NANOMATERIALS: Causes of Changes in Properties and Introduction to Quantum Mechanics

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What is nanotechnology?

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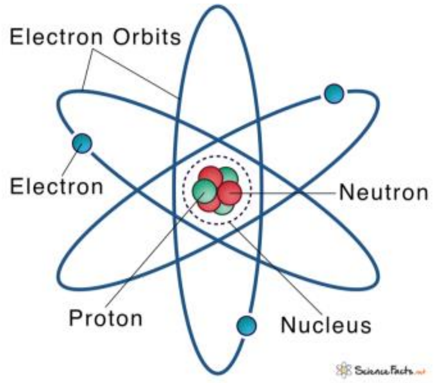
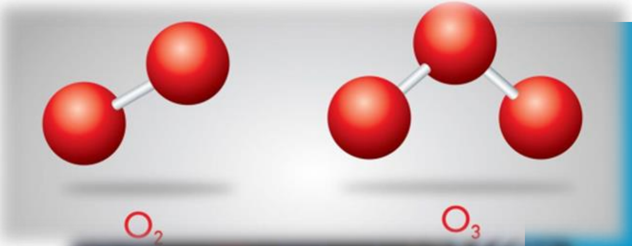


Nanotechnology is the science of manipulating *atoms* and *molecules* to make *advanced nanomaterials*

Atom is the basic building block of all matter.

Atoms can combine with other atoms to form *molecules* but cannot be broken down into smaller pieces by ordinary chemical processes.



Molecule is a group of two or more atoms forming the smallest identifiable unit that retains the composition and chemical properties of that substance.

Advanced nanomaterials are new materials with enhanced properties designed to provide superior performance.

Nanotechnology is the understanding and manipulation of matter in sizes ranging from approximately 1 to 100 nanometers, where unique phenomena enable new applications

Nanotechnology is an emerging, interdisciplinary field involving:

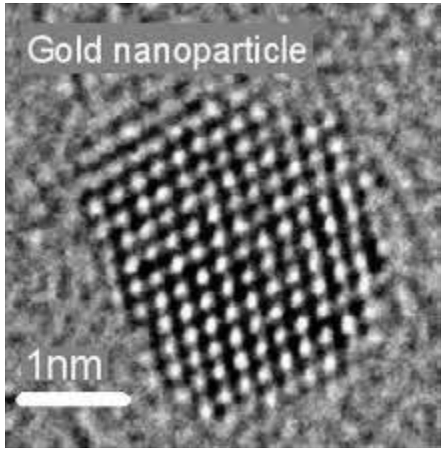
physics, chemistry, biology, engineering, materials science, computer science

One of the major scientific advances of the 21st century laid the foundation for advanced nanomaterials.

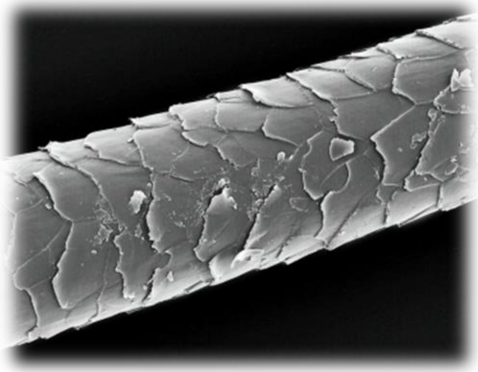
Nano

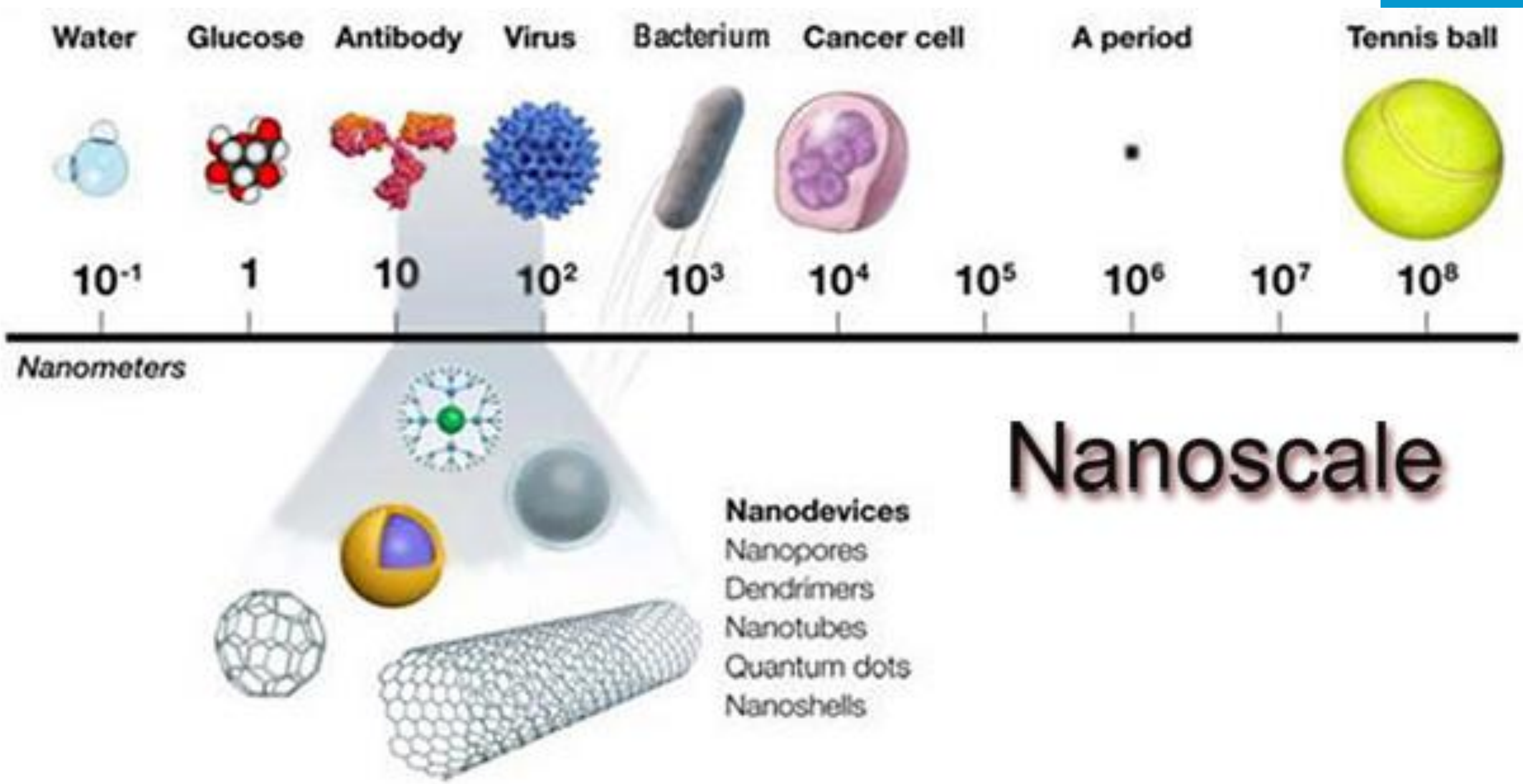
Nano is a millionth of a millimeter or a billionth of a meter, i.e. 1 nm = 10^{-9} m.

Atom is about 0.1 nanometer - 10 atoms side by side make up 1 nm.



Human hair:
50,000–100,000 nm in diameter.





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Nanomaterials

Nanomaterials - in the range of 1-100 nanometers in at least one dimension.

Classification: based on the number of free dimensions

0D *nanomaterial*: all three dimensions are in the nanoscale.

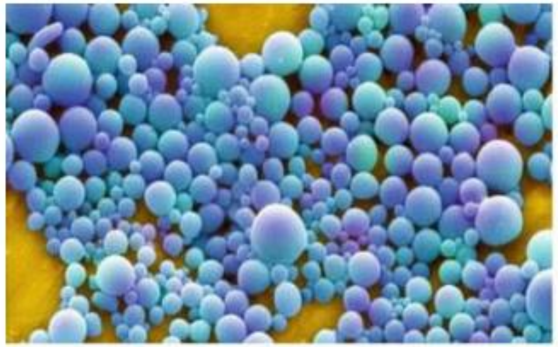
(Nanoparticles, Colloids, Quantum dots)

1D *nanomaterial*: one dimension beyond the nanoscale and two other dimensions in the nanoscale. (Nanowires, Nanorods, Nanotubes & Biopolymers).

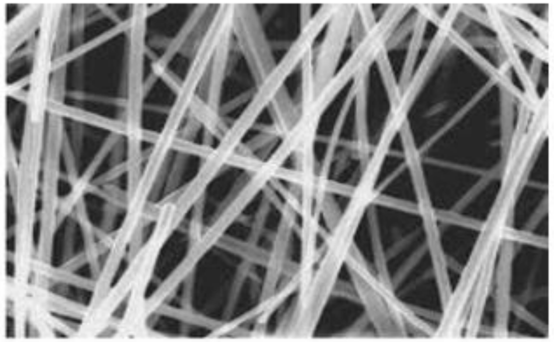
2D *nanomaterial*: any two dimensions can be outside of the nanoscale and one dimension in the nanoscale. (Plate-like shapes - nanolayers, surface coatings and thin films).

3D *nanomaterial*: all three dimensions can be outside of the nanoscale. Made of a nanomaterials.

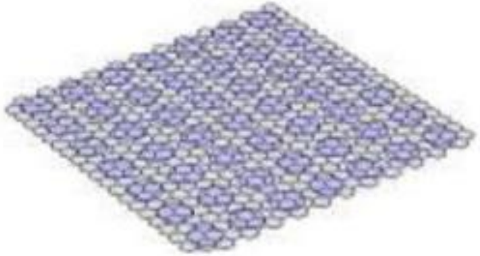
(nanoparticle dispersions, nanowire/ nanotube bundles & multiple nanolayers).



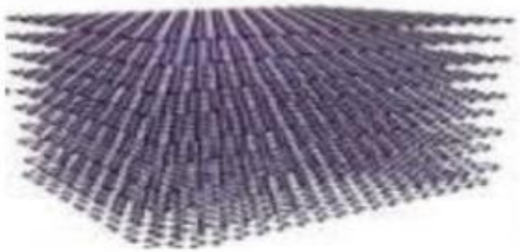
0D(Nanoparticle)



1D(Nanowire)

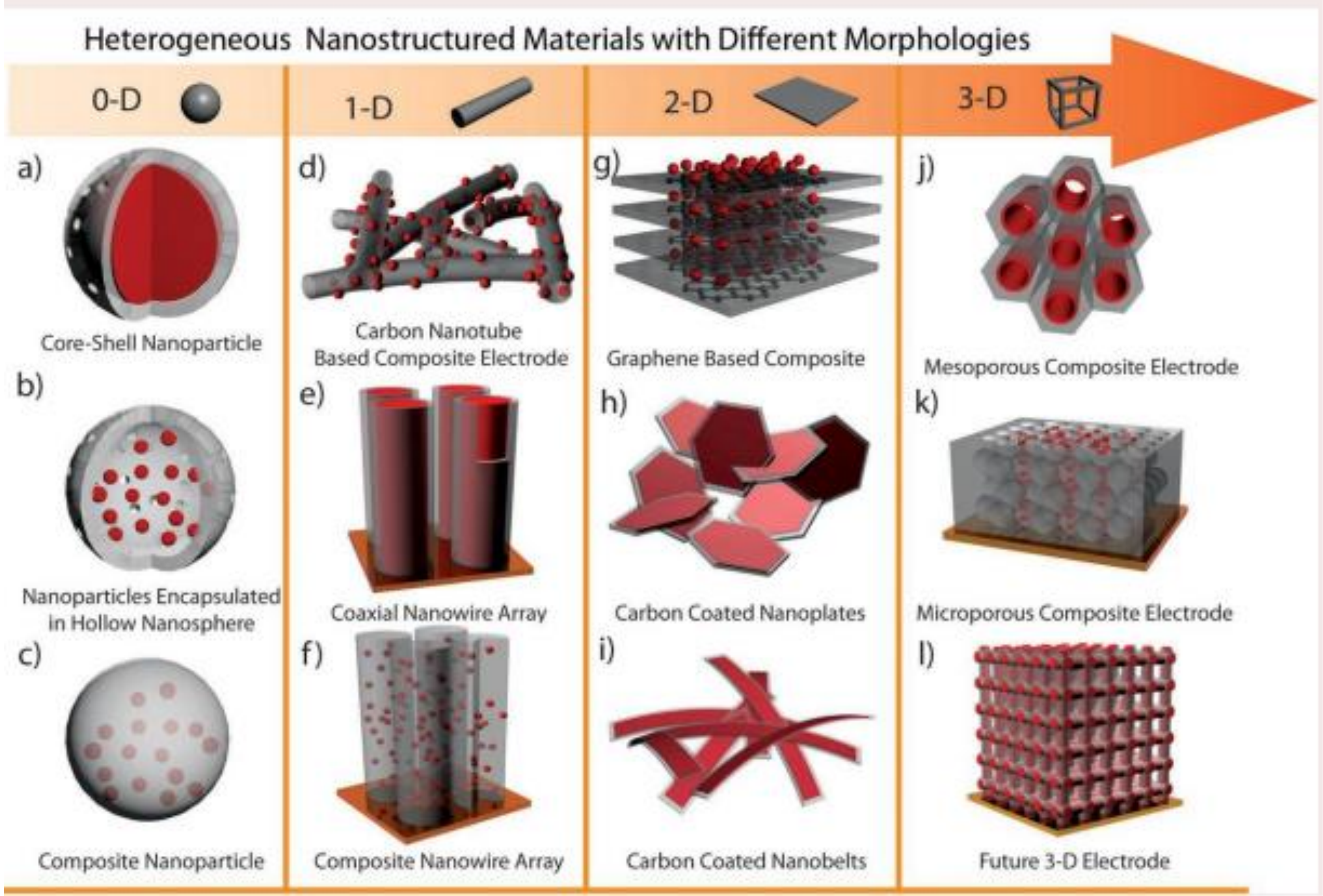


2D Nanomaterials (plate)



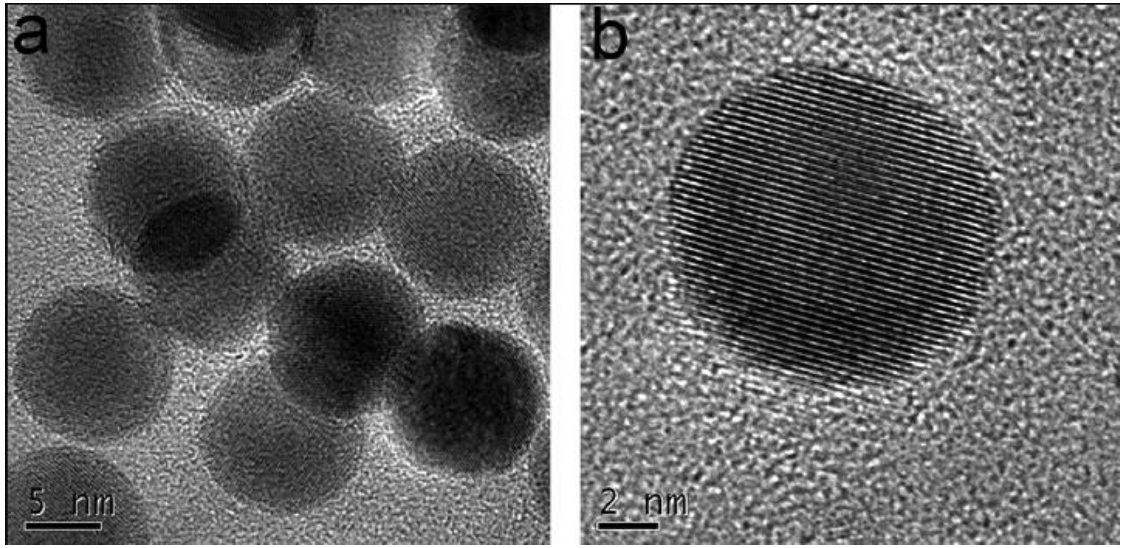
3D Nanomaterials

Nanomaterials: compex forms

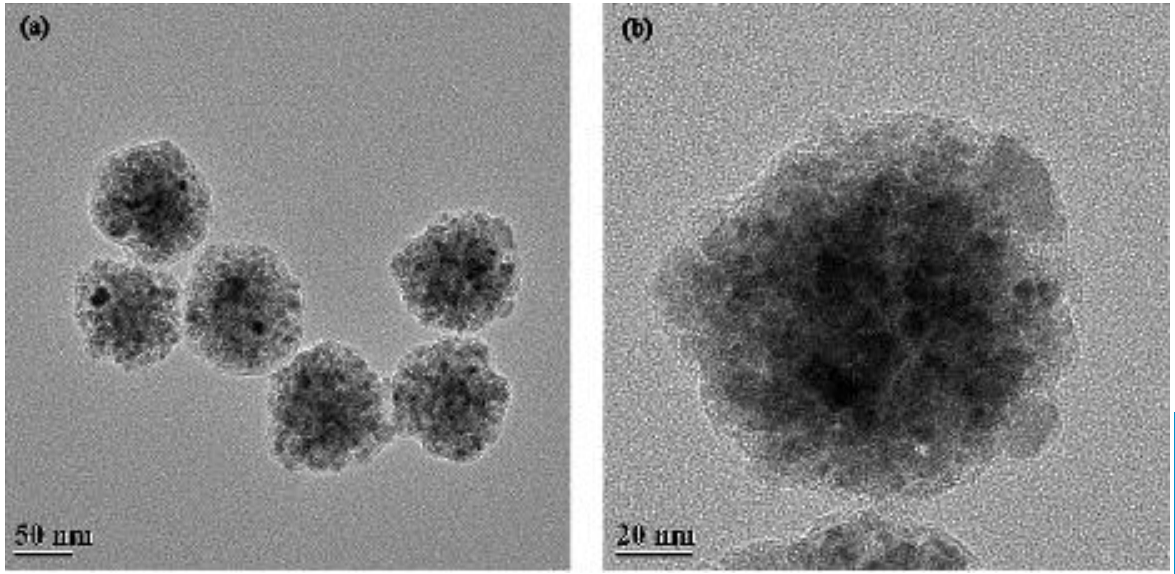


There is a wide spectrum of different morphologies of NM.
The morphology can be explained as a combination of geometric characteristics.

Nanomaterials: Gallery

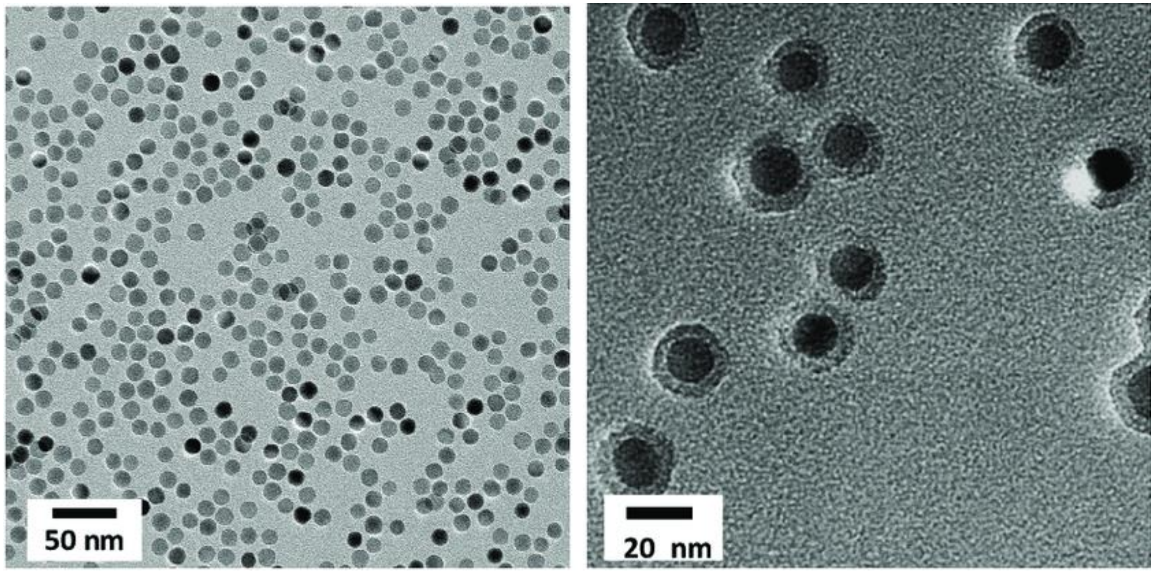


single



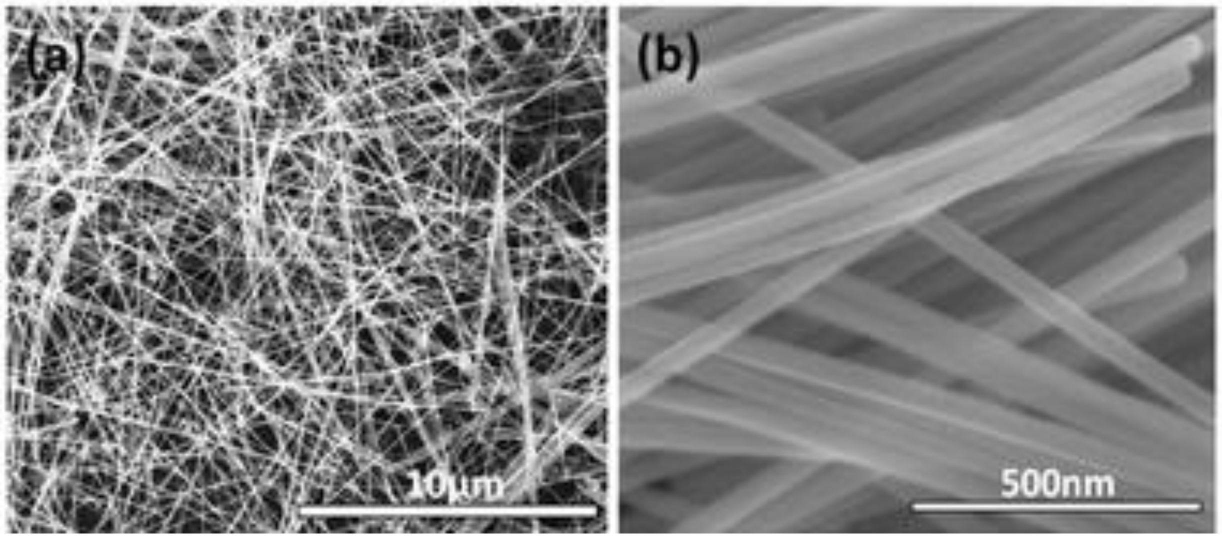
composite

0D nanoparticles
single/composite/coated

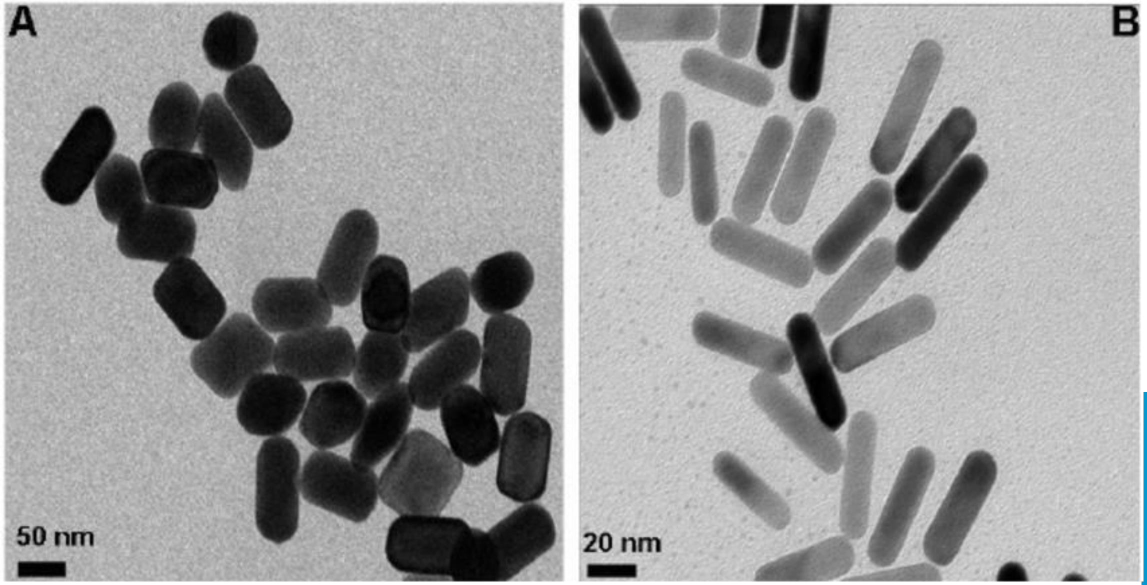


coated

Nanomaterials: Gallery

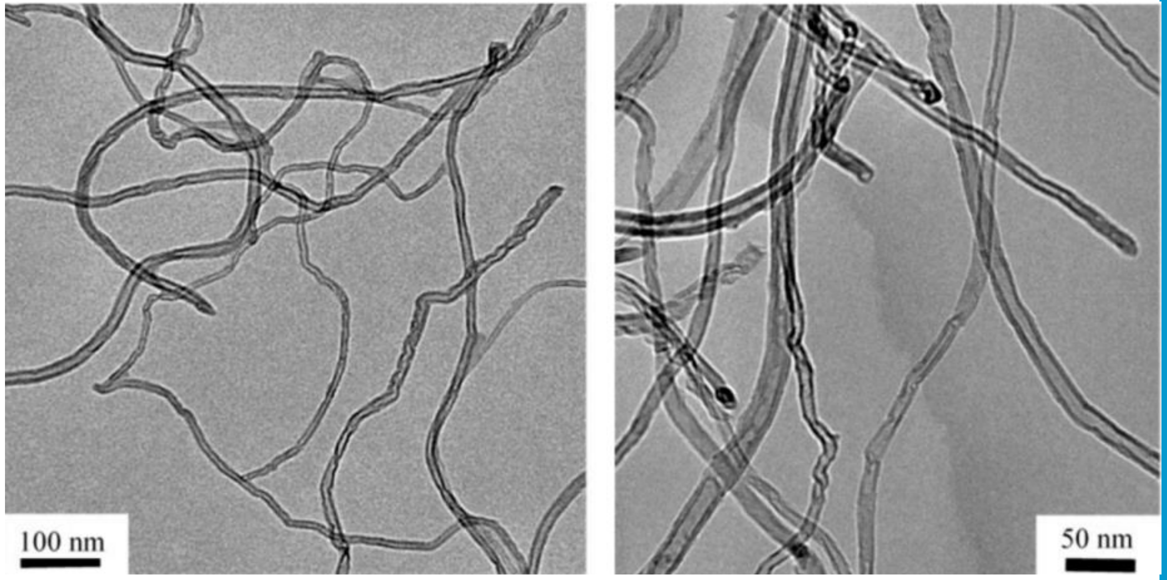


Nanowires



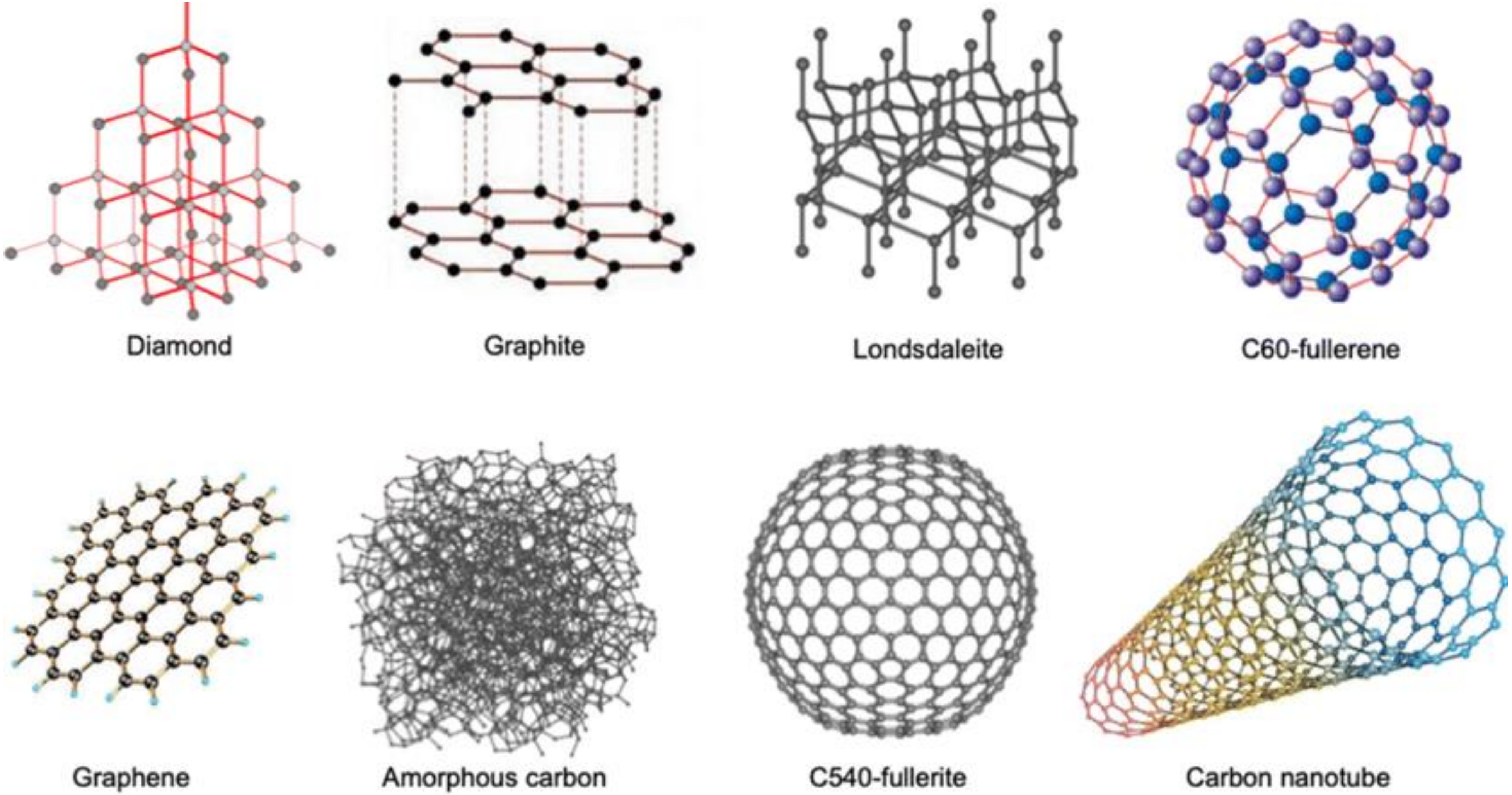
Nanorods

1D nanoparticles
nanowires/ nanorods/ nanotubes



Nanotubes

Nanomaterials: Gallery



Carbon: allotropes of carbon: 0D to 3D

Nanomaterials: History

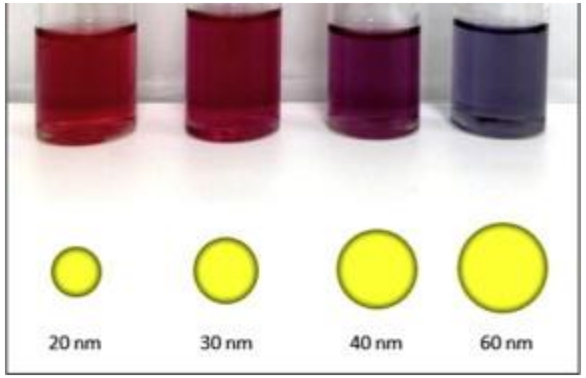
Roman glaziers (4th century) made a "Lycurgus cup" of soda-lime glass dyed with Au and Ag nanoparticles that appears green (in reflected light) and red (in transmitted light).

In the Middle Ages: multi-colored window panes of churches were stained with nanoparticles of various metals.

In the 16th and 17th centuries, an extremely strong yet flexible Damascus sword was made using carbon nanotubes and iron carbide (Fe_3C) nanowires. They were unusually strong, yet flexible enough to bend from hill to tip.

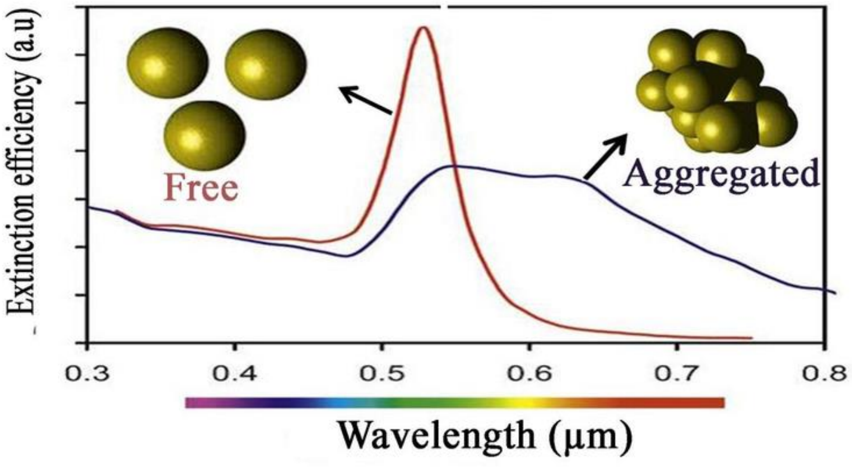
Nanomaterials: History - Optical Properties

Michael Faraday (1857) attributed the color of stained-glass windows to the presence of metallic nanoparticles. He prepared red gold nanoparticles (stored at the Royal Institution in London).



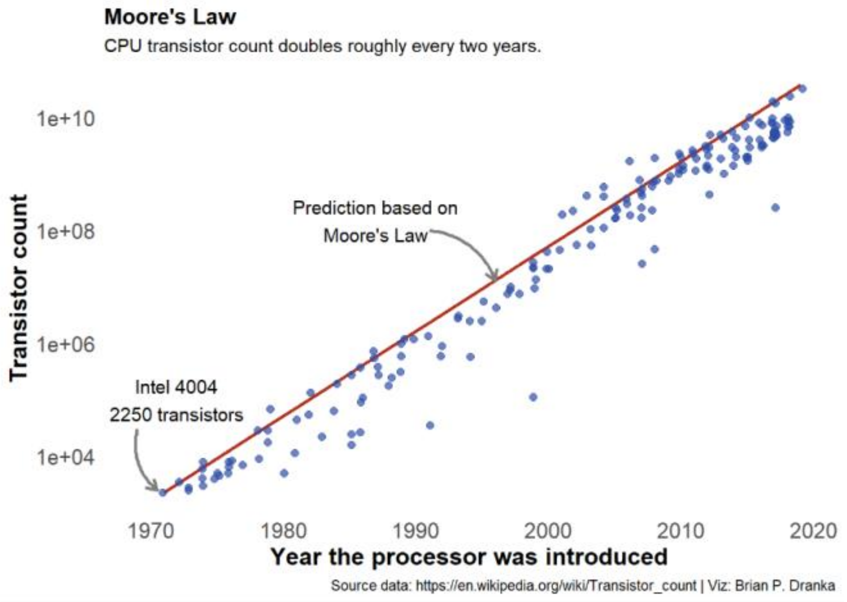
G. Mie (1908) explained the change in the color of glasses by the size of metal particles scattered in glasses.

R.A. Zsigmondy (first decade of the 20th century) studied the optical properties of gold and other nanoparticles and received the Nobel Prize in Chemistry in 1926.

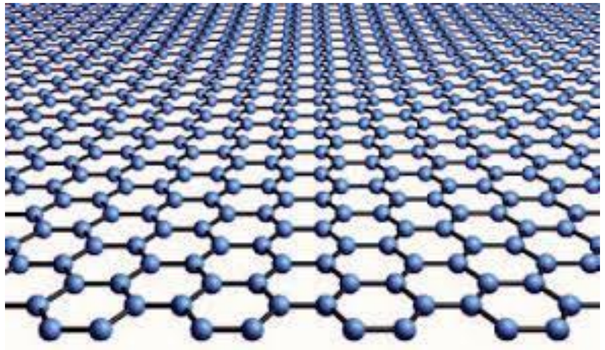


Nanomaterials: Persons

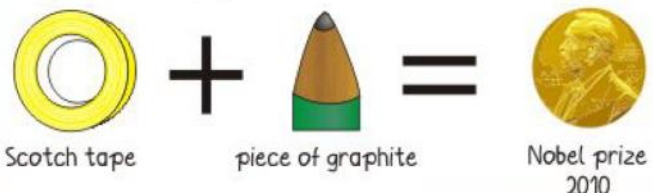
In 1959, the American physicist Richard Feynman, in his famous speech "There's plenty of room at the bottom," gave an idea of nanotechnologies, foresaw the possibilities and potentialities of nanotechnologies (denser computer circuitry, "swallowing the doctor")



Gordon E. Moore (1965), co-founder of Intel Corporation, made an amazing prediction: the number of transistors on a chip of a given area will double every 1.5 years, that is, the size of a transistor decreases by 2 times every 1.5 years. The size of the transistor is reduced by 2 times every 1.5 years. His prediction indicated that today's transistors would be 1-2 nm in size (this is true, but we have some problems)



The Nobel Prize in Physics 2010 has been awarded to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene".



Bulk vs Nano

Material properties describe how a material behaves under certain conditions.

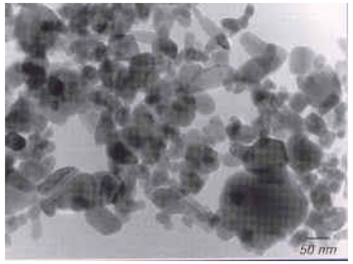
Optical Properties: Example:
Zinc Oxide (ZnO)

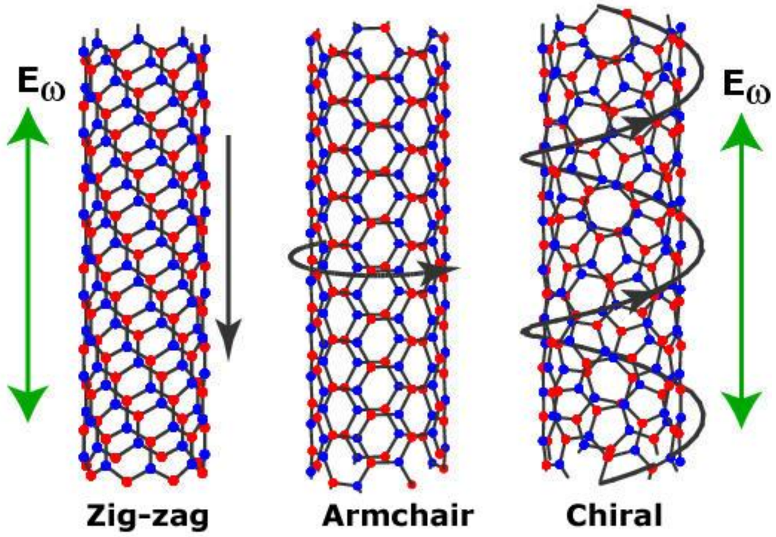
Large ZnO particles : block UV light, scatter visible light, appear white,

Nanosized ZnO particles: block UV radiation, are so small compared to the wavelength of visible light that they do not scatter it, appear transparent

Application for sunscreen

vs



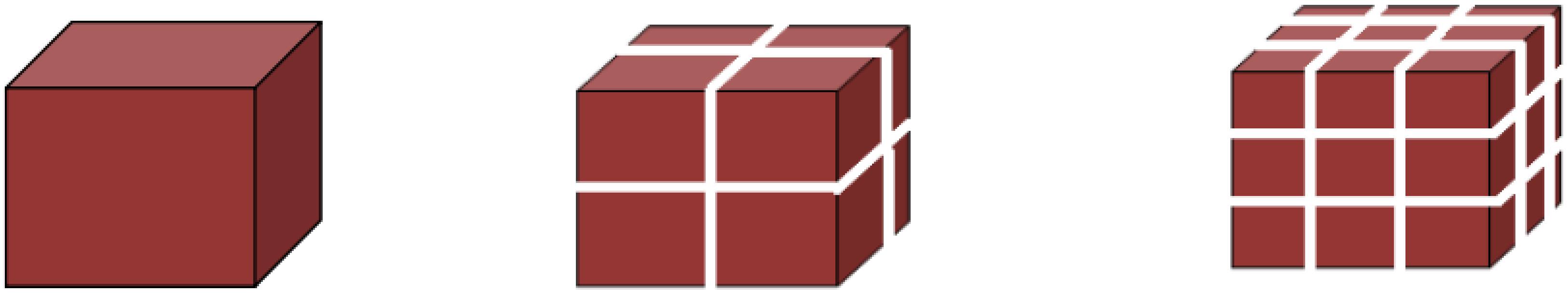


Mechanical and Electrical Properties Example:
Carbon Nanotubes

Nanotubes are long, thin cylinders of carbon. They are 100 times stronger than steel, very flexible, and have unique electrical properties. Their electrical properties change with diameter, “twist”, and number of walls. According to their electrical behavior, they can be conducting or semi-conducting.

Reasons for Special Properties of Nanoscale Materials

1 Increasing the surface area to volume ratio

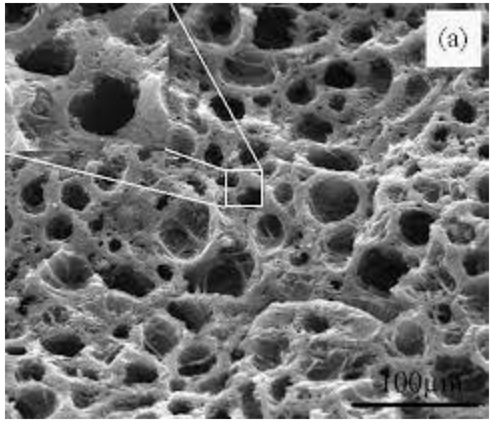


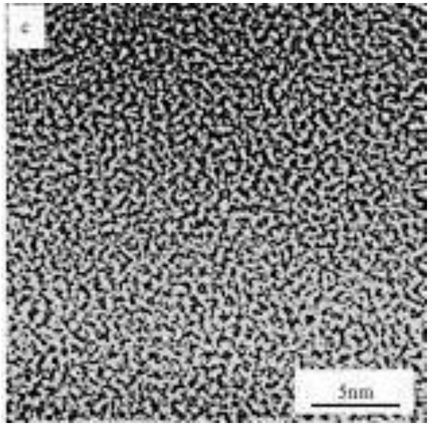
Area = 6 x 1cm^2 = 6 cm^2

Area= 6 x (1/2cm)^2 x 8 =12 cm^2

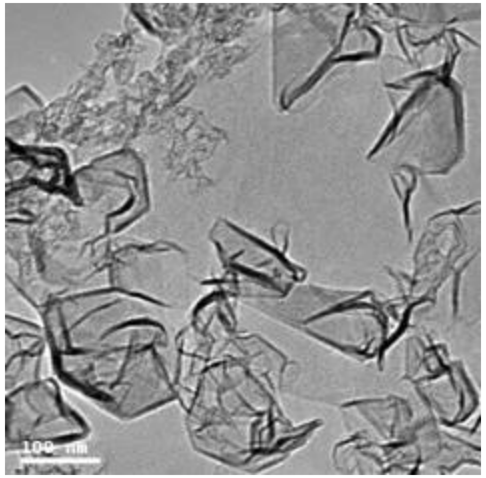
Area= 6 x (1/3cm)^2 x 27 =18 cm^2

Activated carbon – specific surface area up to 3550 m^2/g





Graphene – specific surface area up to 2630 m^2/g



Reasons for Special Properties of Nanoscale Materials

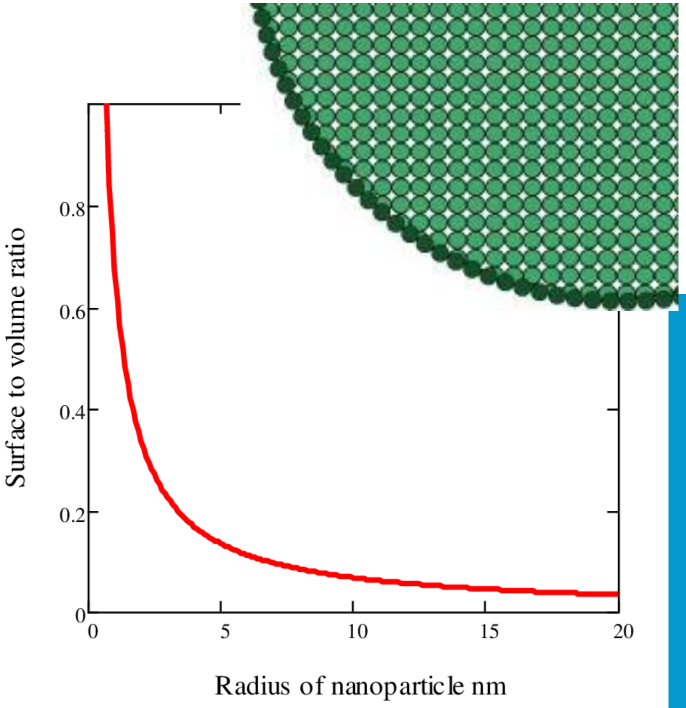
2. Surface tension effect

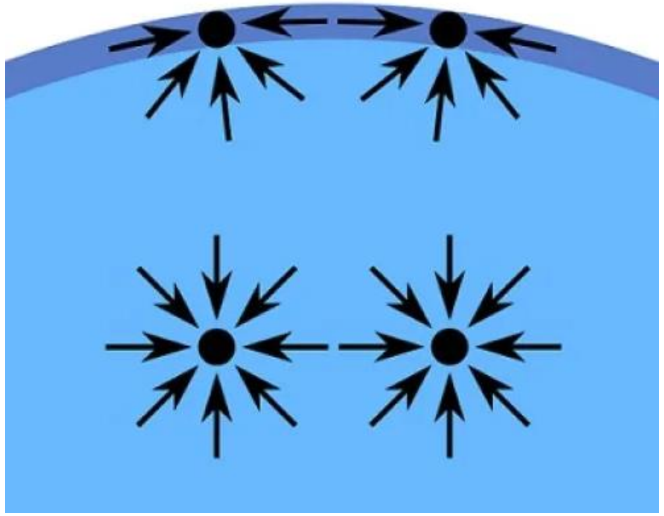
The larger the sample, the smaller the fraction of atoms on the surface.

Atoms on the surface have fewer neighbors than atoms inside

(Students at the edge of the classroom have fewer neighbors than students at the center)

Only atoms on the surface can interact with another material and take part in a chemical reaction (increase in reactivity).





The surface layer has excess energy (surface free energy) compared to the bulk. Reducing the particle causes an increase in its surface energy, which leads to a change in properties.

Reasons for Special Properties of Nanoscale Materials

3. Size effect (particle sizes approached the characteristic length for this material)

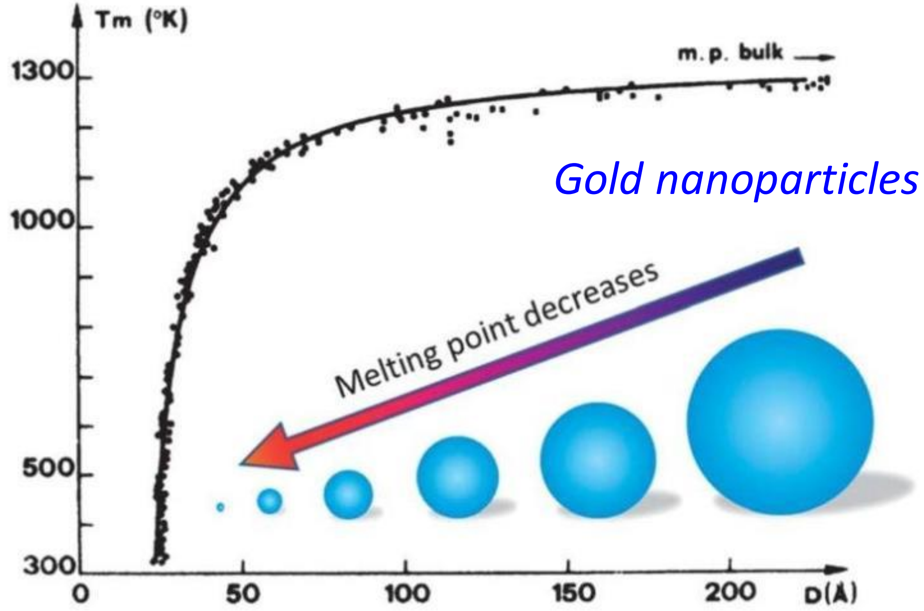
At the nanometer scale, properties become dependent on size.

(1) Chemical properties – reactivity, catalysis
(2) Thermal properties – melting temperature
(3) Mechanical properties – adhesion, capillary forces
(4) Optical properties – absorption and scattering of light
(5) Electrical properties – tunneling current
(6) Magnetic properties – superparamagnetic effect

Melting point example

MP is the temperature at which the atoms in a substance have sufficient energy to overcome the interatomic forces that hold them in a "fixed" position in a solid.

On a scale of macroscopic length, the melting point material does not depend on size - both the ice cube and the glacier melt at the same temperature.



- Surface atoms require less energy to move because they are in contact with fewer atoms of matter.

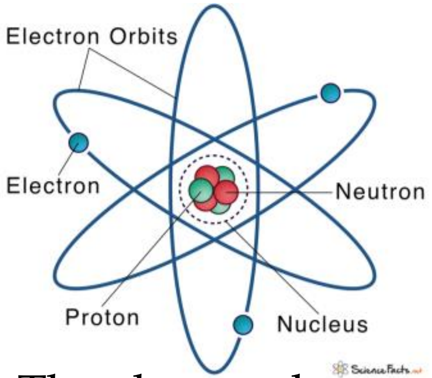
Nanocrystal decreases → surface energy increases → → melting point decreases

Heat transfer in materials is carried out by two different mechanisms: lattice vibration waves (phonons) and free electrons. Size effects will be observed when the particle size becomes close to the phonon or electron free path.

Quantum Physics

To explain the effect of *quantum size*, we have to take a small leap and imagine what quantum physics is dealing with.

Quantum Physics is a set of laws that explain observations of the tiny building blocks of all matter.
The quantum world should be able to explain the classical world we live in.
To understand the quantum world, we need to understand and believe in the equivalence of a single atom and an electromagnetic wave.



Rutherford's classical model of atom

Observations show that the atom is basically empty space with a dense central positively charged structure in the center.
The electrons exist outside this nucleus and revolve around it like planets around the sun.

The problem with the classical model

The electron has a negative charge and revolves around a central positive nucleus.
The nucleus has a charge and therefore has a magnetic field.
Charged particles lose energy when passing through a magnetic field.
According to the classical electromagnetic theory, an electron must lose energy in its orbit and fall into the nucleus.

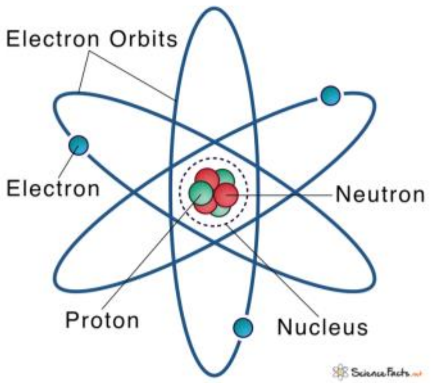
Observations

An atom is a stable structure made up of subatomic particles that do not normally decay during our lifetime.

Conclusion

Because the observation does not match the theory…. either classical physics is wrong, or Rutherford's model is wrong/incomplete.

Quantum Physics



What is easier to believe?

Hundreds of years of laws and theories of physics are wrong.

OR

Rutherford's classical model of the atom of our atom is wrong.

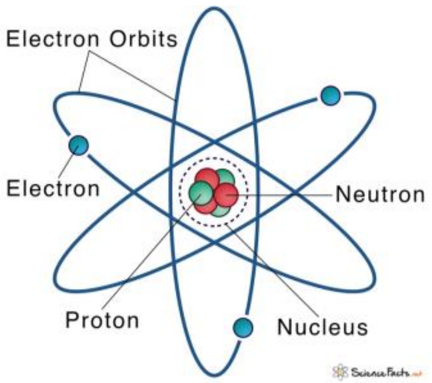
Answer :

Both classical physics and Rutherford's model have some flaws.

But this is our idea of the atom for the most part wrong ....

The ingenious ideas of Max Planck (1918 Nobel Prize for the discovery of the quantum nature of energy)

Quantum Physics



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The ingenious ideas of Max Planck (1918 Nobel Prize for the discovery of the quantum nature of energy)

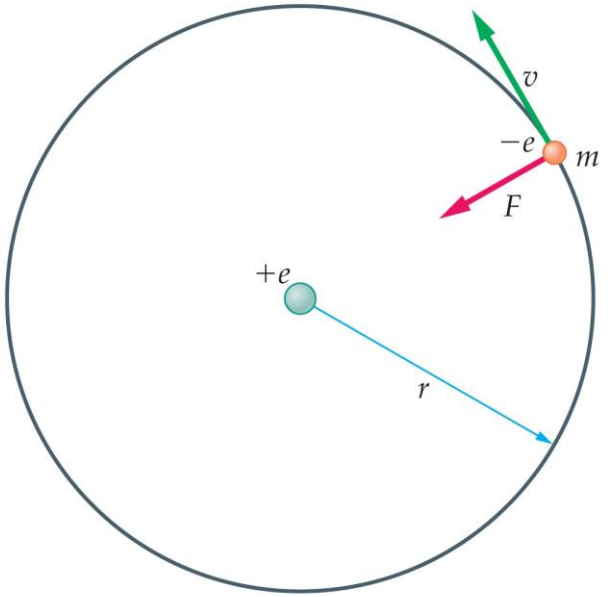
Energy is not a continuous stream but consists of chunks or discrete packets.
Energy is quantized (quanta flow)

Electrons can only have a certain discrete amount of energy
Each energy quantum can be defined as $E = hf$

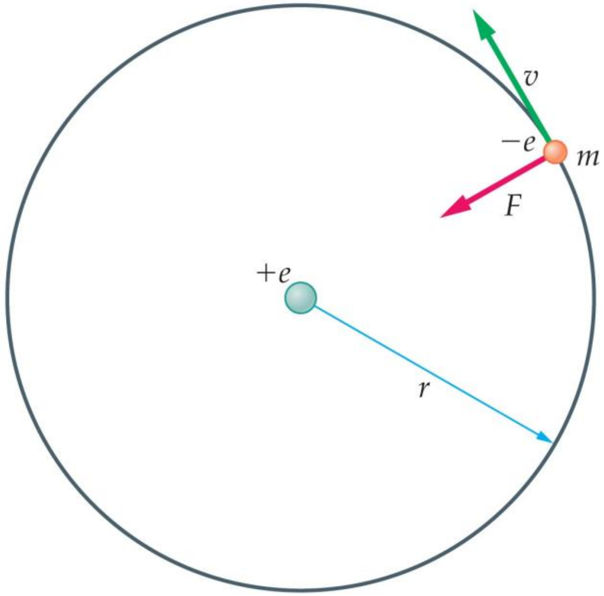
E is the energy of the quanta (J or eV)
f is the frequency of vibration
h is Planck's constant (6.626×10^{-34} Js)

Quantum Physics: Atom

Bohr model of the atom



Quantum Physics: Atom



Bohr model of the atom

1. An electron in an atom moves in a circular orbit around the nucleus,

m, υ and e are the mass of the electron, the speed in the orbit and the charge,

r is the radius of the orbit

As a result, the electron experiences a centripetal acceleration towards the nucleus of magnitude $a = \upsilon^2/r$.

We know from Newton's second law that a force $F = ma$ is required to create an acceleration.

In this case, the force is an electrostatic force $F = ke^2/r^2$ (*k is constant*).

Combining these results, we have the following relation: $ke^2/r^2 = mv^2/r$

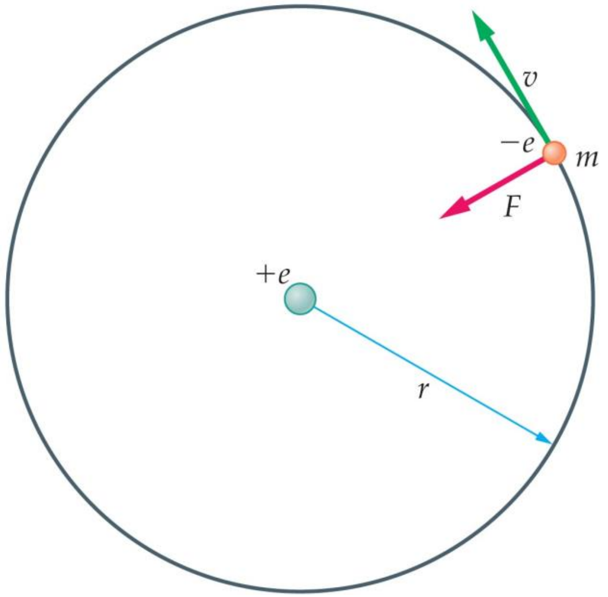
Bohr then suggested that the angular momentum in the allowed orbit should be an integer n (the quantum number) times $h/2\pi$, where h is Planck's constant. Since the electron moves with a speed v in a circular path of radius r, its angular momentum is $L = m\upsilon r$.

Thus, this condition is $m\upsilon r = n(h/2\pi) = n\hbar$

Combining the force and angular momentum equations allows us to find the radii of the allowed orbits. The result is $r_n = (h^2/(4\pi^2mke^2))n^2 \quad n = 1, 2, 3, \ldots$

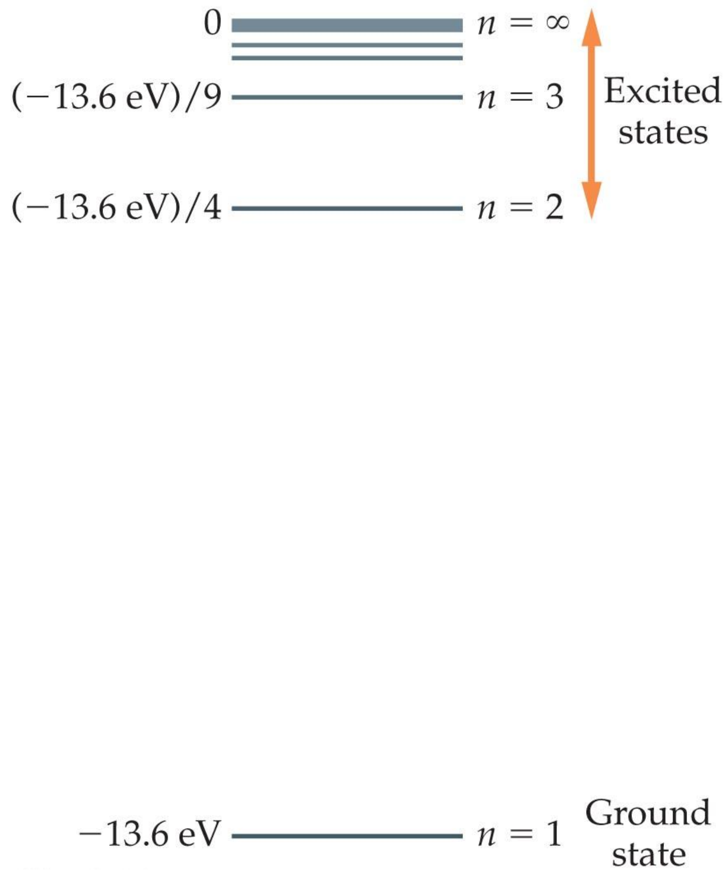
Conclusion : Only certain circular orbits are allowed (!!) but this is just a starting point

Quantum Physics: Energy of Atom



The total energy of the hydrogen atom is also quantized. In fact, a direct calculation combining the kinetic energy ($m\upsilon^2/2$) and potential energy ($-ke^2/r$) shows that the total energy of the nth Bohr orbit is

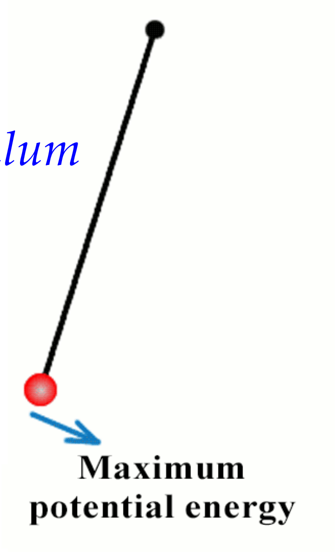
$$E_n = -(2\pi^2 mk^2e^4/h^2)/n^2 = -constant/n^2$$



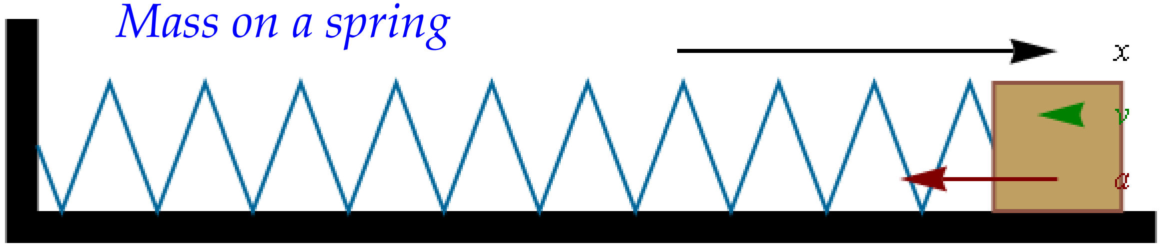
These energies are shown in the figure for various values of n

Oscillator

Pendulum

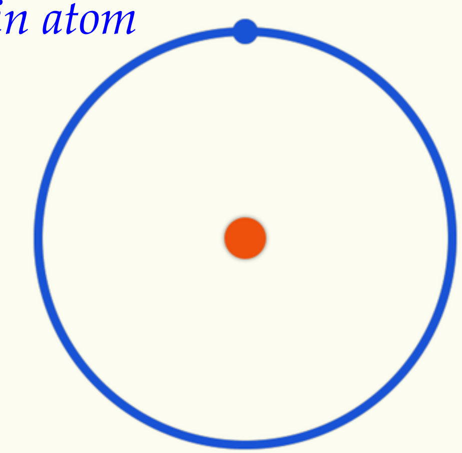


Mass on a spring



Oscillation is a periodic movement in which the state of the system is repeated at regular intervals.

Electron in atom



Examples of harmonic oscillators
Yes, the orbiting electron is an oscillation

Description of Periodic Motion

The duration of one cycle is the period T

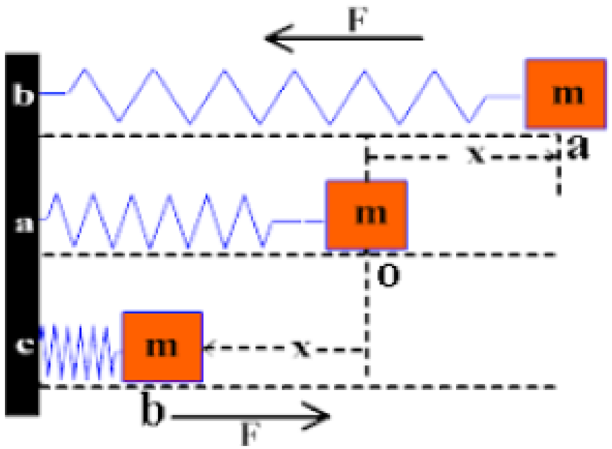
The reciprocal of the period is the frequency $f = 1/T$

Frequency is how many cycles per unit of time (1 second) the system goes through

The maximum displacement is determined by the amplitude A

Angular frequency $\omega = 2\pi f = 2\pi/T$ is how many cycles the system goes through in 2π

Oscillator: Classical Approach



Classical Harmonic Oscillator

If the spring is unbalanced and released, it will make a harmonic motion.

Pull the spring to the right and it will try to regain its length: For $\boldsymbol{x} > \boldsymbol{0}$*,* $\boldsymbol{F} < \boldsymbol{0}$ *(Left force)*
In equilibrium: $\boldsymbol{x} = \boldsymbol{0}$*,* $\boldsymbol{F} = \boldsymbol{0}$ *(No force)*
Move the spring to the left and it will try to regain its length: For $\boldsymbol{x} < \boldsymbol{0}$*,* $\boldsymbol{F} > \boldsymbol{0}$ *(Right force)*
This is summarized by Hooke's Law: $\boldsymbol{F} = -\boldsymbol{kx}$*, k is spring constant [N/m]*

$$F = -kx$$

$$F = ma = m\frac{d^2x}{dt^2}$$

$$m\frac{d^2x}{dt^2} = -kx$$

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x \equiv -\omega^2 x$$

$$\omega = \sqrt{\frac{k}{m}}$$

Natural angular frequency of a harmonic oscillator

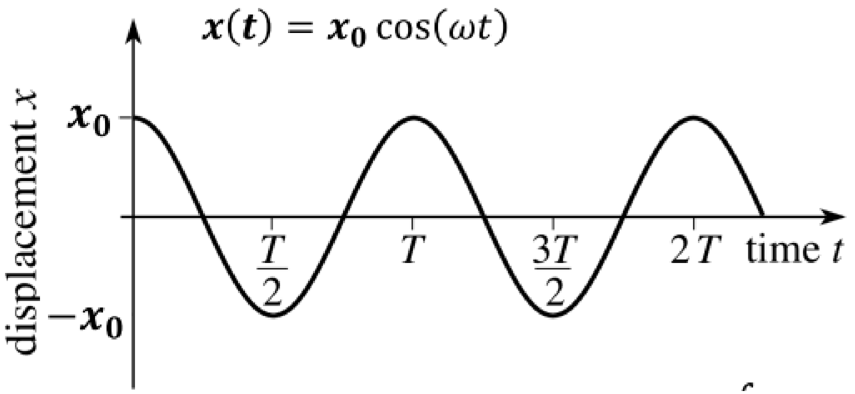
The solutions to this 2nd order differential equation are the sines and cosines

$$x(t) = A\sin(\omega t) + B\cos(\omega t)$$

Initial conditions

$$x(0) = x_0 \text{ and } \dot{x}(0) = 0$$

$$B = x_0 \text{ and } A = 0$$



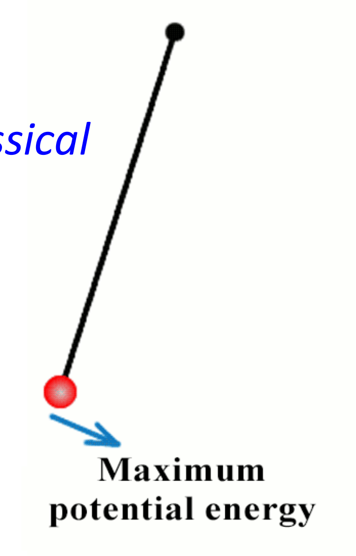
Mass on a spring

Potential energy (interaction) $V(x) = \frac{1}{2}kx^2$

Kinetic energy (motion) $T(x) = \frac{1}{2}m\dot{x}^2$

Harmonic oscillator - Classical to Quantum Transition

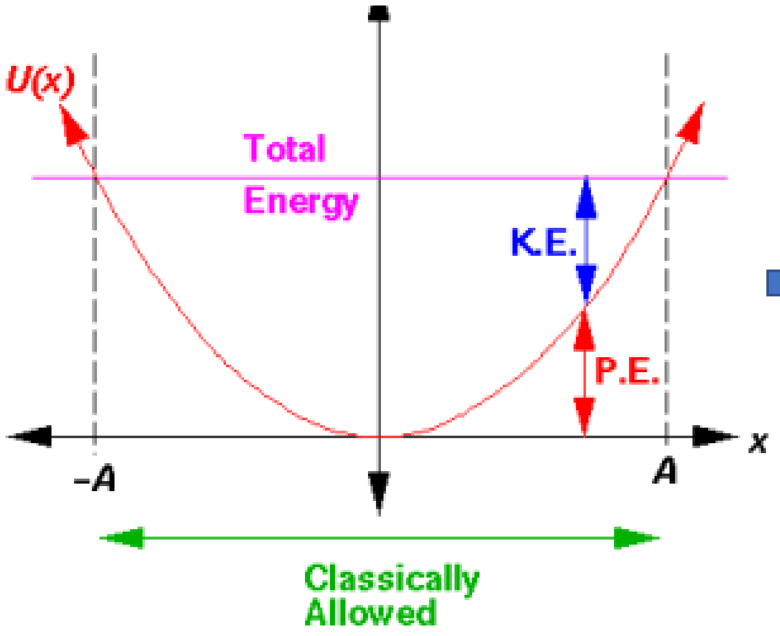
Classical



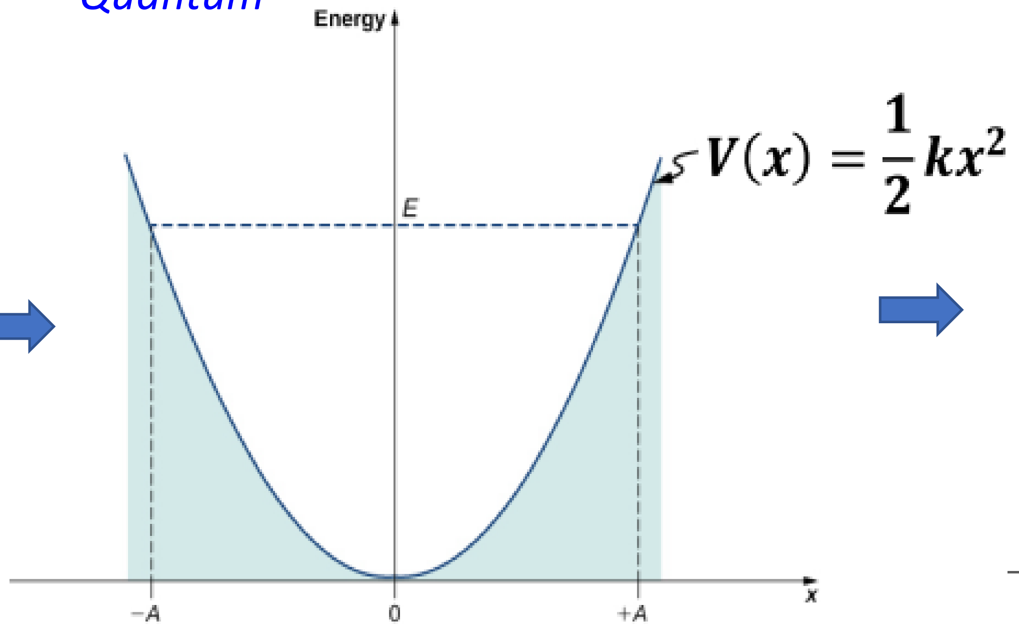
The energy of the pendulum (*harmonic oscillators*) at any time is equal to the *sum of the potential and kinetic components*

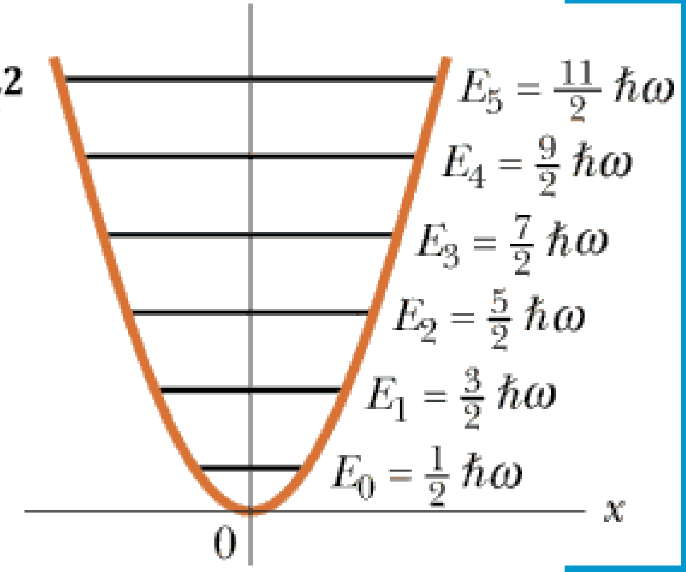
$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \text{ where } n = \mathbf{0}, 1, 2, 3, \ldots$$

*Note that **n** starts at 0*

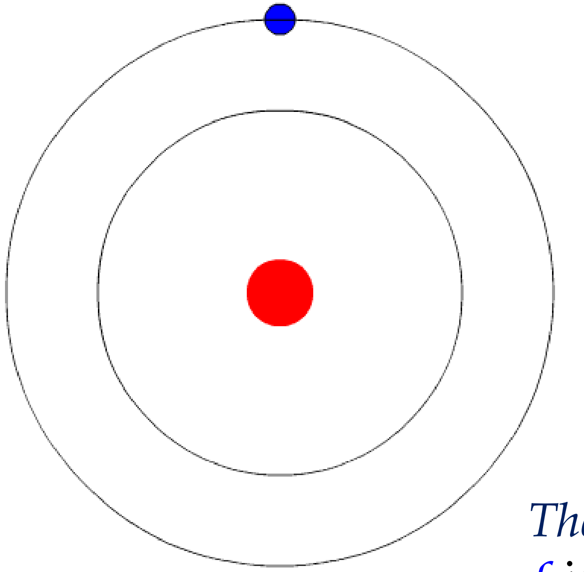


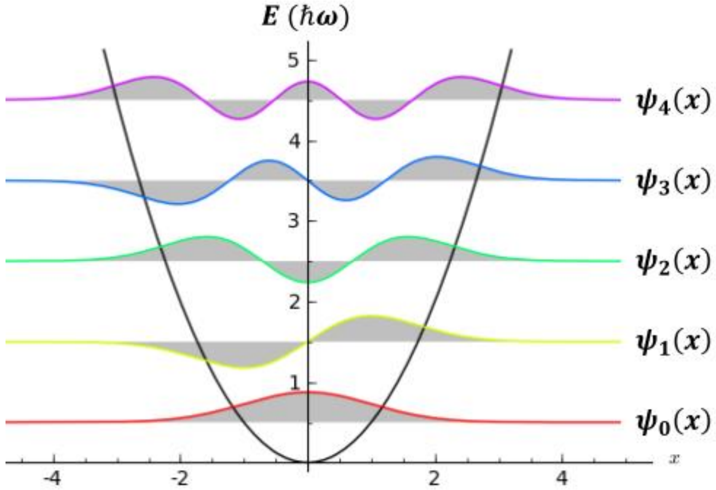
Quantum

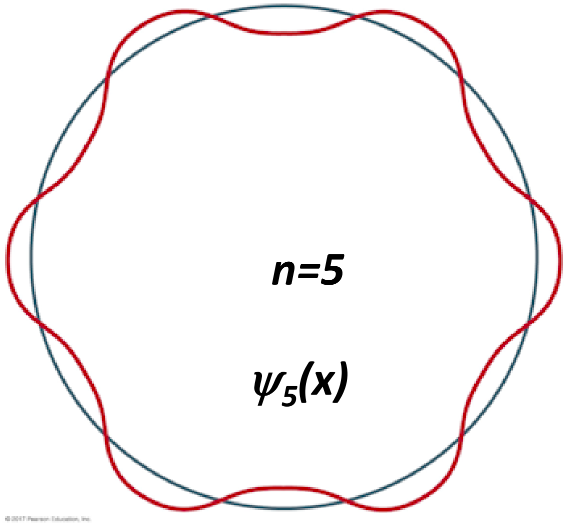




Energy of Electron in Atom





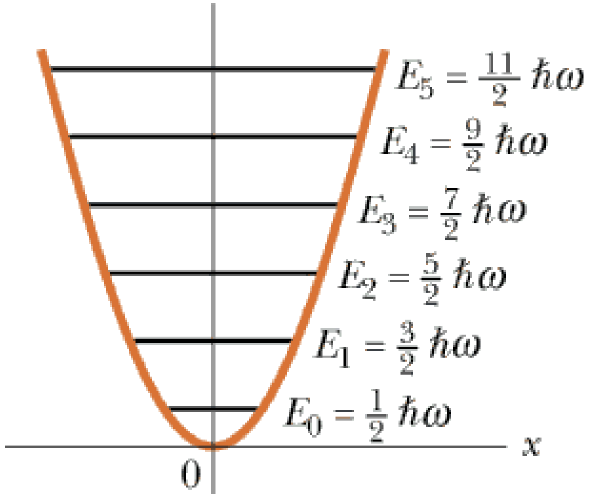


The energy of an oscillator (electrons in an atom) can only have certain discrete values of E_n

f is oscillation frequency, h is Planck's constant,

Energy is quantized, each discrete value of energy corresponds to different orbitals and different quantum states.

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \text{ where } n = 0, 1, 2, 3, \ldots$$



Important conclusions

1. *An electron in an orbital is equivalent to a standing wave propagating along the orbital.*
2. *When electrons behave like standing waves, they no longer radiate energy in the form of radiation - as this applies to particles (de Broglie's idea)*
3. *A change in the energy of an electron is equivalent to a change in the quantum state*
4. *A change in the energy of an electron is possible due to the emission or absorption of energy by an atom in the form of electromagnetic waves*

Particle = Wave

Any piece of matter moving at any speed can exhibit wave properties
Effects for classical particles are too small to be observed
A quantum particle, an electron, is not only a particle, but also exhibits a wave nature.

$$E = mc^2 = hf$$

$$f = \frac{mc^2}{h}$$

The de Broglie wavelength of the particle is $\lambda = \frac{h}{m\upsilon}$

TASK!

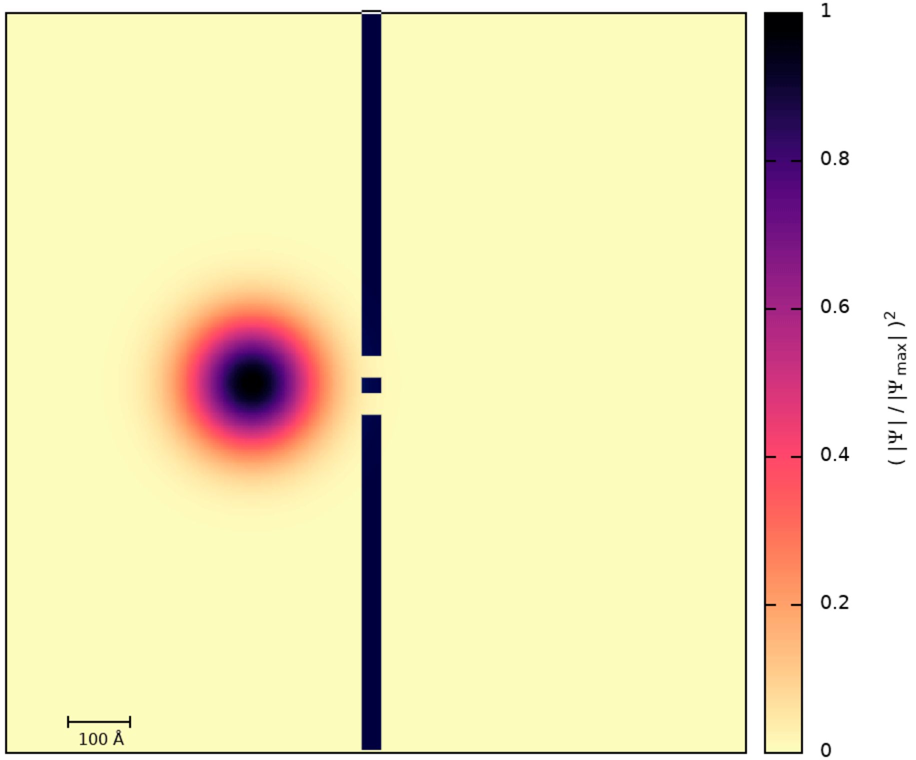
Find the de Broglie wavelength for a person with a mass of 70 kg traveling at about 1 m/s

Particle = Wave

Davisson-Germer Experiment

If the particles are of a wave nature, then under the right conditions they should exhibit diffraction effects.
Davisson and Germer measured the wavelength of electrons.
This confirmed the hypothesis, advanced by Louis de Broglie in 1924, of wave-particle duality

The principle of complementarity states that the wave and corpuscular models of matter or radiation complement each other.
None of the models can be used solely to adequately describe matter or radiation.



The Uncertainty Principle

In classical mechanics, one can make measurements with an arbitrarily small uncertainty

Quantum theory predicts the fundamental impossibility of simultaneous measurements of the position and momentum of a particle with infinite accuracy.

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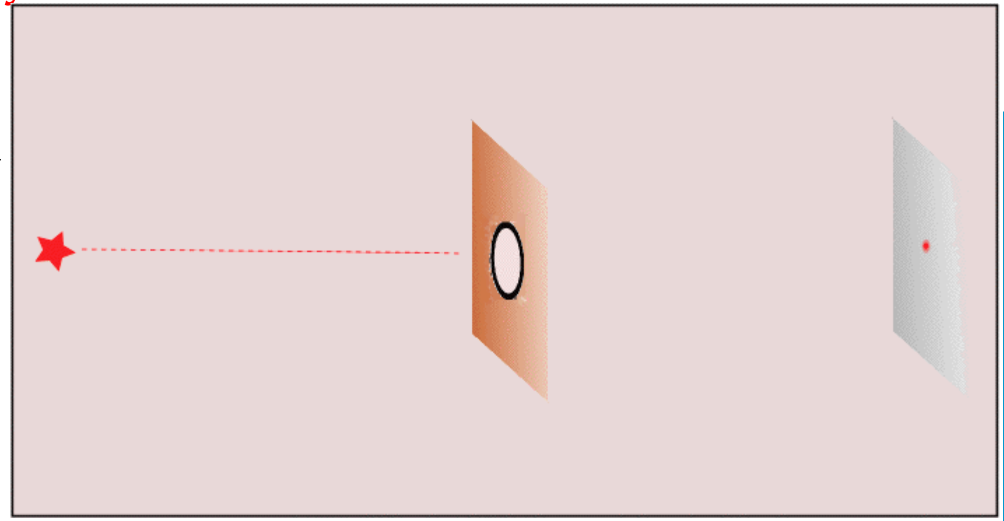
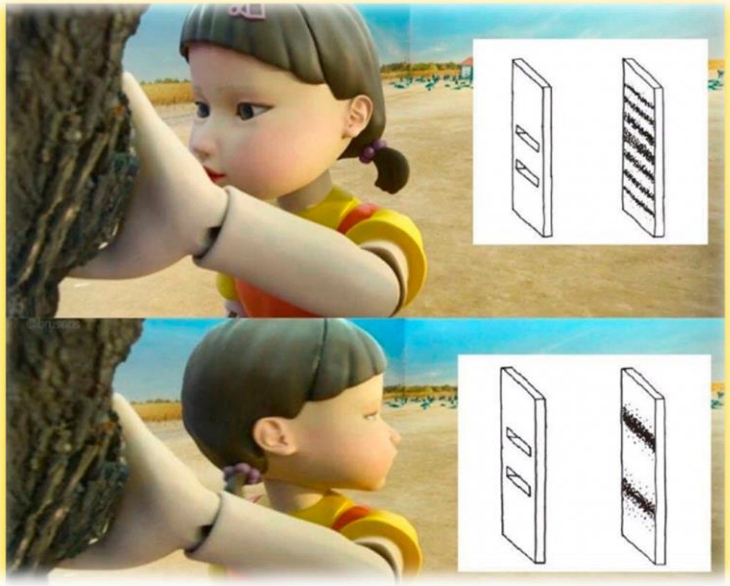
Quantum theory predicts the fundamental impossibility of simultaneous measurements of the position and momentum of a particle with infinite accuracy.

The Heisenberg uncertainty principle states that if a particle's position is measured with an uncertainty Δx and its momentum x-component is simultaneously measured with an uncertainty Δp_x, the product of this two uncertainties can never be less than n $\hbar/2$





Quantum system - electron trajectory after diffraction is statistically *uncertain*

Uncertainties arise from the quantum structure of matter.

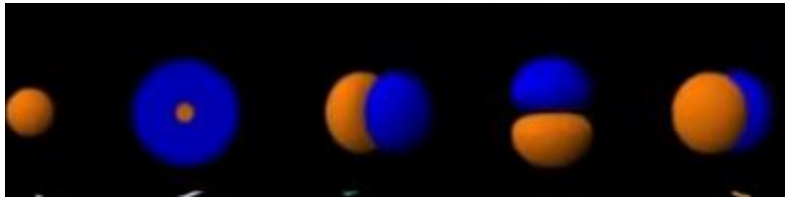
Classical system - electron trajectory after slit is *definite*

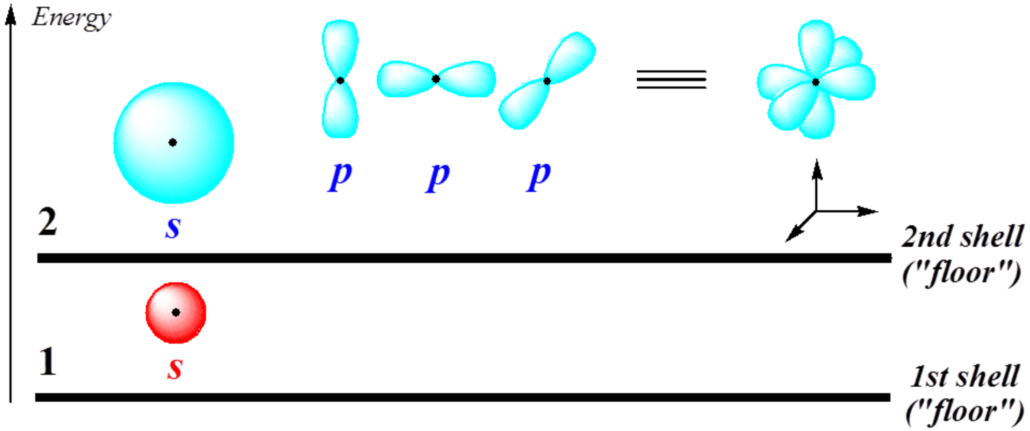
Electrons in Atom

Each electron shell is composed of subshells, which in turn are made up of orbitals. The electronic system of the atom can be compared to a multistorey hotel building. Each floor of the hotel has rooms of different types (classes). All rooms within each class are identical, but different from rooms in another class.

So, we think like this:

- The hotel building = *atom*
- Each floor of the building = *electron shell*
- Each set of identical rooms (of the same class) within a floor = *electron subshell*
- Each room, regardless of its type = *orbital*
- Each hotel guest = *electron*





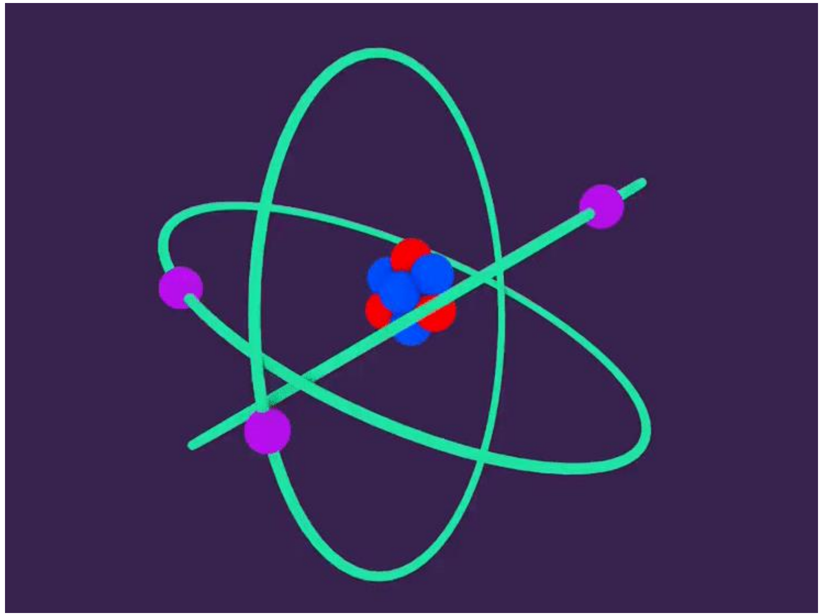
Our "1st floor" is the first electron shell (n = 1), which is the lowest in energy (closest to the nucleus). This "floor" (shell) has only one "room" (orbital), which is spherical in shape (s-orbitals).

While there is only one "room" (orbital) and, consequently, only one "type of room" (one subshell) on the "1st floor" (1st shell), the "2nd floor" (2nd shell) has a total of four "rooms" (four orbitals) of two different "classes" (two subshells). One of the four is another spherical orbital (s-orbital). The remaining three orbitals of the 2nd shell are slightly higher in energy and have a "dumbbell" shape. Orbitals of this shape are referred to as p-orbitals. All three p-orbitals are identical, except for their orientation in space - three are perpendicular to each other.

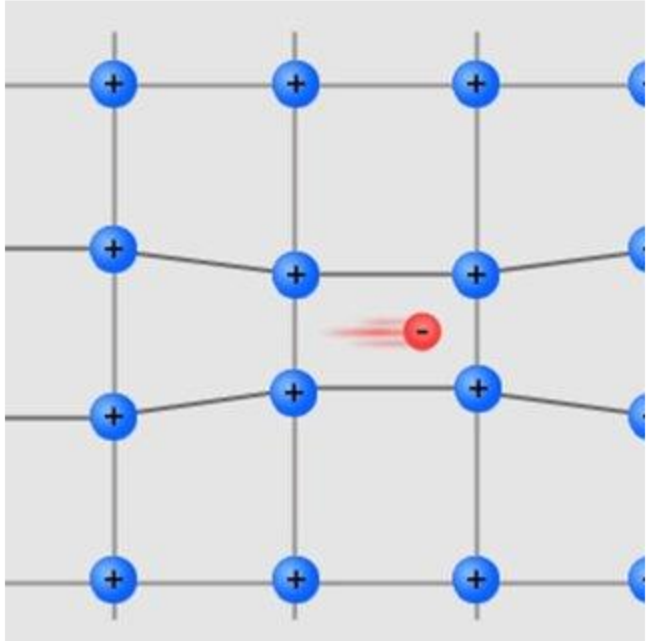
The orbital of an electron is a part of space where the probability of finding an electron is non-zero !!!!!

Electrons in Atom

We are still preparing to explain the quantum size effect



Now we imagine electrons in an atom and understand that this gif is not perfect)



The next jump is an electron in crystals

REGINNA 4.0

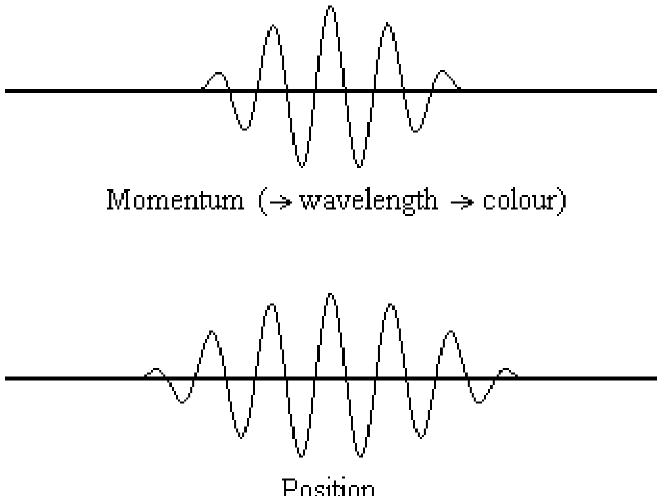
Quantum Particle

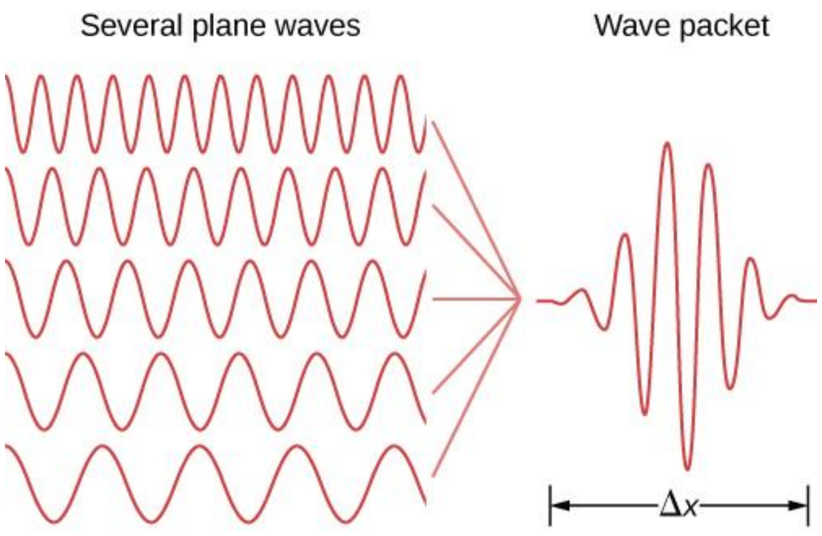
A quantum particle has both corpuscular and wave characteristics.

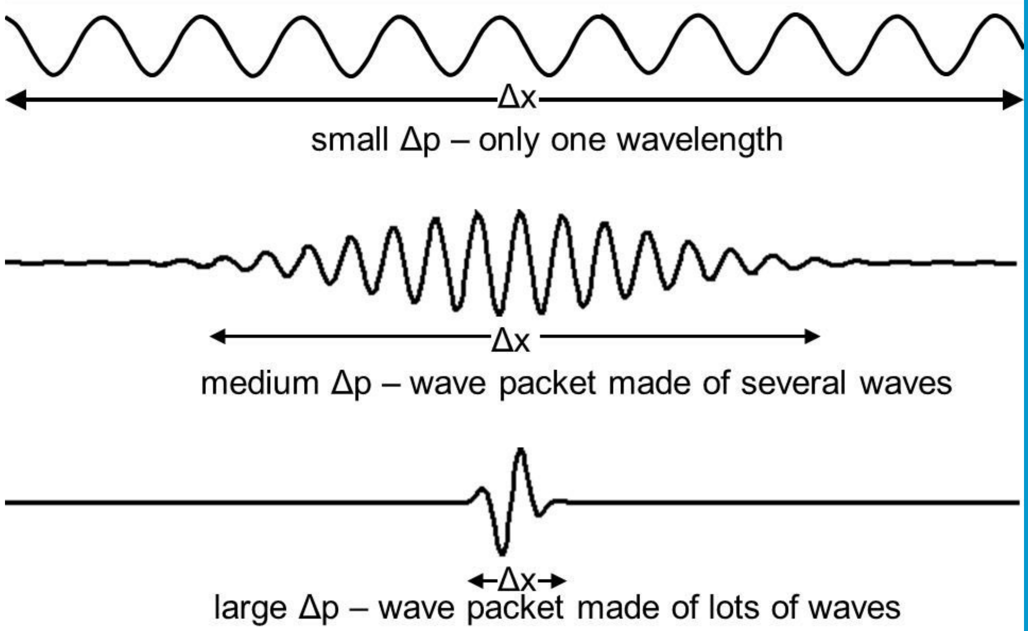
An ideal particle has zero size
Therefore, it is localized in space
An ideal wave has a single frequency and is infinitely long
Therefore, it is unlocalized in space
A localized entity can be built from infinitely long waves

Multiple waves are superimposed so that one of its crests is at x = 0
The result is that all the waves add constructively at x = 0
There is destructive interference at every point except x = 0
The small region of constructive interference is called a wave packet

The wave packet can be identified as a particle



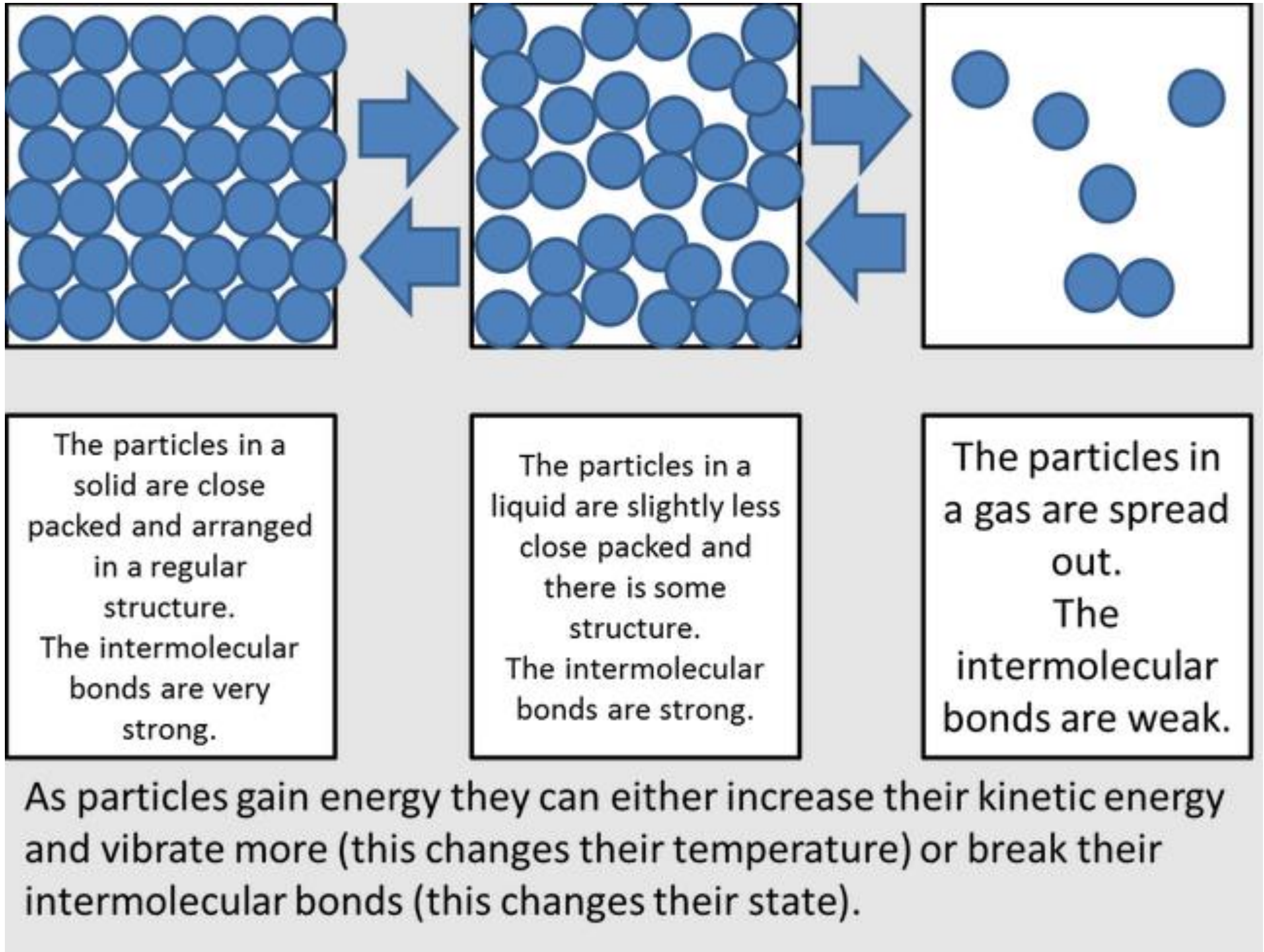




Condensed Matter Physics

Condensed matter physics deals with systems of large number of interacting particles and explores macroscopic behavior of matter based on its microscopic properties

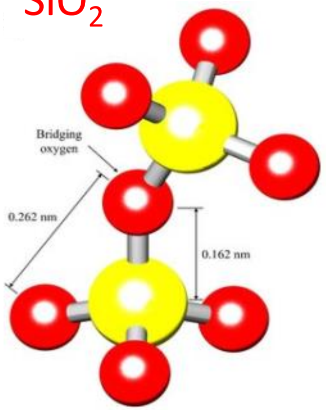
Study of microscopic properties (electrical, thermal, magnetic…) of solids. Solid: a system with a large number of particles (atoms, molecules, ions) in strong interaction (unlike a gas)

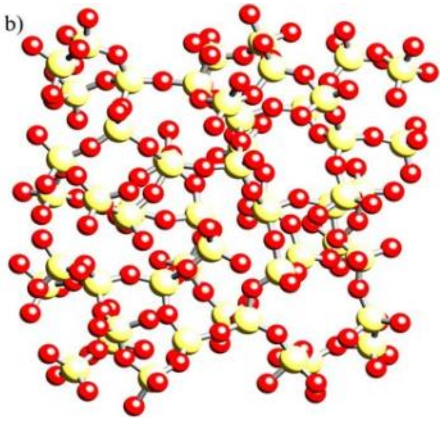


Crystals

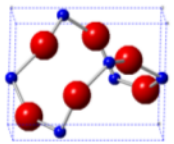
Crystalline materials are characterized by the long-range ordered periodic arrangements of atoms.

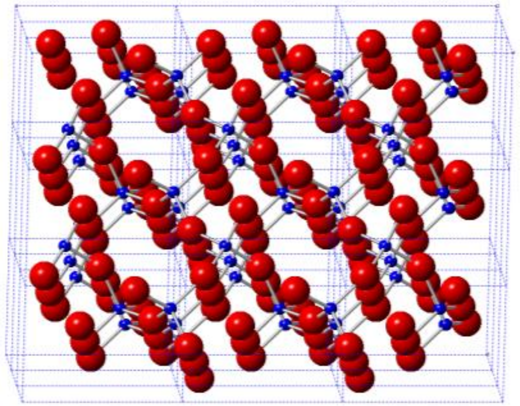
SiO_2





The unit cell is the basic repeating unit that defines the crystal structure. The unit cell contains the symmetry elements necessary for the unambiguous determination of the crystal structure.
The unit cell might contain more than one molecular unit (not molecules!!!!).
The crystal system describes the shape of the unit cell.
The lattice parameters describe the size of the unit cell





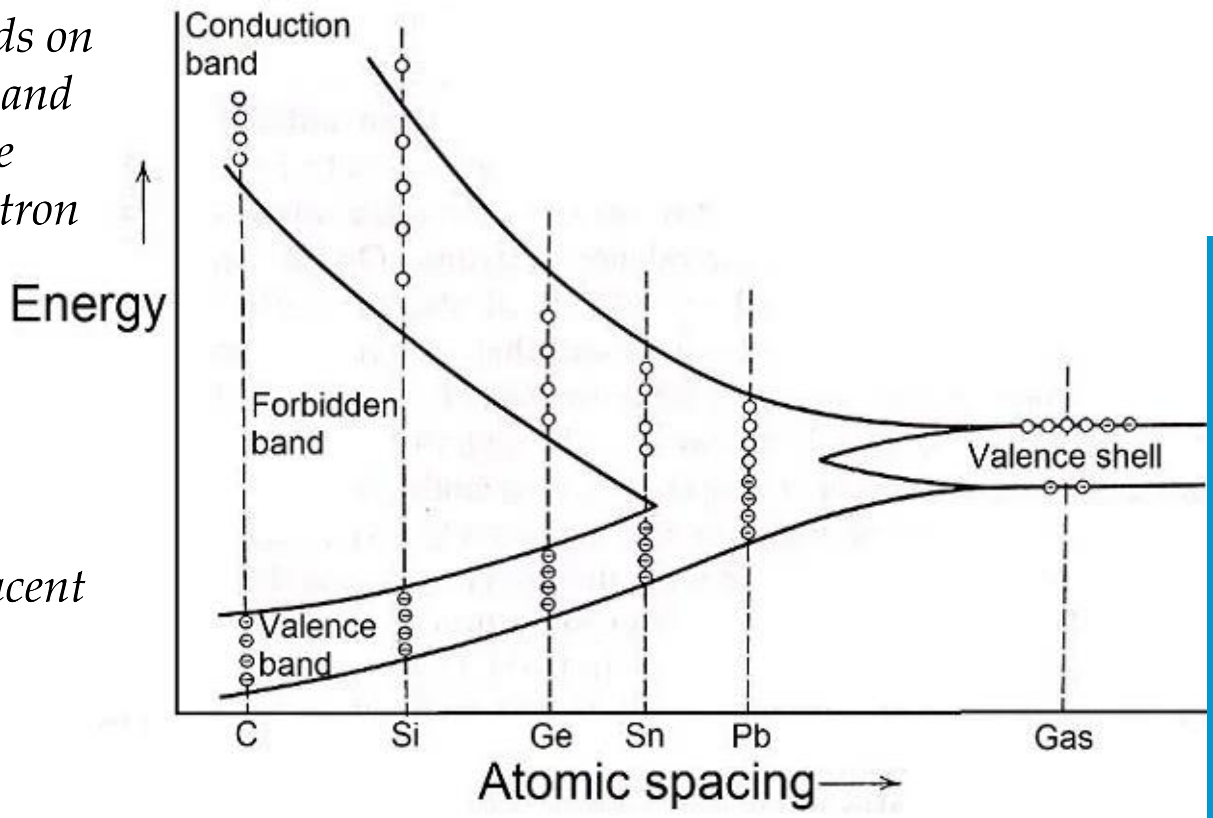
Lattice Parameters:
4.9134 x 4.9134 x 5.4052 Å
(90 x 90 x 120°)

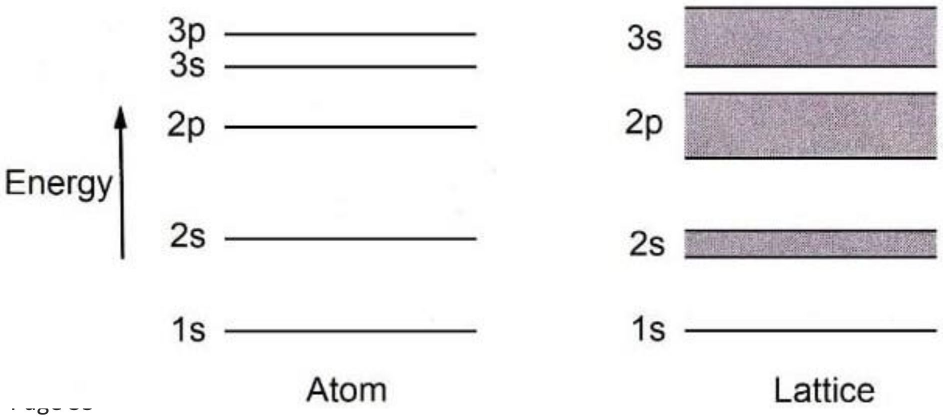
Band Structure Formation

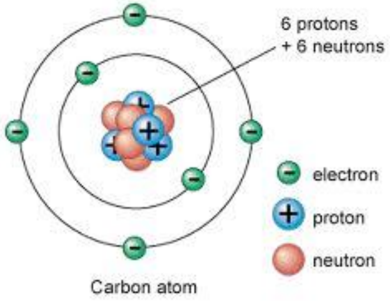
The magnitude of the influence of neighboring atoms depends on the type of atoms (the number of electrons in atomic shells and protons in nuclei), the environment of each atom (lattice symmetry and distance), and also on the location of an electron within a group of atoms.

In accordance with the Pauli exclusion principle, when a system consists of many identical atoms, the individual energy levels of the electrons of individual atoms turn into energy bands.

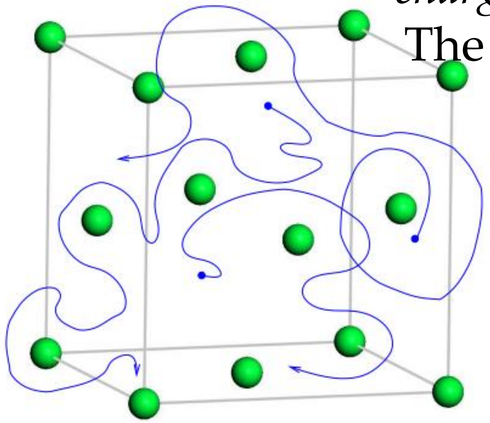
An energy band is an energy range with many allowed adjacent energy levels very close to each other.







Electrons in Crystals



An electron in a crystal is in a periodic electric field, which is created by the nuclei of atoms (positively charged) and electrons in the shells of atoms (negatively charged)

The periodicity scale is of the order of the de Broglie wavelength of an electron, about 0.1 nm.

Periodicity is idealization: impurities, defects, thermal fluctuations

The Schrödinger equation, which determines the position of an electron, depends on both energy and time. The solution to the Schrödinger equation is a wave function that gives the probability of finding an electron in a given location.

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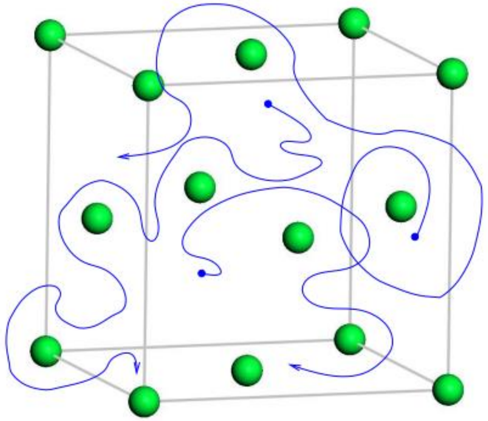

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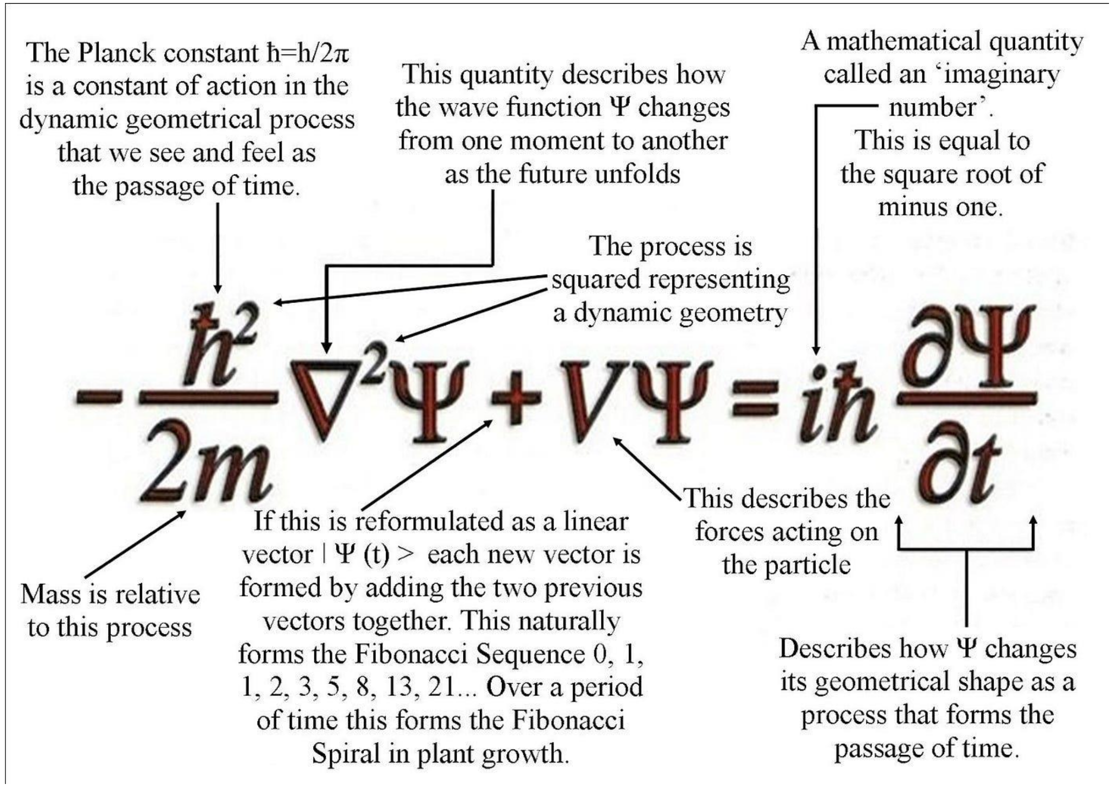


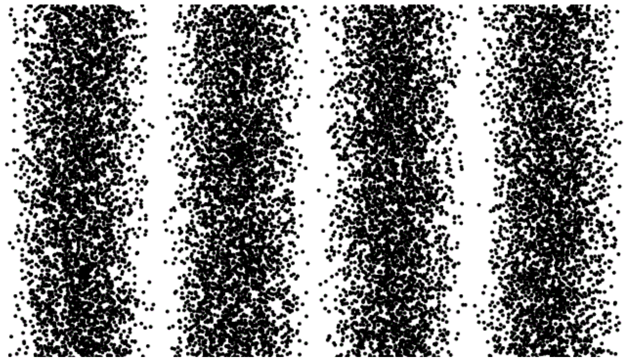
Independent electronic approximation:

Schrödinger equation for a single electron:

$$\frac{-\hbar^2}{2m}\nabla^2\Psi(\mathrm{r}) + V(r)\Psi(\mathrm{r}) = E\Psi(\mathrm{r})$$

Kinetic Energy + *Potential Energy* = *Total Energy*

Electrons in Crystals



The wave function doesn't tell you where the electron is - as in the case of classical physics - it tells you the probability that the electron is here, or there, or somewhere else.

To visualize a wave function, think of it as a probability cloud.

Wave function can be interpreted as the probability amplitude of finding a particle at a specific point in space at a specific moment in time.

Electrons in Crystals

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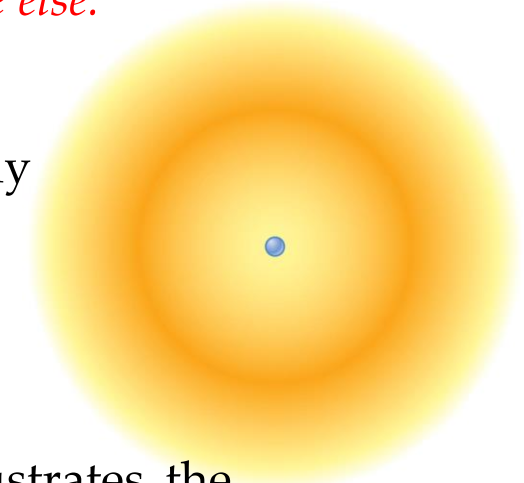
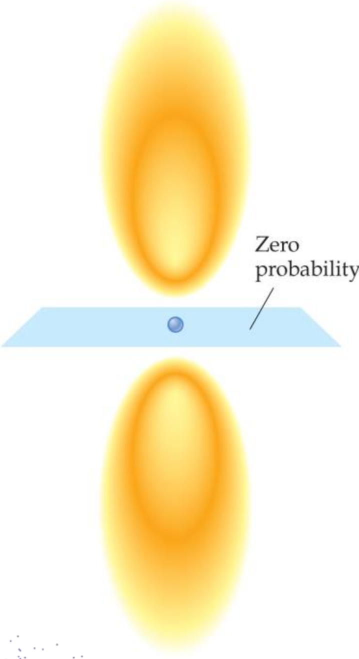
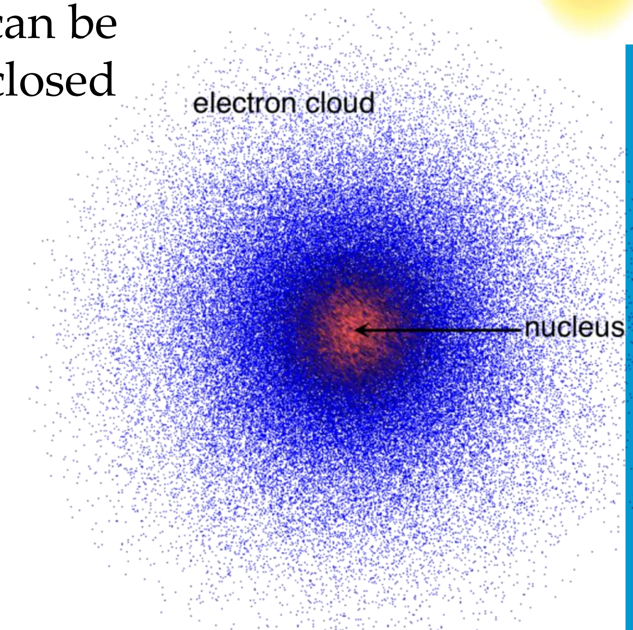
To visualize a wave function, think of it as a probability cloud.

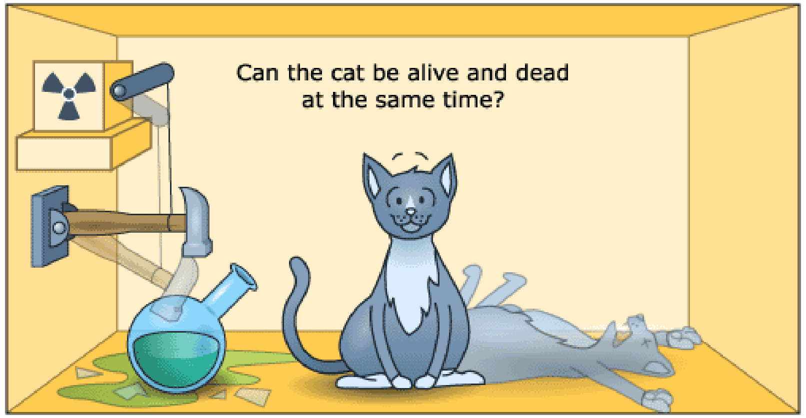




The interpretation of the probability cloud is simple: the electron is most likely to be found where the cloud is densest.
The probability of finding an electron near the nucleus or far from it is small.
The probability clouds for the excited states of hydrogen have the same interpretation as for the ground state, but their shape is more interesting.

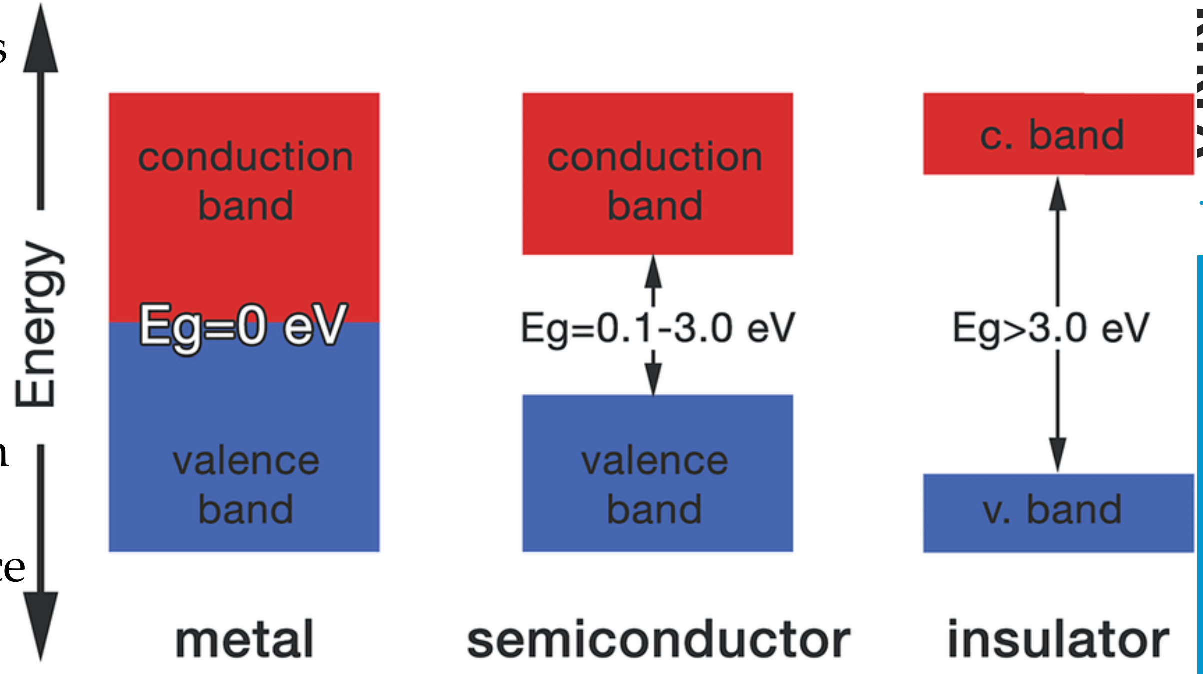
In quantum mechanics, Schrödinger's cat is a thought experiment that illustrates the paradox of quantum superposition. In the thought experiment, a hypothetical cat can be considered simultaneously both alive and dead, while not being observed in a closed box, since its fate is tied to a random subatomic event that may or may not occur.





Energy Bands

Electrons in the same orbit have different energy levels.
The grouping of these different energy levels is known as an ***energy band***.
There are three types of bands:
Valance band: the energy band consisting of the energy levels of the valence electrons is known as the valence band.
Conduction band: the energy band consisting of the energy levels of free electrons is known as the conduction band.
Forbidden energy gap: the energy gap between the valence band and the conduction band.
The energy difference between the valance band and the conduction band is known as the **band gap**.



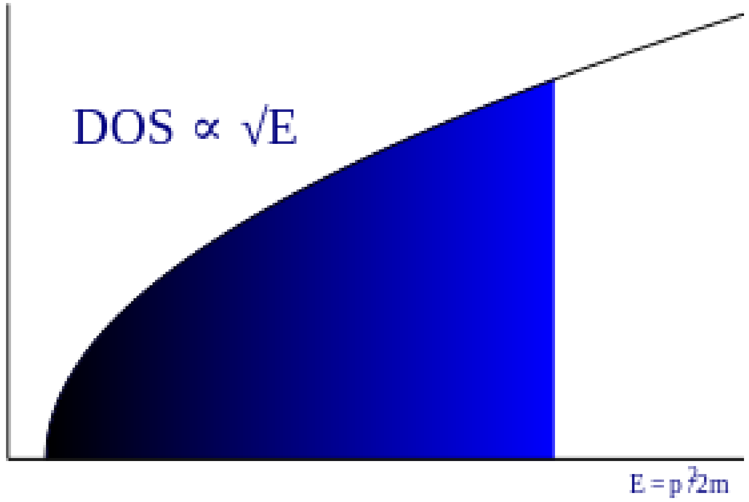
One electron volt is defined as the energy gained by an electron when it is accelerated through a potential difference of 1 volt.

$1eV = 1.6\times10^{-19}$ Joules

Due to the band gap, materials can be divided into three groups:
Conductor: The valence band and conduction band overlap.
Semiconductor: There is a small band gap between the valence band and the conduction band.
Insulator: There is a large band gap between the valence band and the conduction band.

Density of States

The density of states (DOS) is the number of different states (cells) at a certain energy level that electrons can occupy, that is, the number of electron states per unit volume per unit energy.

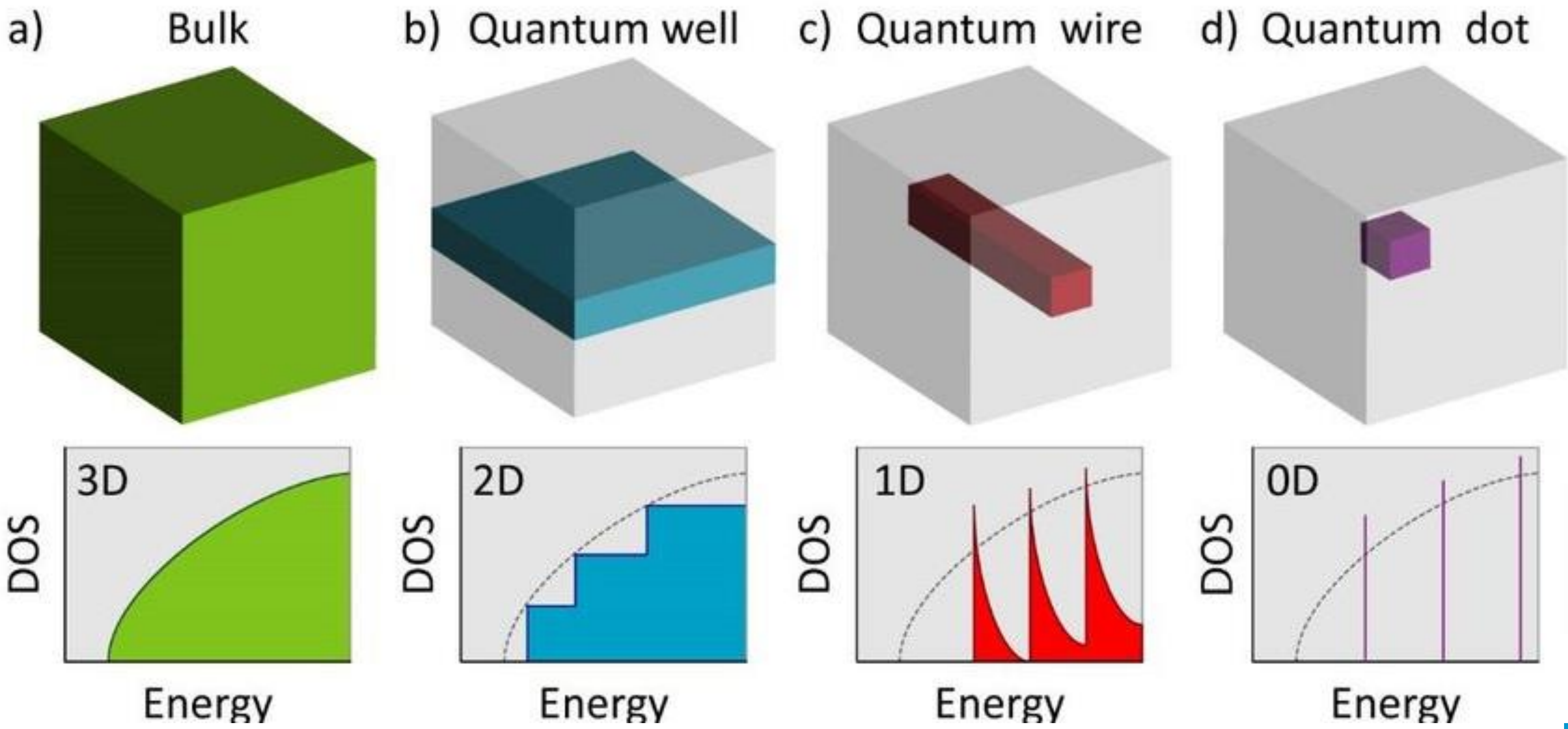


The parabolic relation is predicted for DOS vs Energy (E) dependence

Generally, the density of states of matter is continuous. In isolated systems however, such as atoms or molecules in the gas phase, the density distribution is discrete

Quantum Confinement Effect and DOS for Nanomaterials

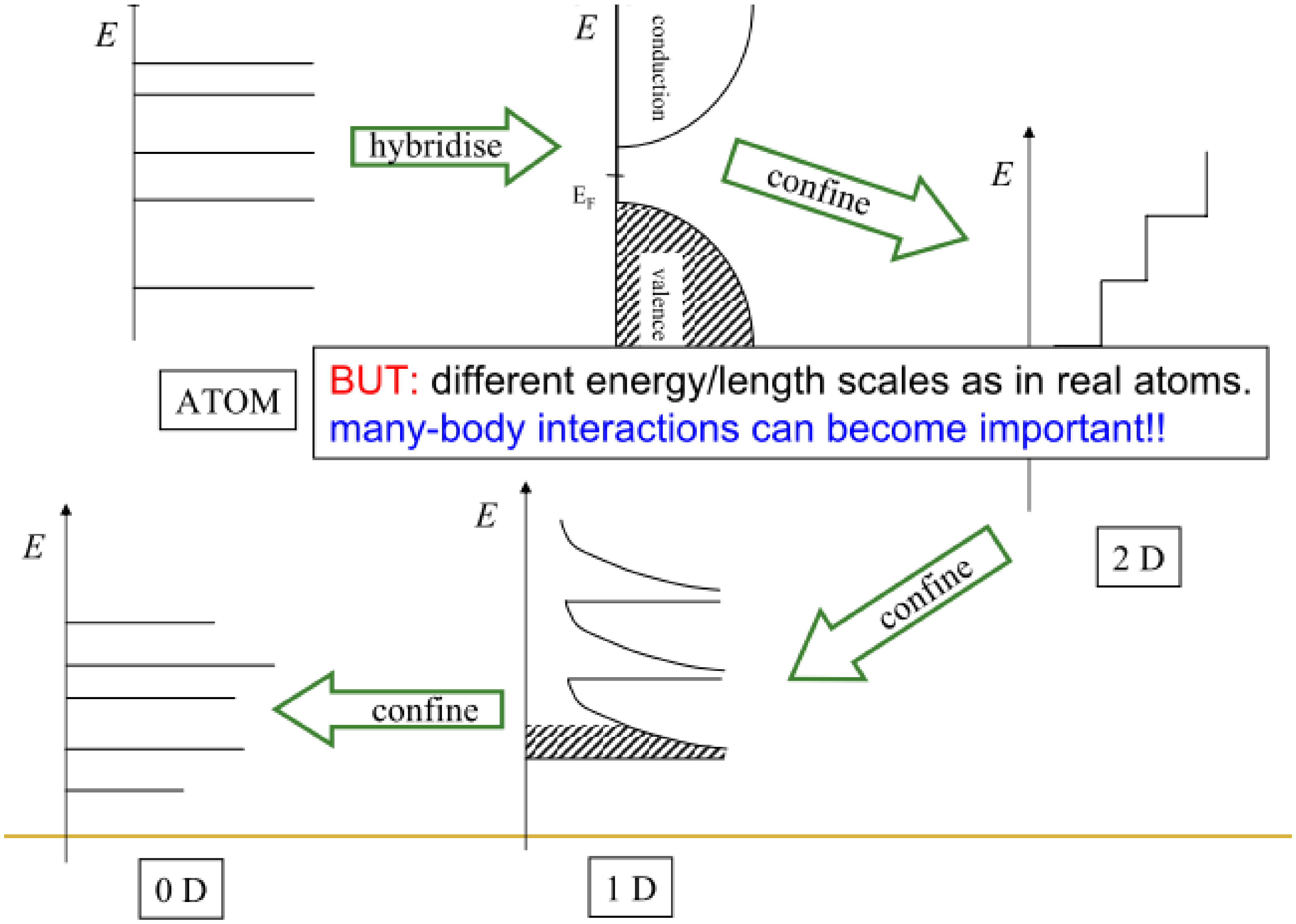
When the length of a particle is reduced to the same order as ***the wave packet*** , i.e., to a few nanometers, quantum confinement effect occurs, and the materials properties are modified. Depending on the dimension of the confinement, three kinds of confined structures are defined: *quantum well*, *quantum wire* and *quantum dot*



The reduction in dimensionality caused by confinement of electrons from bulk (3D) to a thin crystal layer (2D) leads to a sharp change in their behavior and transformation of DOS. A further decrease in the dimension of the electron environment to a one-dimensional quantum wire (1D) and eventually to a zero-dimensional quantum dot (0D) leads to formation of an ***atom-like system***.

The energy distribution of electrons in a quantum dot is similar to the energy level of atoms - there is no band structure, but the density of single levels is greater.

QD as Artificial Atoms

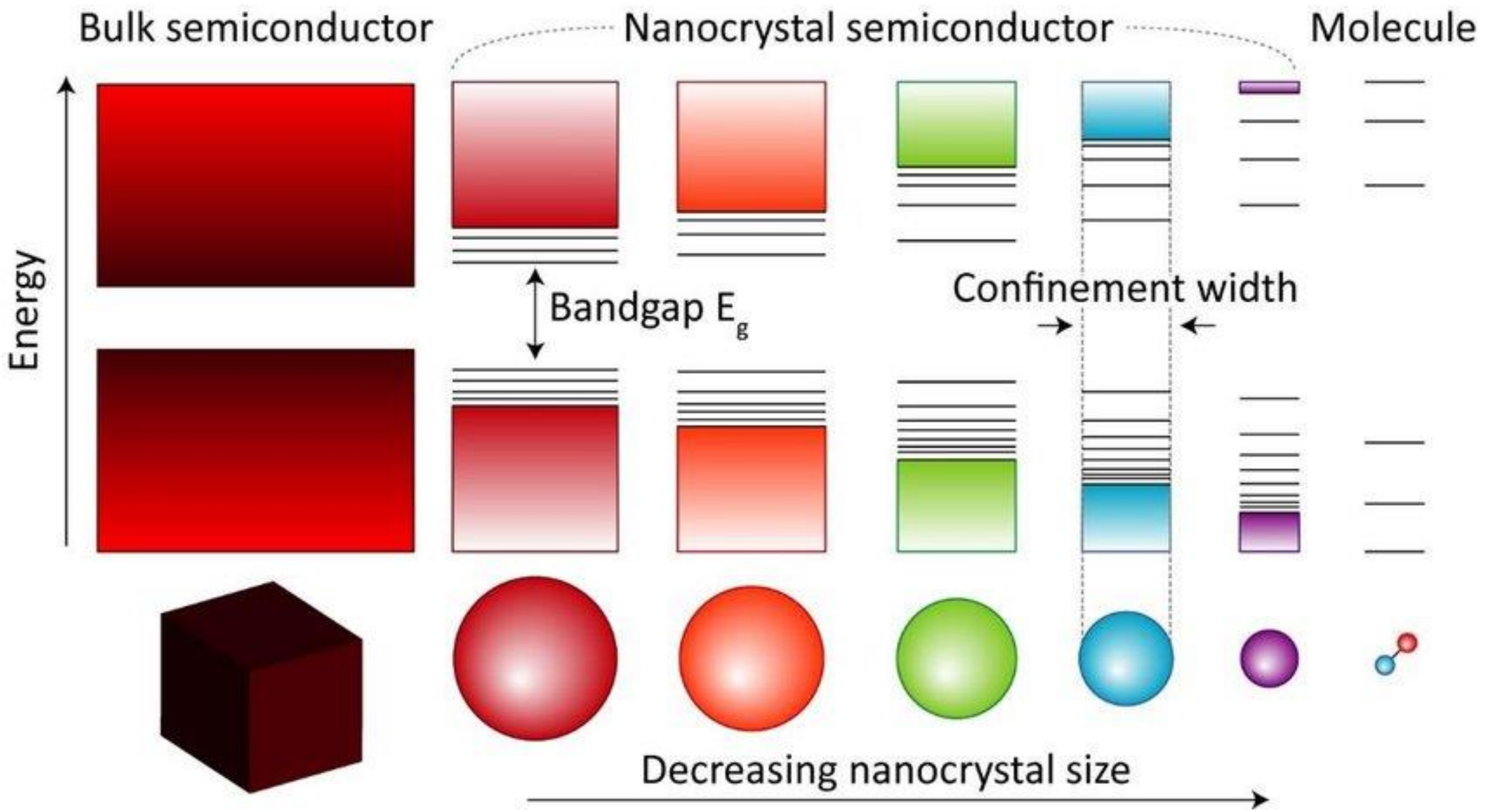


BUT: different energy/length scales as in real atoms.
many-body interactions can become important!!

Semiconductor nanocrystals are called *artificial atoms* due to their atom-like discrete electronic structure resulting from quantum confinement. *Artificial atoms can also be assembled into artificial molecules or solids, thus, extending the toolbox for material design.*

Quantum Confinement

The size of the nanoparticles decreases from left to right, and the corresponding increase in the band gap is reflected in the change in the color of the photoluminescence from red to violet.



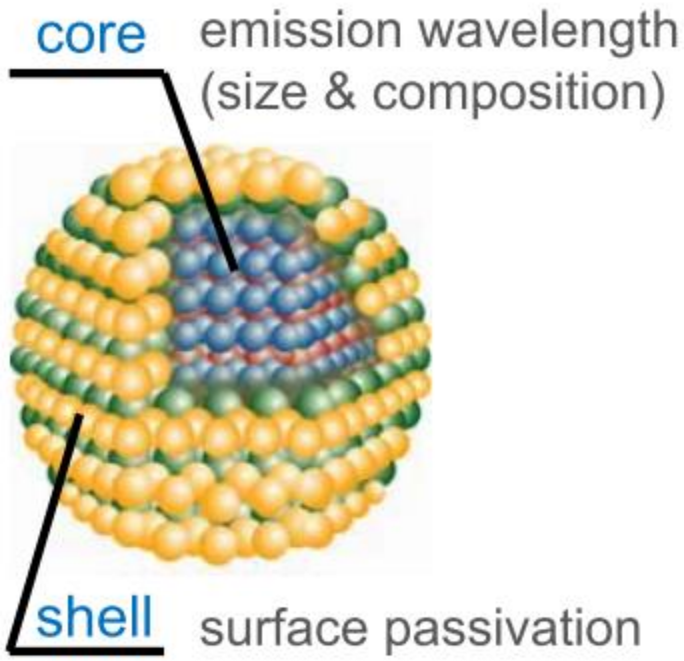
Quantum confinement is responsible for increasing the energy difference between the energy states and the band gap.

A phenomenon tightly related with the optical and electronic properties of the materials.

Quantum Dots

Quantum dots are fragments of a semiconductor with a bulk bond geometry and with surface states eliminated by enclosure in a material that has a larger band gap

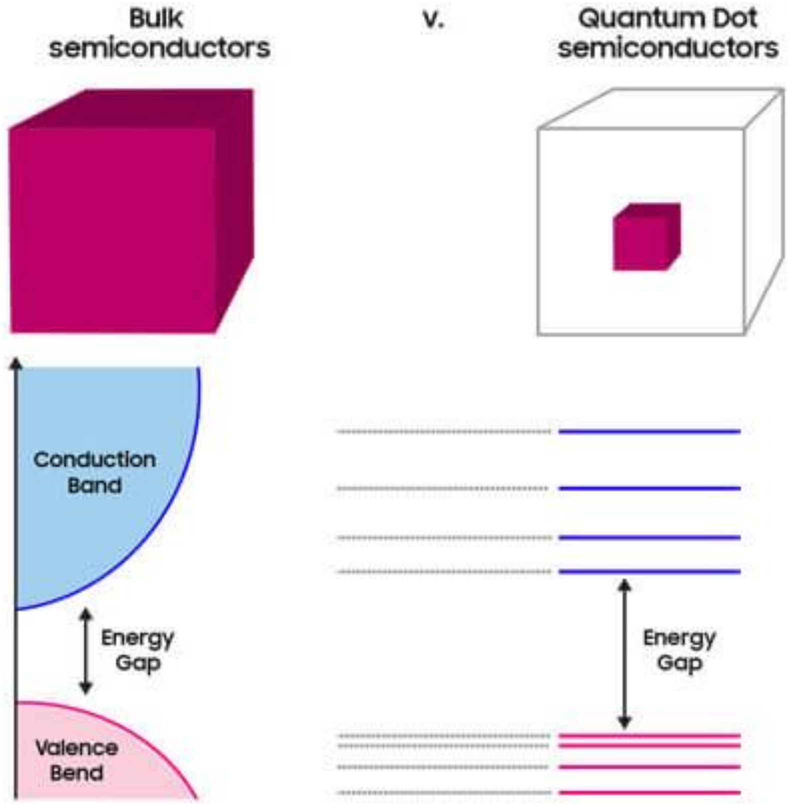
QDs contain 100 to 1000 electrons and are 2 to 10 nanometers in diameter, or 10 to 50 atoms. Changing the band gap of semiconductors is the most attractive due to fundamental and technological importance. Widely tunable bandgap semiconductors are considered materials for new generation flat panel displays, photovoltaic, optoelectronic devices, lasers, sensors, photonic bandgap devices, etc.



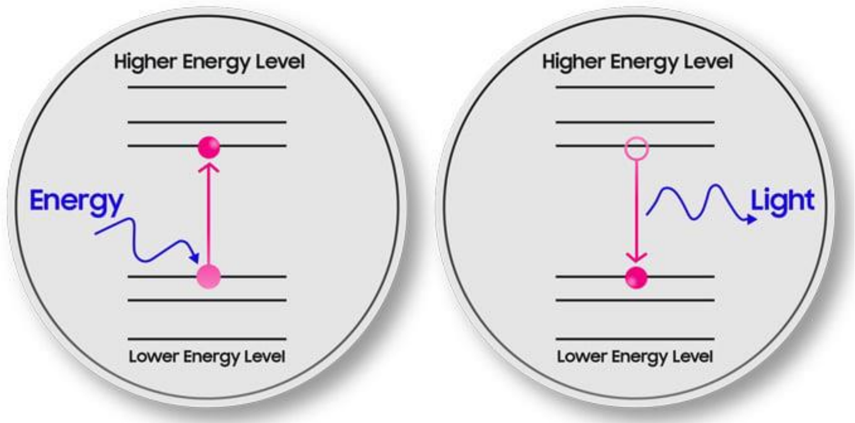
Properties of quantum dots

High extinction coefficient
High electron mobility
Bandwidth and position adjustment
Solution process capabilities

Quantum Dots



The release of confinement energy is a key property of a quantum dot, which explains the positive relationship between the QD size and the frequency of the light it emits.



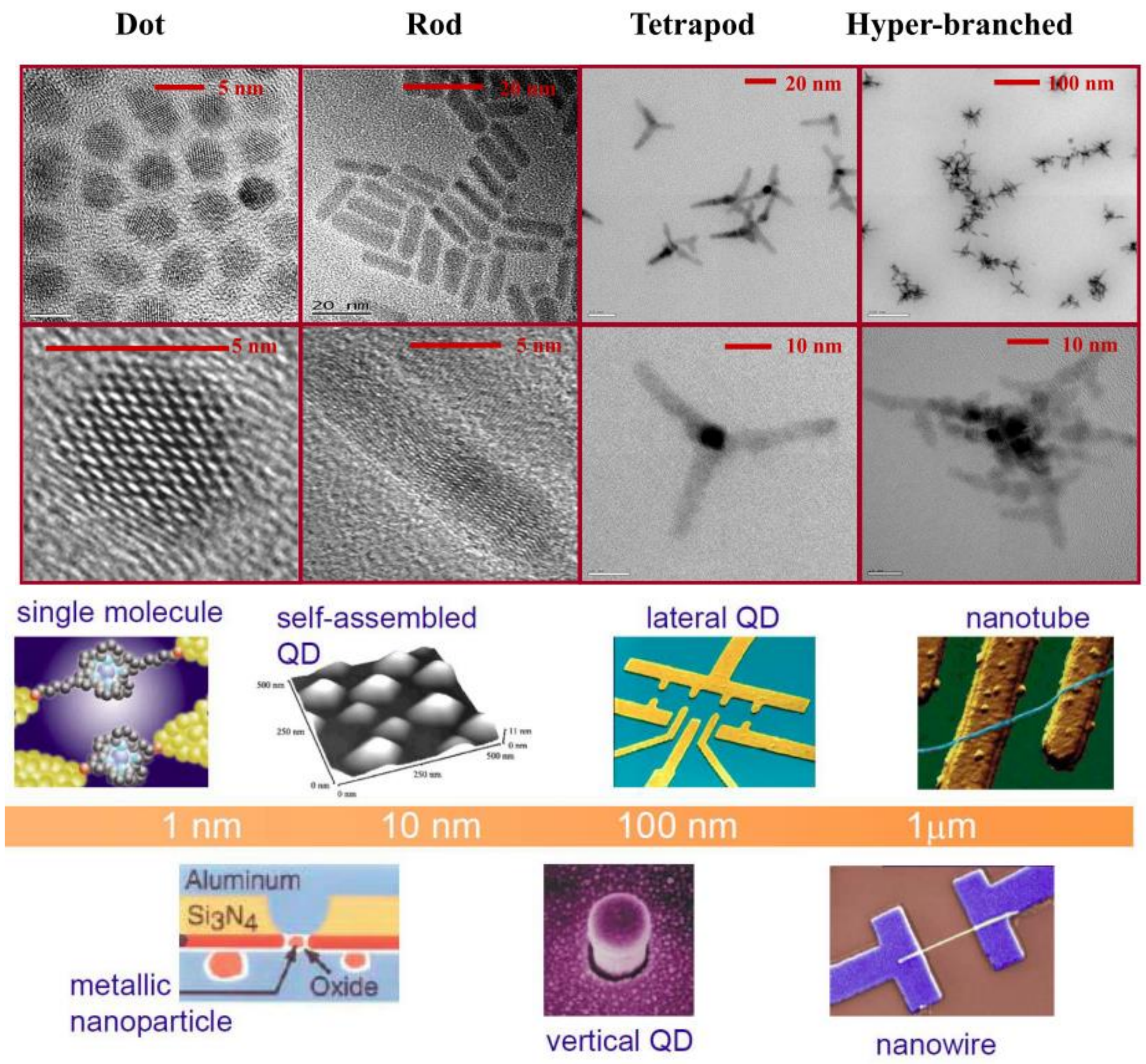
Unlike bulk semiconductors, which have continuous energy levels within the bands, the quantum confinement effect creates a large band gap with observed discrete energy levels. And because of this quantized band gap, a quantum dot can emit light at a very constant wavelength, which can be fine-tuned by changing the size of the quantum dots (or in other words, changing the energy levels).

Schrödinger:
electrons in confined systems occupy quantized energy levels

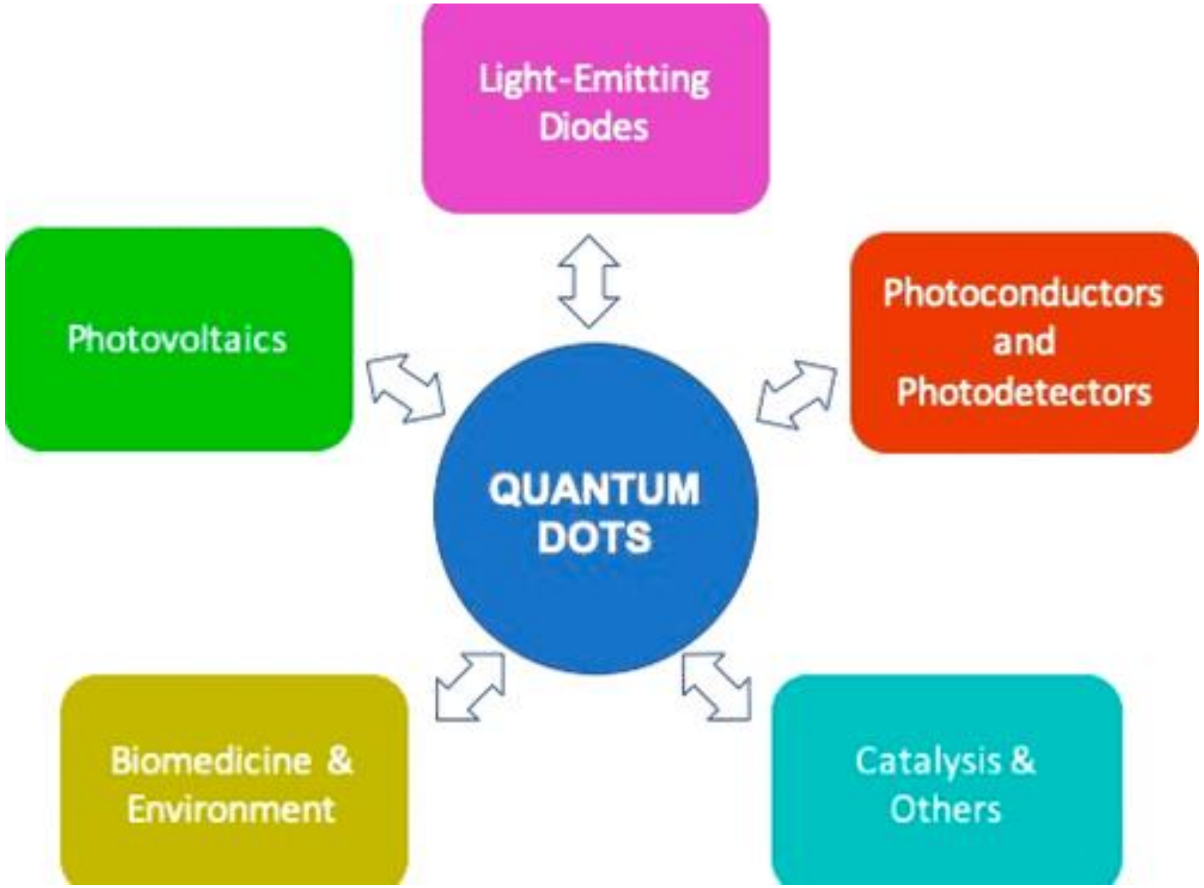
Quantum Dots

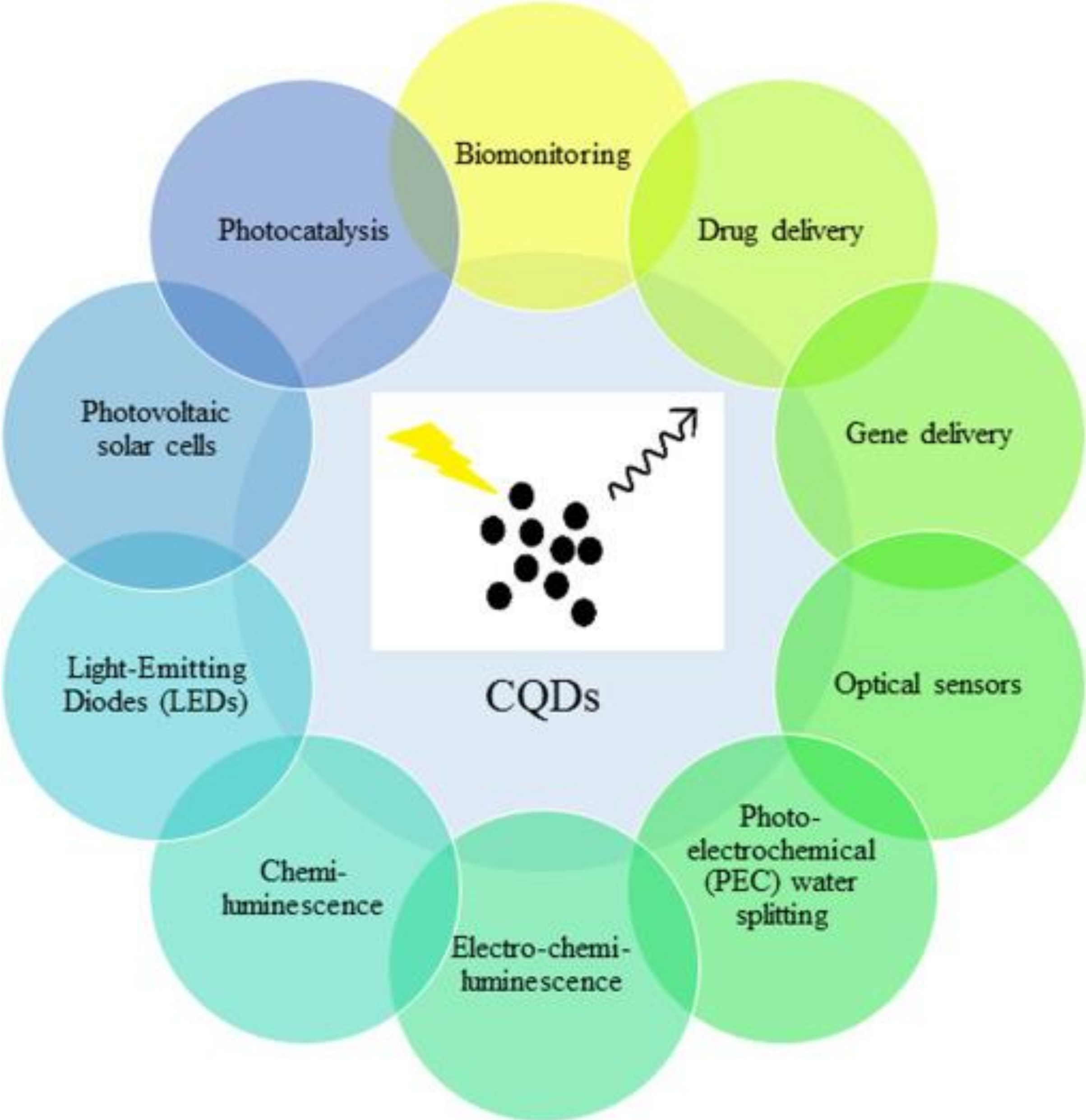
These images allow us to visualize the different geometry of QD as nanoparticles

At the same time, QD can be considered as structure – from molecules to devices



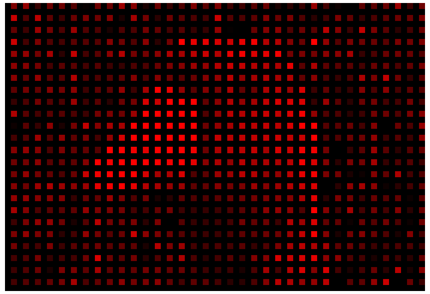
Quantum Dots

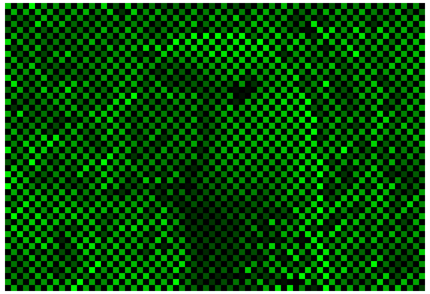


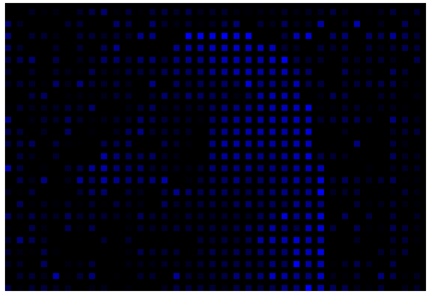


Quantum Dots

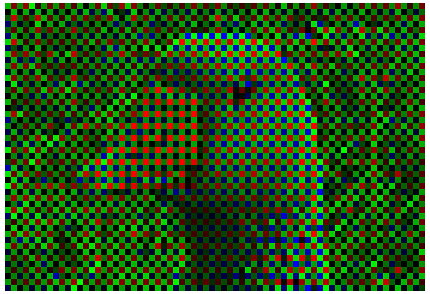
RGB (red, green and blue) refers to a system representing the colors used on a digital display screen. Red, green and blue can be combined in various proportions to obtain any color in the visible spectrum. The RGB model uses 8 bits each - from 0 to 23 - for red, green and blue colors.

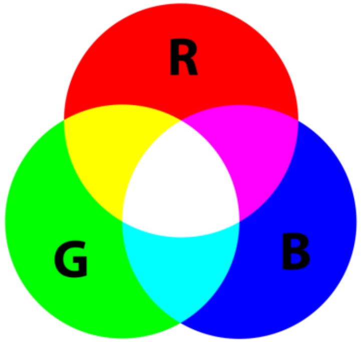


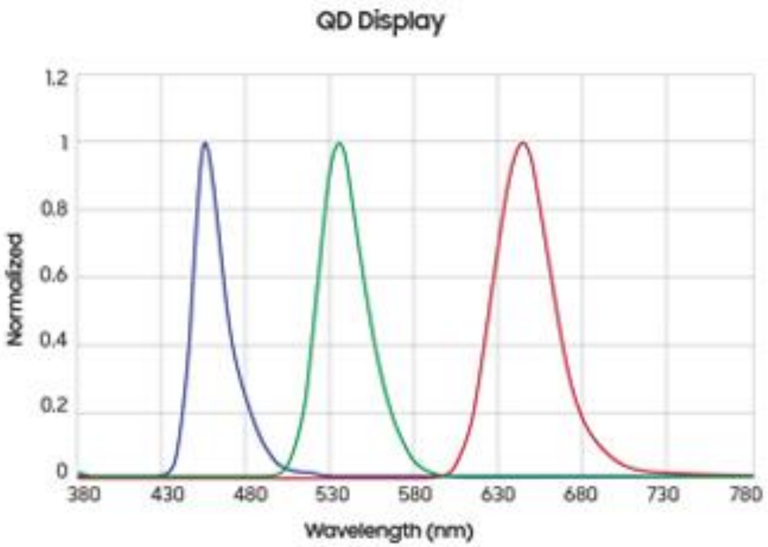


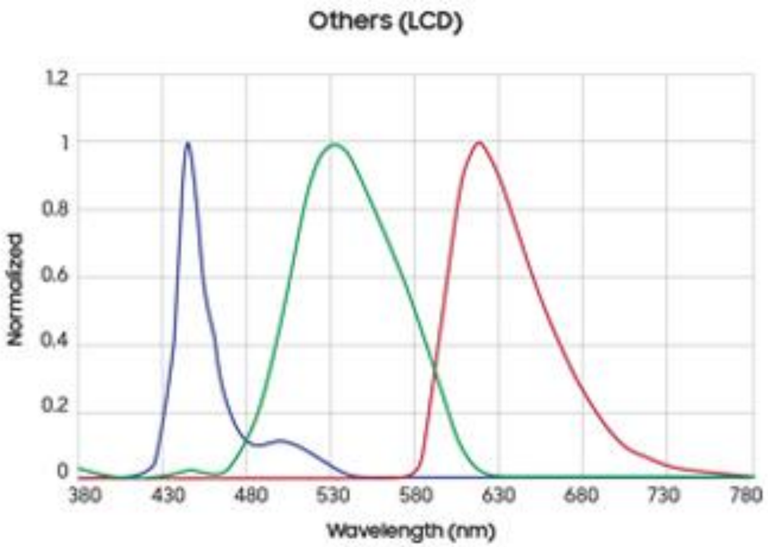


A new goal of improving the three primary colors of the display is to minimize the problem of color mixing. QDs allow the production of light sources with a narrow spectrum without overlap



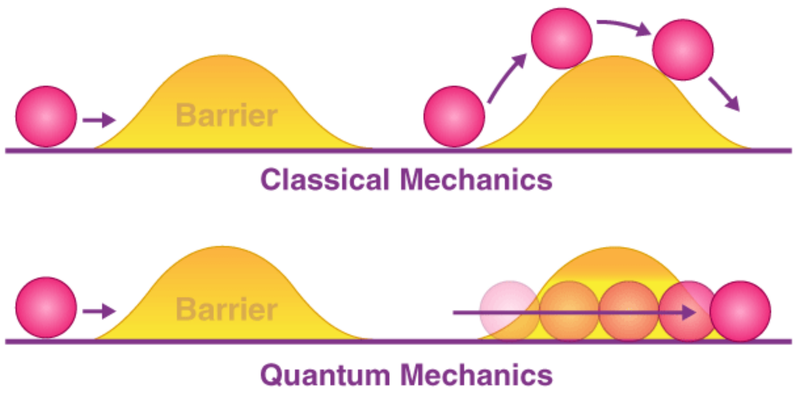


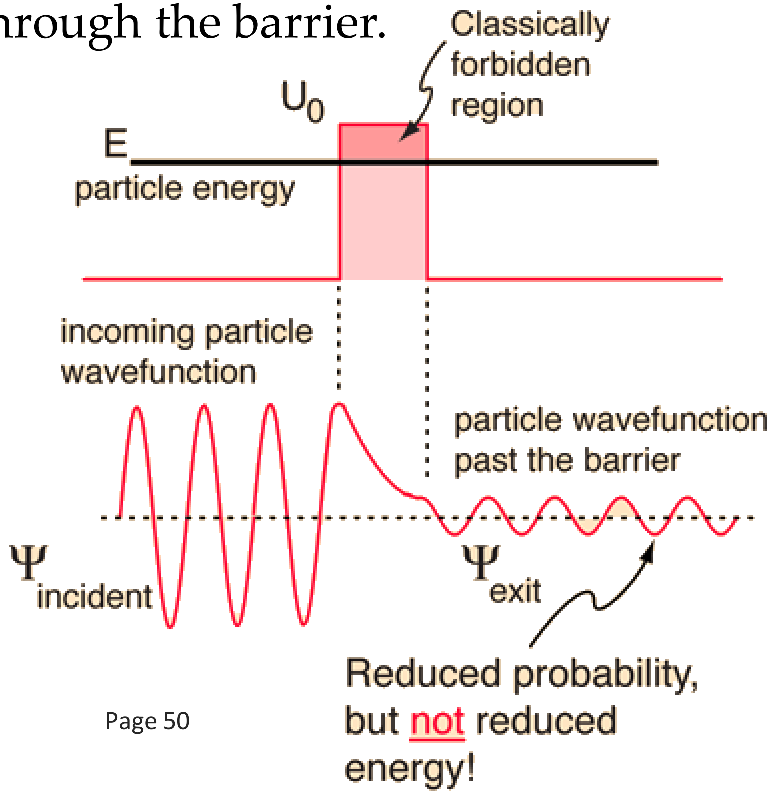




Quantum Tunneling

According to classical physics, a particle with energy E less than the barrier height U_0 cannot penetrate—the region inside the barrier is classically forbidden. But the wave function associated with the free particle must be continuous at the barrier and will exhibit an exponential decay inside the barrier.
The wave function must also be continuous on the far side of the barrier, so there is a finite probability that the particle will tunnel through the barrier.





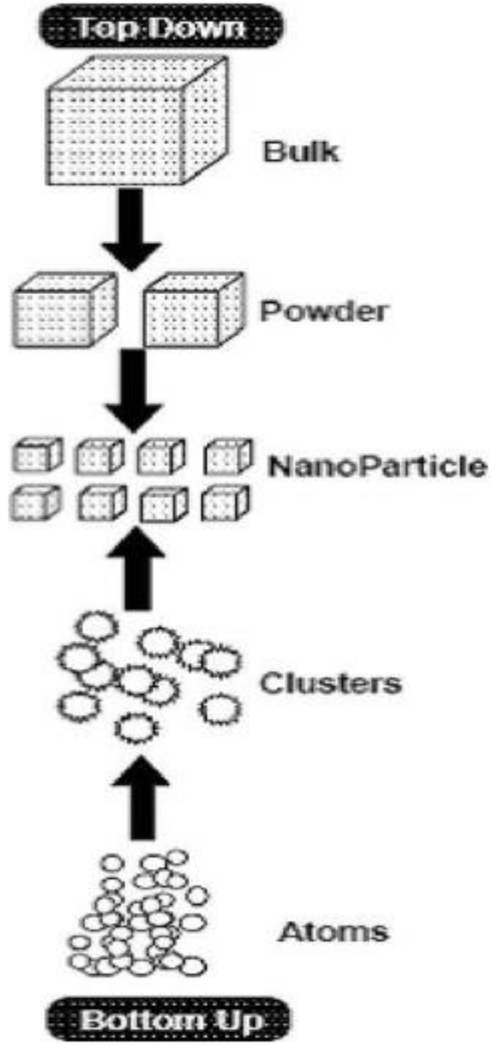
Wave functions have a probability of disappearing on one side and reappearing on the other side.
The first derivative of the wave functions is continuous.
Neither the wave nor the particle disappears.
Tunneling occurs at a barrier thickness of about 1–3 nm.

Quantum tunneling cannot be explained using the laws of classical mechanics, where a dense potential barrier needs potential energy.
This phenomenon is extremely important for development of new nanoelectronic devices.

Prepared Nanoparticle

The two basic approaches to creating nanomaterials in a controlled and repeatable manner are the "top-down" and "bottom-up" techniques, either for atoms to assemble (break) or disassemble (dissociate) bulk solids into small pieces or to get on a few atoms from them.

In the physical methods, mechanical methods offer the least expensive ways to produce nanomaterials in bulk (break the particles into nanostructures). But chemical fabrication methods are always easy to upscale and many, such as anodizing, are widespread industrial processes. **Top-down approach** is the process of making nanostructures that start with larger structures and break away to nanosize to form nanomaterials. Methods of deposition and nanopatterning of thin films are more advanced, and this approach has been pushed further into the nanofabrication. Also, applying the top-down assembly process of nanocomponents over large areas is difficult and expensive.



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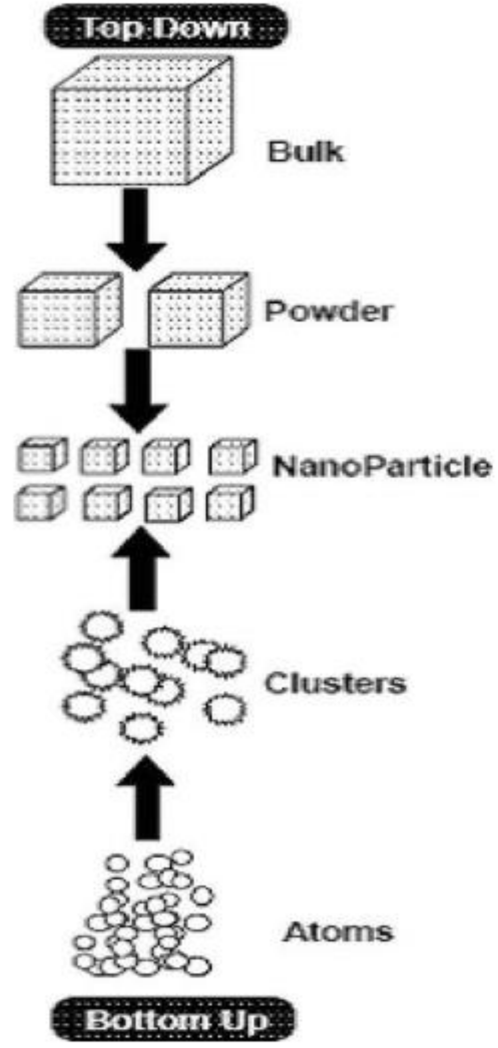
Prepared Nanoparticle

The building of nanostructures starting with small components such as atoms or molecules is called **bottom-up approach**. The bottom-up techniques make use of self-processes for ordering of supramolecular or solid-state architectures from the atomic to the mesoscopic scale. The methods of bottom-up include gas-phase and liquid-phase methods. For two methods, fabrication of nanomaterials was controlled when starting from the single atom or molecule. Chemical vapor deposition (CVD) and plasma arcing are called gas-phase methods, whereas liquid-phase represented by the most established method is sol-gel synthesis. Also, a new method called molecular self-assembly emerged. The areas of application for nanotechnology have different fields such as photonics, electronics, chemical sensors, biological sensors, and energy storage, and catalysis nanomaterial requires the manipulation into functional materials and devices.



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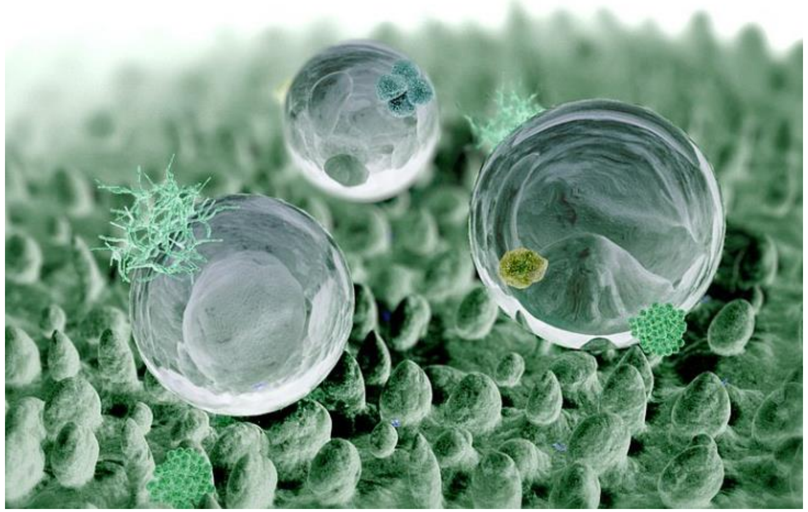
Nanotechnologies in Nature

Nilufer (lotus) leaf effect

The lotus grows in small lakes and ponds, ponds and puddles, and the surfaces of its leaves are always bright, clean and smooth, as if untouched by polluted water. It symbolizes pure cleanliness, as there is no bacteria and pathogen formation on the lotus leaves, which do not usually accumulate water on them. The water drops act like a drop of “mercury” on the lotus leaf and slide slowly over the surface, thus sweeping away any dirt and dust accumulated on the surface, leaving a clean surface behind.

Dirt particles are picked up by water droplets due to the micro- and nanoscopic architecture on the surface, which minimizes the droplet's adhesion to that surface.

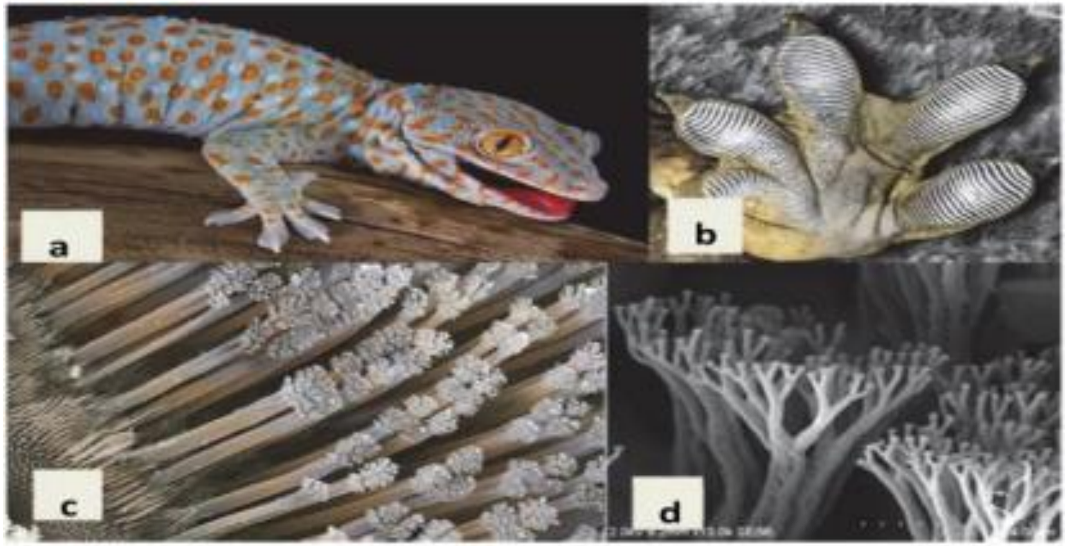


Based on the concept of the lotus effect, nanotechnology uses examples for industrial and everyday life

Nanotechnologies in Nature

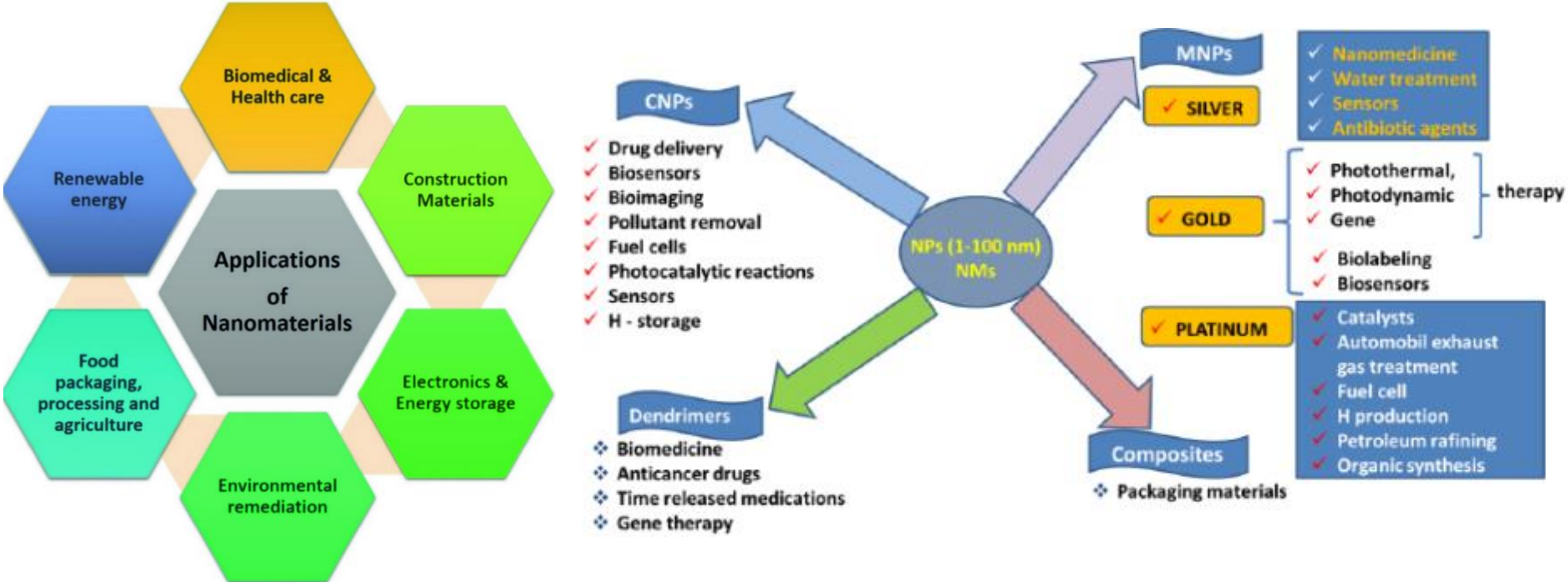
Gecko effect

As a result of billions of years, we are able to examine in detail the most developed form and structure examples that are most suitable for living conditions with modern electron microscopy techniques. One of these is the ability of lizards, known as the "Gecko Effect", to move rapidly in all conditions (humid, dusty, rainy, and other) vertically and inverted on any surface, defying gravity



a) Gecko, b) bottom of the foot, c) hairy area at the bottom of the foot, d) SEM image of the hairs on the lower part of the gecko foot

Nanomaterials – Modern Applications



The fields of application of NPs are extremely wide and continue to expand every day. A very good analogy is spheres with an increasing diameter, because it exhibits non-linear changes in applications. Thus, the most notable areas of application of new materials are medicine and biotechnology, obtaining materials with special properties, new materials for the production and storage of energy.

Nanotechnology Applications

Automotive

Nanostructured materials are of great importance for the automotive industry. Above all, nanomaterials play a critical role in efforts to reduce vehicle weight, increase structural strength and flexibility, and improve vehicle safety and reliability. With the help of nanotechnology, scratch-resistant, non-polluting and self-healing automotive paints can be applied to the exterior surface of the car.

Nanomaterials in cars make vehicles more environmentally friendly and improve the performance of automotive parts. Automobiles commonly use nanomaterials such as aluminum-carbon nanotube composites, carbon nanotubes, aluminum-silicon-carbide composites, and graphene.

Nanotechnology Applications

Energy

Pyroelectric ZnO nanowires can convert time-dependent temperature differences into electricity by spontaneous polarization in the conversion based on temperature difference. The nanogenerator developed here will be able to meet the energy requirements of nano devices by converting balanced and waste energy.

Nanotechnologies have great potential for cleaner, more efficient and environmentally friendly energy generation. Energy-related technologies where nanotechnologies can play important roles are as follows: lighting, heating, transport, renewable energy, energy storage, fuel cells, hydrogen production and storage.

Nanotechnologies are used in lithium-ion batteries, which are emphasized for hybrid and electric vehicles, and significant improvements have been made in efficiency and effectiveness

REGINNA 4.0

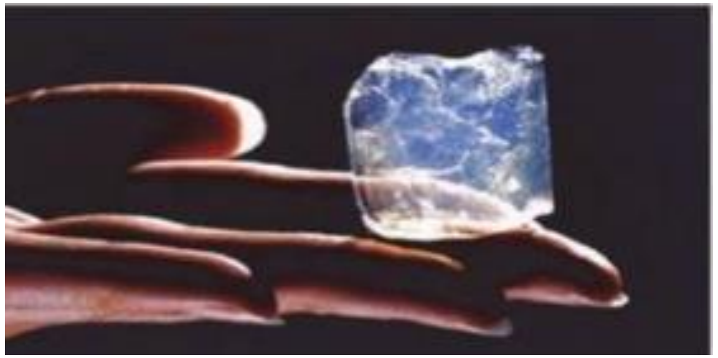
Nanotechnology Applications

Environment

Nanosensor applications that can continuously measure and give warnings and alarms in case of deviation from the given threshold values are becoming widespread in order to monitor air, water and environment pollution. Nanosensors play an indispensable role in monitoring the ecological quality of air, water and environment with precise data. Various nanostructured materials have been developed for the detection of different components.

Environmental cleaning (remediation) consists of works that are free from chemical and radiological contaminants and do not endanger human health, together with separation and other processes. Faster and cost-effective cleaning-purification is possible with nanomaterial applications. The most appropriate approach in nanotechnological methods is selectivity and cleaning and elimination of organic / inorganic pollutants

Aerogels that can effectively clean water, sea-ocean, soil against oil spills, various aerogels and silica aerogels samples



Nanotechnology Applications

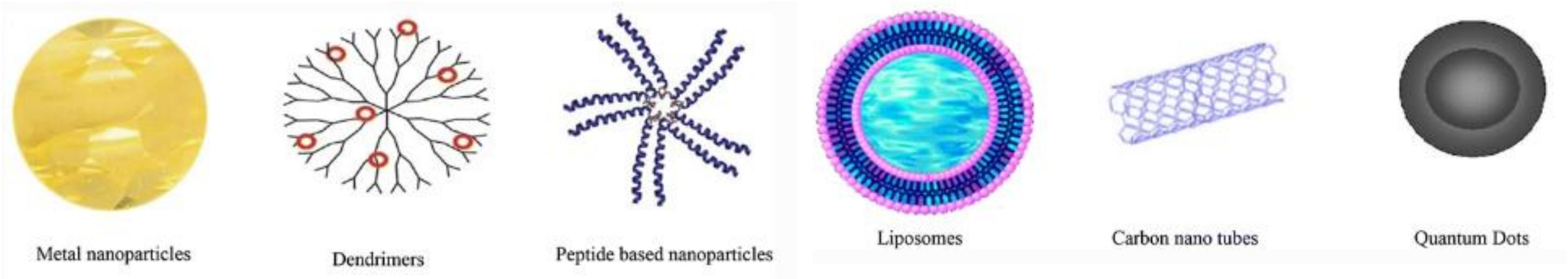
Nanomedicine and drug delivery

Due to the advantage of their size, nanospheres have been shown to be robust drug delivery systems and may be useful for encapsulating drugs and enabling more precise targeting with a controlled release.

Nanoparticles are organic or inorganic structures similar to antibodies and DNA plasmids. Significant work has been done in past decades in the field of nanotechnology; now it is possible to fabricate, characterize, and modify the functional properties of nanoparticles for medical diagnostics and biomedical application.

The most promising application of nanomaterials is the promise of targeted, site-specific drug delivery. The potential of eliminating a tumorous outgrowth without any collateral damage through nanomaterial-based drug delivery has created significant interest and nanoparticles form the basis for bio-nano-materials and major efforts in designing drug delivery systems are based on functionalized nanoparticles.

Modifying or functionalizing nanoparticles to deliver drugs through the blood brain barrier for targeting brain tumors can be regarded as a brilliant outcome of this technology.



Common types of nano-drug carriers.

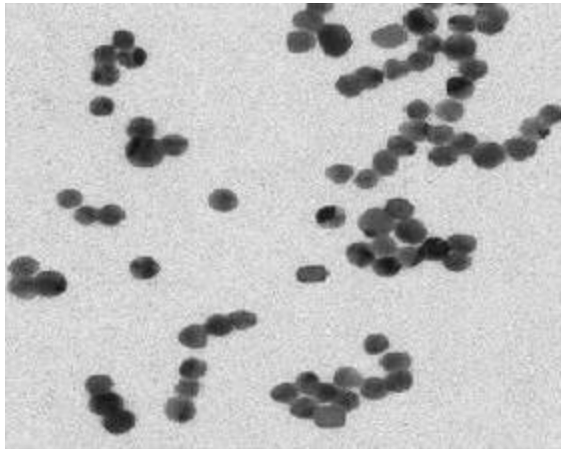
Nanotechnology Applications

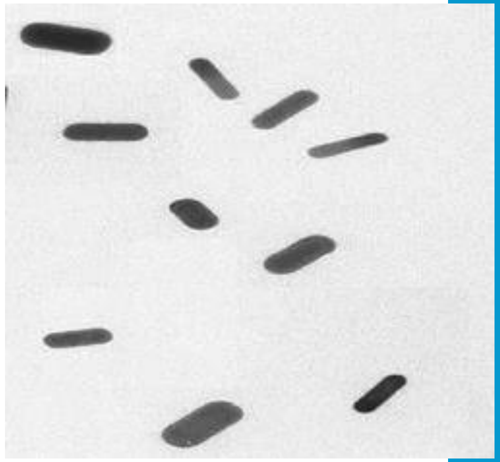
Nanomedicine and drug delivery

Due to their size, shape and functionality, nanoparticle systems play a pivotal role in creation of DNA delivery vectors. They can penetrate deep into tissues and are absorbed by the cells efficiently. Nano-sized colloidal carriers of drugs can be regarded as an advanced development in pharmacotherapy. They act as potential carriers for several classes of drugs like anti-cancer, anti-hypertensive and hormones, etc.

Submicron colloidal particles have been used as nanoparticles for the purpose of drug delivery and also used for the diagnosis of diseases. Nanoparticles have widened the scope of pharmacokinetics for insoluble drugs. For example, the trans-retinoic acid nanoparticle coated by $CaCO_3$ was developed as a new drug delivery system.

Gold nanoparticles and nanorods have many unique properties, which have been explored for potential applications in bio-molecular detection.





TEM images of gold nanoparticles and nanorods

Let's summarize

- The surface area to volume ratio increases as 1/R, and surfaces and interfaces become the main factor influencing material properties, thermodynamic behavior, and dynamics of energy carriers at the nanoscale.
- Diffusion of atoms to surfaces and interfaces changes the conditions of thermodynamic equilibrium.
- Solid-state transfer of heat, matter, charge carriers, photons - they all change at the nanoscale, because scattering centers are farther apart than nanoscale.
- The electronic density of states becomes discontinuous when the dimensions are reduced to quantum wells, quantum wires and quantum dots. This leads to new physical concepts such as energy filtering, "pocket engineering" of carriers, and electronic transitions (such as semimetal-semiconductor transitions).
- Size-dependent energy levels due to quantum confinement change the energy of doped semiconductor nanocrystals
- Liquid transport in nanoscale channels can be improved by atomic smoothness, changing the contact angle, and molecular ordering of transported molecules.

Thank you for your attention!

Liliia Turovska

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