the hydroxylation of hydrocarbons, including ferriporphyrin. Reactions of cytochrome P450 go through a number of changes in spin states. On the basis of quantum-chemical calculations based on the spin-orbit interaction electronic mechanisms to overcome the spin prohibition in enzymatic activation of molecular oxygen in several heme-containing enzymes, peroxidases, monooxygenases, hemoglobin, myoglobin, cytochromes and other flavoproteins, as well as glucose oxidase activity that is essential for biochemical reactions, have been studied [9, 32].

Changing of the spin states in biomolecules is one of the essential properties of living matter, which is characterized by self-organization. Therefore, the quantum wave properties of nanoparticles with their high ability to change the spin states appear to be useful in considering the pharmacological action of these drugs. Quantum nanopharmacology should detect this kind of quantum transitions in medical action of nanoparticle based medications [14].

Therefore it's possible to develop a hypothesis that electron and molecule spin is one of crucial characteristics of wave properties of nanoparticles that prevail over corpuscular ones.

Optical properties

Optical phenomena in nanoparticles of gold and other noble metals are based on quantum size effects and play a significant role only when the particle size is substantially smaller than 10 nm. However, changes in optical properties occur even if the size of metal nanoparticles is smaller than the wavelength of visible light, i. e. smaller than 500 nm [10].

Resonant tunneling diode uses tunneling effect, discovered by G. A. Gamow, – an ability of electrons to pass through the potential barrier, if their width is comparable to the wavelength of L. de Broglie. Resonant tunneling diode consists of two barriers separated by an area of low potential energy – quantum well. One or more allowed discrete energy levels of electron exist here. A typical width of barriers and wells between them is a few nanometers. Areas on the left and right side of barriers act as reservoirs of conduction electrons. The mechanism of resonant tunneling is driven by properties of electron that penetrates into the region between barriers, is delayed there for a long time, and as a result of multiple reflections from the left and right barriers significantly increases the probability of tunneling [35].

Magnetic properties Magnetic properties of nanostructured materials are intensively studied by world's scientists [17]. Particular attention is paid to investigation of magnetic properties of ferromagnetic materials, such as iron, nickel and cobalt. Electron has an important quantum-mechanical characteristic – an intrinsic moment of momentum, or spin, which has not been given sufficient attention of developers and researchers until recently. This research direction is called «spintronics». The aim of spintronics (spin electronics, or magnetoelectronics) is development of devices, based on the employment of electron spins' properties. This is a novel field of science and technology in which both charge and electron spin are used in creation of new functional devices [22].

Discovery of a giant magnetoresistance contributed to development of new scientific [34] and technological direction – spintronics, in which much attention is paid to the electron spin – a quantum-wave characteristic, reflecting the intrinsic momentum of a particle [22].

Another important phenomenon that occurs in case of a further decrease in the magnetic particles' size and which is a characteristic of nanoscale magnetic particles is superparamagnetism [30].

Superparamagnetism is one of the outstanding properties of nanoparticles, which led to their experimental discovery in the mid-twentieth century. Phenomenon of superparamagnetism can be understood by considering the behaviour of isolated single-domain magnetic particles. Superparamagnetism is a type of magnetism, which is a characteristic of ferromagnetic or ferrimagnetic materials' nanoparticles, and in which the magnetic moment of single-domain particles spontaneously and accidentally changes its orientation due to thermal fluctuations. A key premise, in which nanoparticles are superparamagnetic, is a temperature value that exceeds the so-called blocking temperature – the temperature that corresponds to the maximum magnetization [24].

Thus, according to the mentioned above, the effectiveness of nanoparticles in most applications is the highest in condition that nanoparticles' size is less than a critical value, which in turn depends on their chemical composition, and is usually about 10–20 nm. As a result, each nanoparticle becomes a single magnetic domain and receives superparamagnetic properties. We can assume that the phenomenon of superparamagnetism is caused by the predominance of the wave properties over the corpuscular ones in nanomaterials.

Surface tension Experimental data has shown that at high nanoparticles' concentrations the surface tension increases with the elevation in particles' concentration in all cases. However, at low particles' concentrations the trends are different for different base fluids, and in case of addition of surfactants or without their addition. Nanoparticles tend to accumulate at the gas-liquid interface. This indicates that the concentration of nanoparticles in/near the surface of gas-liquid will be higher than in the middle of drops [37, 38].

For deionized water containing Al_2O_3 the surface tension remains constant at a low concentration of particles. This is because in such dilute suspensions the distance between the particles is much larger than the particle size, and therefore the interaction forces between particles in/near the surface of gas-liquid interface have little effect on the surface energy. However, in case of elevation in particles' concentration, particles become closer to each other, and strength of van der Waals interaction increases. This leads to enhancement of free energy on the surface and elevation of the surface tension [36].

Nanothermodynamics Nanothermodynamics as a separate field of physics was founded in 2001, when T.L. Hall formed the first law of thermodynamics for small systems [26], which also include nanosystems. The scientist used the first law of thermodynamics for macrosystems:

$$dU = TdS - pdV + \Sigma_i \mu_i dN_i,$$

where U – internal energy of the system, T – absolute temperature, S – entropy, p – pressure, V – change of volume, in which the chemical potential of systems component μ_i, and the amount of matter N_i were added.

Since in case of small systems the number of individual components has a great importance, T. L. Hall increased contribution of $\Sigma_i \mu_i dN_i$ summand in the result of the equation and introduced the concept of "subdivisional potential", which is the chemical potential of a single small system:

$$dU = TdS - pdV + \Sigma_i \mu_i dN_i + EdN,$$

where E is "subdivisional potential", the effect of which increases with elevation of N – the number of individual small systems (e. g., nanoparticles). The above mentioned equation is an attempt in formulation of the first law of thermodynamics for small systems, including nanomaterials.

In the search for the thermodynamic laws of nanosystems' existence it has been established the need to introduce so-called local thermodynamic functions: local pressure, temperature, chemical potential, etc. [21, 27]. This approach has been called as «quasi-thermodynamic assumption» [33].

Moreover, with decreasing of particle's size, the laws of its thermodynamic quantities, including surface energy, change too. When the particle's size is 1–10 nm, its thermodynamic properties require a precise investigation. But when the particle's size is less than 1 nm, it acquires the properties of the surface. It is important to understand the dimensions of inhomogeneity of such systems, as when transiting from the macroscale to the nanoscale the influence of some physical parameters decreases (e. g., gravity) and the influence of others, such as the capillary diameter, surface tension, Tolman length (a quantity, describing the decrease in surface tension of a drop of fluid at the transition from micro- to nanoscale), grows [2].

Thermal conductivity is one of the characteristics of nanomaterials' thermodynamics. This value is sensitive to changes in structure, including the factors of dimension. As materials' size significantly decreases their thermal conductivity also decreases due to scattering of electrons on the intergranular boundaries. For instance, thermal conductivity of nanocrystalline silver 20–47 nm is 3.5–4.0 times lower than in a case of conventional coarse-crystalline silver [3].

For nanomaterials with the size of structure of several nanometers Hall–Petch relationship fails to work. Additionally, there is an inverse Hall–Petch relationship: as soon as the size of the structure is reduced to 10 nm, the grain boundaries of polycrystalline nanomaterials are starting to slide [23]. It can be assumed that changes in thermodynamics of nanomaterials are due to the predominance of the wave properties over the corpuscular ones.

Conclusion. Despite the fact that a great number of phenomena that occur during the transition of matter into nanoscale have been established, many mysteries remain. Unique mechanical, physical, chemical, physico-chemical, electromagnetic, electrical, pharmacological, toxicological, and other properties of nanomaterials are already working for the benefit of mankind. A lot of medicines based on nanoparticles have been created, such as Sylix (silica nanoparticles as a powder), nanosilver (ointment), nanoiron (solution for injection or capsules), and liposomes. However, one cannot allege that their therapeutic properties can be fully explained by existing knowledge in physics, chemistry, biochemistry or pharmacology. The discovery of new quantum properties of nanoparticles will be particularly intriguing, because it is known that with decreasing of the object's size the role of nanomaterials' quantum wave effects increases. The predominance of the wave properties of nanomaterials over corpuscular ones causes a significant change in their physical and chemical characteristics and enhances their pharmacological activity.

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ХВИЛЬОВІ ВЛАСТИВОСТІ НАНОЧАСТИНОК: ПОГЛЯД НА ПРОБЛЕМУ

І. С. Чекман (Київ)

Отримані результати дослідженя нанофармакології дозволили висловити гіпотезу: з позицій квантової механіки підвищення фармакологічної активності нанопрепаратів зумовлено переважанням у них хвильових властивостей над корпускулярними. У нанорозмірних структурах домінує коливально-енергетична активність таких речовин. Згідно з отриманими результатами, зміна спінових станів у молекулах є однією з невід'ємних властивостей живої матерії, для якої характерна самоорганізація, для наноструктур – також саморегуляція. Тому квантово-хвильові властивості наночастинок з їх високою здатністю до зміни спінових станів визначають виражену фармакологічну дію нанопрепаратів. На даному етапі досліджень отримані наукові факти не дозволяють експериментально або математично обґрунтувати висунуту гіпотезу. Переконаний, що припущення, висловлене в цій статті, буде тим наномотором, який залучить учених світу до продовження наукових досліджень з метою експериментально довести висунуту гіпотезу – хвильові властивості наночастинок визначають їх високу активність.

Ключові слова: хвильові властивості, наночастинки, спінові стани, висока активність.

ВОЛНОВЫЕ СВОЙСТВА НАНОЧАСТИЦ: ВЗГЛЯД НА ПРОБЛЕМУ

И. С. Чекман (Киев)

Полученные результаты исследований по нанофармакологии позволили высказать гипотезу: с позиций квантовой механики повышенная фармакологическая активность нанопрепаратов обусловлена превалированием в них волновых свойств над корпускулярными. В наноструктурах колебательно-энергетическая активность таких веществ доминирует. Согласно полученным результатам, изменение спиновых состояний в молекулах является неотъемлемым свойством живой материи, для которой характерна самоорганизация, для наноструктур – также саморегуляция. Поэтому квантово-волновые свойства наночастиц с их высокой способностью к изменению спиновых состояний способствуют высокой фармакологической эффективности нанопрепаратов. На этом этапе исследований полученные научные факты не позволяют экспериментально или математически обосновать данную гипотезу. Убеждён, что предположение, высказанное в данной статье, будет тем наномотором, который привлечёт внимание учёных мира к продолжению научных исследований с целью экспериментального доказательства выдвинутой гипотезы – высокую активность наночастиц определяют их волновые свойства.

Ключевые слова: волновые свойства, наночастицы, спиновое состояние, высокая активность.