

# **NanoSciences-Questions**

**2023**

Topics in Nanosciences  
End Semester Exam: Monsoon 2023  
IIT-Hyderabad

Full Marks: 100

Time: 3 hr

Important notes:

1. Use of non-programmable scientific calculators is allowed.
2. Some constants, formulas, equations, etc. are given at the end of the question paper. You should pick and use them for your answers. Do not forget to name/define the terms used in these expressions while using them.

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Q1. (a) Mention two currently available commercial products that use nanoparticles in it and write the names of the nanoparticles. [2]

(b) Compare the top-down and bottom-up approaches of synthesis and give examples. [5]

(c) What is meant by 'sintering'? How is it related to nanoscale properties? [3]

Q2. "Hot injection" technique is used to produce monodispersed colloidal nanocrystals." Justify this statement with the help of appropriate mathematical equations and schematic diagrams for the growth rate function. [10]

Q3. (a) Define heterogeneous nucleation. [1]

(b) Draw a schematic diagram showing the comparison of the free energy barriers as a function of the particle size between homogeneous and heterogeneous nucleations. Comment on the salient features of the plot. [4]

(c) Discuss how the affinity (wettability) of the substrate with the "heterogeneous" nucleus controls the energy barrier of the heterogeneous nucleation. [5]

Q4. (a) Mention two microscopy (nanoscopy) techniques that can measure/image surface topography of nanomaterials. [1]

(b) Why are high energy electrons used in electron microscopy techniques? [2]

(c) Name a nanoscopy technique whose work environment can be air or liquid, not necessarily vacuum. Describe the working principle of this nanoscopy technique. [1,4]

(d) What is expected to happen to the peak position and width for the silver nanocrystal (111) plane XRD reflection ( $2\theta=38.20$ ) as the crystallite size reduces from 20 nm to 2 nm? [2]

Q5. (a) Derive an expression that shows how the density of states (DOS) function depends on the energy of a 1D material. Show the graphical plot of the 1D DOS function vs. energy. [4,1]

(b) Name two classical material properties that can show quantized behaviour in nanowires. Confirm it by deriving simple mathematical equation. [1,4]

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1-

A:

### **MRI Contrast Agents**

- **Nanoparticles Used:** Superparamagnetic Iron Oxide Nanoparticles (SPIONs)
- **Example Product:** Feridex (ferumoxides)
- **Purpose:** Used as a contrast agent in MRI to enhance imaging of liver and lymph node tissues.

### **Drug Delivery Systems**

- **Nanoparticles Used:** Liposomes and Polymeric Nanoparticles (e.g., Poly(lactic-co-glycolic acid) - PLGA)
- **Example Product:** Doxil, a liposome-based formulation for delivering the chemotherapy drug doxorubicin.
- **Purpose:** Nanoparticles improve the targeted delivery of drugs, enhancing therapeutic effects while reducing side effects.

B:

Aspect	Top-Down Approach	Bottom-Up Approach
<b>Definition</b>	Breaks bulk material into nanostructures.	Builds nanostructures atom by atom or molecule by molecule.
<b>Control</b>	Less precise control over structure.	High precision in structure and properties.

Example: top down: ball milling and for bottom up: co precipitation

top down: bulk  $\rightarrow$  thin film  $\rightarrow$  nano , bottom  
up  $\rightarrow$  nano  $\rightarrow$  molecules  $\rightarrow$  proteins  $\rightarrow$  structures

C:Sintering is a process where powdered materials are pressed and heated to temperatures close to their bulk melting points, but not below, to compact the particles into a solid shape. This method ensures materials with uniform composition while enhancing their mechanical, electrical, and thermal properties. The nanoscale protrusions on the rough surfaces of powdered particles have lower melting temperatures than the bulk material. During sintering, these protrusions melt and diffuse to neighboring particles, reducing surface energy by decreasing the solid–vapor interface. Upon cooling, the particles solidify into a single cohesive mass.

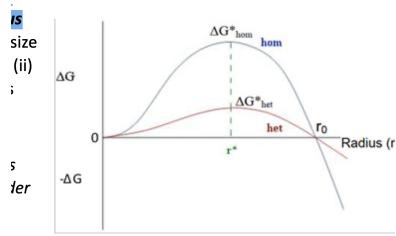
3:

A-

Heterogeneous nucleation occurs when a condensed phase forms on a preexisting condensed phase, typically at specific sites such as grain boundaries, edges, or corners of foreign bodies or solid structures, which facilitate the nucleation process.

b-

C-



Heterogeneous nucleation occurs more readily than homogeneous nucleation due to partial affinity between the particle-forming solid and the foreign solid surface, which releases energy by partially eliminating preexisting interfaces, reducing the free energy barrier. This makes heterogeneous nucleation easier and more frequent, even at lower supersaturation levels. However, in the case of complete nonaffinity, the free energy of heterogeneous nucleation equals that of homogeneous nucleation. Conversely, with complete affinity, such as nucleation

on a seed particle in a supersaturated solution of the same solute, the free energy of nucleation becomes zero.

→ tell using that formula where  $f(\theta)$  gets multiplied hence reducing

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4: same as 2022 → afm and sim for topography and high energy for resolution. and dls

DLS working principle: Dynamic Light Scattering (DLS) is a technique used to measure the size and dynamics of particles in a solution by analyzing fluctuations in the intensity of scattered light caused by the random Brownian motion of the particles. A beam of monochromatic light is directed through a colloidal solution, where particles scatter the light. Larger particles scatter more light and move more slowly than smaller ones. The time-dependent fluctuations in scattering intensity are analyzed through autocorrelation to calculate the diffusion coefficient,  $D$ , and the particle size using the Stokes-Einstein equation. DLS is widely used for nanoparticle size determination, studying colloids, and analyzing particle distribution changes during processes like coating or crystallization.

As the crystallite size of silver nanocrystals decreases from 20 nm to 2 nm, the following changes are expected in the XRD reflection for the (111) plane:

- **Peak Position:** The peak position may slightly shift to a lower  $2\theta$  value due to increased lattice strain caused by surface stress in smaller nanocrystals.
- **Peak Width:** The peak width will increase (broaden) because of the reduction in crystallite size. This broadening is related to the Scherrer equation, which links the peak width inversely to the crystallite size.

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5-

➤ This kind of analysis for the **1-dimensional (nanowire) case** (with  $n^2=n_z^2$ ) gives

$$\text{➤ } N_{tot} = 2 \times \frac{1}{2} \times (n) = n = \left[ \frac{2mEL^2}{\hbar^2\pi^2} \right]^{\frac{1}{2}} = \left[ \frac{2m}{\hbar^2\pi^2} \right]^{\frac{1}{2}} \cdot L \cdot E^{\frac{1}{2}}$$

➤ We have multiplied by 2, since each state can be occupied by two electrons of opposite spin. Also, we have divided by 2 corresponding to the two directions (positive and negative) of the wire.

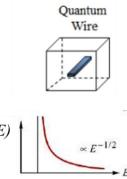
$$\text{➤ } \frac{dN_{tot}}{dE} = \left[ \frac{2m}{\hbar^2\pi^2} \right]^{\frac{1}{2}} \cdot L \cdot \frac{1}{2} \cdot E^{\left(-\frac{1}{2}\right)}$$

$$\text{➤ } \frac{1}{L} \cdot \frac{dN_{tot}}{dE} = \frac{\sqrt{m}}{\hbar\pi\sqrt{2}} \cdot E^{\left(-\frac{1}{2}\right)}$$

➤ The **density  $D(E)$  of states** near energy  $E$  is therefore given as:

$$\text{➤ } D(E)_{1D} = \frac{\sqrt{m}}{\pi\hbar\sqrt{2}} \cdot E^{\left(-\frac{1}{2}\right)}$$

➤ Here the density of states drops as  $E^{-1/2}$ , which reflects the growing spacing of states with



Name two classical material properties that can show quantized behaviour in nanowires.

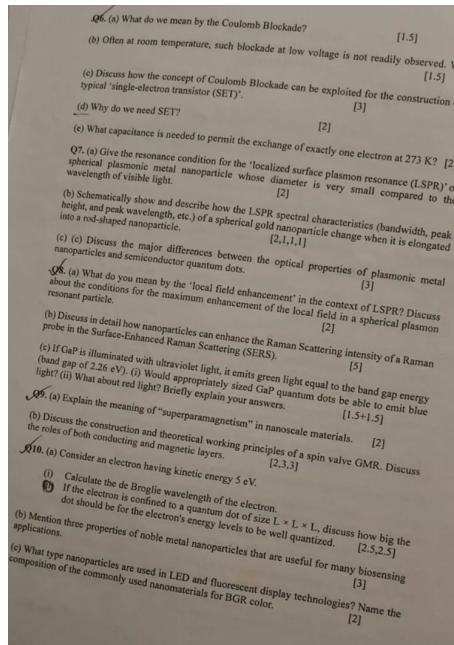
Confirm it by deriving simple mathematical equation.

For this we can consider thermal conductance and resistance and also electrical conductance and resistance  $\rightarrow e^2/2h$  thing we can derive from, done in last year exam, for thermal conductance assign the relation here

electronic contribution of the thermal conductivity ( $\kappa$ ) to the electrical conductivity ( $G_o$ ) of a metal is proportional to the temperature (T).

$$\text{➤ } \kappa / G_o = LT$$

➤ Theoretically, the proportionality constant  $L$ , known as the Lorenz number, is equal to



6-

A: The Coulomb Blockade is a phenomenon observed in nanoscale systems, where the flow of electrons through a device is inhibited due to the charging energy associated with adding an additional electron. This occurs because the capacitance of the system is so small that the energy required to add one electron becomes significant compared to thermal energy.

B-At room temperature, the thermal energy ( $k_B T$ ) is high enough to overcome the charging energy required to add an electron, thus masking the Coulomb Blockade effect.

C-The Coulomb Blockade forms the basis of SETs by controlling the tunneling of individual electrons through a quantum dot between source and drain electrodes. By tuning the gate voltage, the energy levels of the quantum dot can be aligned or misaligned with the electrodes, allowing for single-electron transport.

D-SETs are essential for applications requiring ultra-low power consumption, high sensitivity in charge detection, and nanoscale electronics. They are widely used in quantum computing and advanced sensing technologies.

**(e) What capacitance is needed to permit the exchange of exactly one electron at 273 K?**

The charging energy  $E_c = \frac{e^2}{2C}$  should be comparable to or greater than the thermal energy ( $k_B T$ ) for Coulomb Blockade to occur.

$$C = \frac{e^2}{2k_B T}$$

At 273 K ( $T = 273$  K),

$$C = \frac{(1.6 \times 10^{-19} \text{ C})^2}{2 \times (1.38 \times 10^{-23} \text{ J/K}) \times 273} \approx 2.9 \text{ aF (attofarads).}$$

7-

a

The resonance condition for **Localized Surface Plasmon Resonance (LSPR)** of a spherical plasmonic metal nanoparticle is based on the condition where the frequency of the incident light matches the natural frequency of oscillation of the conduction electrons in the nanoparticle.

$$\lambda_{max}^2 = \lambda_p^2(\epsilon_{\infty} + 2\epsilon_{dielectric})$$

b:

1. **Splitting of the Plasmon Band:**

- The **plasmon absorption** splits into two distinct bands due to the anisotropic shape of the rod-shaped nanoparticle:
- **Longitudinal Mode:** This mode corresponds to the oscillation of free electrons along the long axis of the rod. It experiences a **red-shift** (shift to longer wavelengths) as the aspect ratio  $R$  (length-to-width ratio) of the rod increases. This shift occurs because the longer the rod, the lower the energy required to excite the longitudinal plasmon mode.
- **Transverse Mode:** This mode corresponds to oscillations of free electrons perpendicular to the long axis of the rod. The transverse plasmon resonance is

similar to that of spherical particles and typically shows a resonance around **520 nm**, which coincides with the plasmon peak of spherical gold nanoparticles.

## 2. Peak Wavelength:

- **Longitudinal Mode:** The resonance wavelength for the longitudinal mode is **red-shifted** with increasing aspect ratio  $R$ . The larger the rod, the more pronounced the shift toward longer wavelengths.
- **Transverse Mode:** The resonance wavelength for the transverse mode remains similar to that of spherical particles, around **520 nm**, and does not experience a large shift.

## 3. Bandwidth:

- The **bandwidth** of the plasmon resonance typically increases in rod-shaped nanoparticles compared to spherical ones due to the complexity of electron oscillations along different axes in the anisotropic shape.

## 4. Peak Height:

- The **peak height** tends to decrease for rod-shaped nanoparticles, especially in the longitudinal mode, due to the more complex and spread-out electron oscillations, leading to a less intense peak compared to spherical nanoparticles.

### Schematic Representation:

- **Spherical Nanoparticle:** A single plasmon resonance peak around 520 nm.
- **Rod-Shaped Nanoparticle:** Two distinct peaks—one around 520 nm (transverse mode) and another red-shifted peak (longitudinal mode) that depends on the aspect ratio of the rod.

In summary, elongating a gold nanoparticle into a rod shape leads to a splitting of the plasmon resonance into longitudinal and transverse modes, with the longitudinal mode experiencing a red shift and becoming more dependent on the rod's aspect ratio.

### Difference Between Semiconducting and Plasmonic Metal Nanoparticles:

- **Metal Nanoparticles:** Governed by **Localized Surface Plasmon Resonance (LSPR)**, where the conduction electrons oscillate in response to light.

- **Plasmon Resonance Peak:** Characteristic absorption peak due to collective electron oscillations.
  - **Application: Surface-Enhanced Raman Spectroscopy (SERS)** for enhancing Raman signals.
  - **Semiconducting Nanoparticles:** Governed by **Quantum Confinement Effects**, where electron and hole confinement in small structures results in discrete energy levels.
  - **Absorption and Emission Peaks:** Size-dependent peaks due to quantum effects.
  - **Application: Light Emitting Diodes (LEDs) and fluorescence** due to size-dependent emission.
- 

8 - this is teh condition for maximum ,  $E=E_0 + \epsilon_{neighbour}$

$$E_{loc} = \frac{3\epsilon}{\epsilon + 2\epsilon_m} E_0$$

**Local Field Enhancement** refers to the increase in the electromagnetic field near a nanoparticle when it is in resonance with the incident light, such as in **Localized Surface Plasmon Resonance (LSPR)**. This occurs due to the collective oscillation of conduction electrons on the surface of the nanoparticle when the incident light frequency matches the plasmon resonance frequency of the nanoparticle. This enhancement leads to an amplification of the local electric field around the nanoparticle, which can significantly increase the interaction of the nanoparticle with surrounding molecules.

**Conditions for Maximum Enhancement in a Spherical Plasmon Resonant Particle:**

1. **Resonance Condition:** Maximum field enhancement occurs when the frequency of the incident light matches the natural resonance frequency of the particle, which is determined by the particle's size, shape, and the dielectric properties of the surrounding medium.

B-

Surface-Enhanced Raman Scattering (SERS) refers to the phenomenon where the Raman scattering intensity of a molecule is significantly enhanced when it is placed near a nanoparticle or roughened metal surface. Nanoparticles, particularly those made from plasmonic metals like silver or gold, can enhance the Raman scattering signal by orders of magnitude. This enhancement happens due to two key mechanisms:

1. **Electromagnetic Enhancement:**

- The local field enhancement (described in part a) around the nanoparticle during LSPR leads to a stronger interaction between the incident light and the Raman probe molecule. When the molecule is near the nanoparticle, the oscillating electric field at the surface of the nanoparticle enhances the Raman scattering signal. The intensity of the scattered light increases in proportion to the fourth power of the local field enhancement.
- **Localized Plasmon Resonance (LSPR)** of the nanoparticle, when matched to the frequency of incident light, increases the local electromagnetic field, which boosts the Raman scattering intensity.

2. **Chemical Enhancement:**

- In addition to electromagnetic enhancement, the interaction between the nanoparticle and the molecule can lead to charge transfer between the molecule and the nanoparticle. This interaction can modify the electronic properties of the molecule, making it more likely to scatter light. This chemical enhancement is usually smaller than the electromagnetic enhancement but still contributes to the overall intensity boost.
- The proximity of the molecule to the metal surface also leads to changes in the molecule's electronic structure, further amplifying the Raman signal.

C- so here the solution is that quantum dot would have more energy than the bulk ie the band gap hence smaller wavelength can be emitted hence blue etc not red

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9-

A

**Superparamagnetism** is a phenomenon observed in very small ferromagnetic or ferrimagnetic nanoparticles, where the magnetic moments of individual nanoparticles can randomly flip direction due to thermal fluctuations. This occurs when the nanoparticle size is below a certain critical size (typically less than 10 nm), leading to the behavior of the particles being dominated by the effects of thermal energy rather than the collective behavior of the magnetic domains in larger materials.

In this state, the particles do not exhibit permanent magnetization; instead, they behave like paramagnets at room temperature. The thermal energy is sufficient to overcome the energy barrier that would otherwise maintain a stable magnetic moment. Superparamagnetism is commonly observed in nanoparticles used for applications such as magnetic resonance imaging (MRI) and data storage.

B-

A **spin valve Giant Magnetoresistance (GMR)** device is a type of multilayer structure that exhibits a change in electrical resistance depending on the relative orientation of the magnetization in two magnetic layers. This phenomenon is based on the principle of **Giant Magnetoresistance (GMR)**, which is the change in electrical resistance due to the alignment or misalignment of the magnetization in adjacent magnetic layers.

#### **Construction:**

- **Magnetic Layers:** The spin valve consists of alternating thin layers of **ferromagnetic materials** and **non-magnetic materials**. Typically, there are two ferromagnetic layers separated by a non-magnetic layer, such as copper (Cu).
- **Fixed and Free Layers:**

- **Fixed Layer:** One ferromagnetic layer has its magnetization direction fixed (often pinned by an antiferromagnetic layer or external field).
- **Free Layer:** The other ferromagnetic layer's magnetization is free to rotate with an external magnetic field.
- **Non-Magnetic Layer:** This layer, usually made of copper or another conducting material, separates the magnetic layers and facilitates the spin-dependent scattering of electrons.

### Working Principles:

- **Spin-Dependent Scattering:** The GMR effect arises because the electron scattering depends on the alignment of the spins of the electrons in the current and the magnetization of the ferromagnetic layers. When the magnetization of the two ferromagnetic layers is aligned (parallel), the resistance is low because electron spins easily align with the magnetic moments, leading to fewer scatterings.
- **Antiparallel Alignment:** When the magnetizations of the two ferromagnetic layers are oppositely aligned (antiparallel), the resistance increases. In this case, the electrons are scattered more because the spins of the electrons are opposite to the magnetic moments, leading to greater resistive loss.

### Roles of the Layers:

- **Conducting Layer (Non-Magnetic Layer):** The conducting (non-magnetic) layer, typically copper, allows for electron flow between the magnetic layers. The thickness of this layer affects the efficiency of the GMR effect.
- **Magnetic Layers:** The two magnetic layers (fixed and free) play crucial roles in determining the device's resistance. The free layer's magnetization can switch direction in response to an external magnetic field, while the fixed layer provides a stable reference for the free layer's magnetization.

### Application:

Spin valve GMR devices are widely used in **magnetic sensors** (e.g., in hard disk drives for read heads) and **memory storage devices** because of their sensitivity to magnetic fields and the ability to store data based on the alignment of the magnetic layers.

### 1. de Broglie Wavelength Calculation:

The de Broglie wavelength ( $\lambda$ ) of an electron is given by the formula:

$$\lambda = \frac{h}{p}$$

where:

- $h$  is Planck's constant ( $6.626 \times 10^{-34}$  Js),
- $p$  is the momentum of the electron, which can be related to its kinetic energy ( $E_k$ ) by the equation  $p = \sqrt{2mE_k}$ , where  $m$  is the mass of the electron ( $9.11 \times 10^{-31}$  kg).

Given:

- $E_k = 5 \text{ eV} = 5 \times 1.602 \times 10^{-19} \text{ J}$ ,
- $m = 9.11 \times 10^{-31} \text{ kg}$ .

First, calculate the momentum:

$$p = \sqrt{2 \times 9.11 \times 10^{-31} \times 5 \times 1.602 \times 10^{-19}} \approx 1.52 \times 10^{-24} \text{ kgm/s}$$

Now, calculate the wavelength:

$$\lambda = \frac{6.626 \times 10^{-34}}{1.52 \times 10^{-24}} \approx 4.36 \times 10^{-10} \text{ m} = 0.436 \text{ nm}$$

So, the de Broglie wavelength of the electron is approximately **0.436 nm**.

### 2. Size of Quantum Dot for Well-Quantized Energy Levels:

For the energy levels of the electron in a quantum dot to be well quantized, the size of the quantum dot ( $L$ ) should be small enough that the electron is confined  $\downarrow$  all three dimensions. Typically, the condition for

### (b) Properties of Noble Metal Nanoparticles for Biosensing Applications

1. **Surface Plasmon Resonance (SPR):** Noble metal nanoparticles, like gold and silver, exhibit a strong SPR effect, which can be tuned by adjusting the particle size, shape, and surrounding environment. This allows for highly sensitive detection in biosensing applications.
2. **Biocompatibility:** Noble metals such as gold and silver are biocompatible, making them suitable for use in biological environments without causing toxic effects.
3. **Surface Functionalization:** Noble metal nanoparticles can easily be functionalized with various biomolecules (e.g., antibodies or DNA), enabling targeted interactions for specific biomarker detection in sensing applications.

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### (c) Nanoparticles in LED and Fluorescent Display Technologies

1. **Nanoparticles Used:** **Quantum dots (QDs)** are used in LED and fluorescent display technologies. These nanoparticles are typically made from semiconductor materials like cadmium selenide (CdSe), cadmium sulfide (CdS), or indium phosphide (InP).
2. **BGR Color Nanomaterials:**
  - **Blue:** Indium Gallium Nitride (InGaN) quantum dots.
  - **Green:** Cadmium Selenide (CdSe) quantum dots.
  - **Red:** Cadmium Selenide (CdSe) quantum dots, typically with a larger size for red emission.

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No problem at all! I hope this answers your questions clearly. ↓ u ever want to talk more about nano or anything else, feel free to ask!

**2022**

**Give the increasing order of the (re)activities of kink corner, edge, and surface atoms.**

kink > corner > edge > surface atoms. Surface atom have the highest coordination number Hence it would have lowest reactivity.

**Q.2.** In the following, the chiral vectors of some CNTs are given:

(i)  $c = 9a_1$  (ii)  $c = 9a_2$  (iii)  $c = 9a_1 + 9a_2$  (iv)  $c = 9a_1 + 7a_2$ .

(a) What is the type of nanotube formed in each case? Justify.

(b) Arrange these tubes in the order of increasing diameter.

(c) Which of these tubes is metallic, and which is semiconducting? Why?

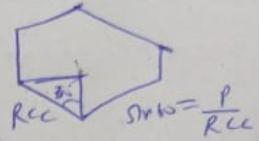
**Solution :**

A) - (n,0) : zig zag, (m,0):zig zag , (m,m):arm chair, (n,m):chiral

C)- iii is arm chair hence metallic apart for I,ii,iv they can be either metallic or semiconductor, I,ii nearly metallic as 3j , while not iv it will be more semiconductors

B) -

$$\begin{aligned}
 \pi \vec{d} &= \vec{C} \\
 \vec{C}^2 &= |ma+nb|^2 \\
 \vec{C}^2 &= |ma|^2 + |nb|^2 + 2|ma||nb| \cos \pi/3 \\
 \vec{C} &= \sqrt{m^2 R_{CC}^2 + n^2 R_{CC}^2 + 2mn R_{CC}^2 \cos \pi/3} \\
 \vec{C} &= 3R_{CC} \sqrt{m^2 + n^2 + 2mn \cos \pi/3} \\
 \vec{C} &= \sqrt{3} R_{CC} \sqrt{m^2 + n^2 + mn} \\
 \pi d &= \sqrt{3} R_{CC} \sqrt{m^2 + n^2 + mn} \\
 d &= \frac{\sqrt{3} R_{CC}}{\pi} \sqrt{m^2 + n^2 + mn}
 \end{aligned}$$



- (I)  $n=9, m=0 \quad d = 9R$   
 (II)  $m=9, n=0 \quad d = 9K$       (III)  $\times$  (IV)  $\Rightarrow i = ii$   
 (IV)  $m=9, n=9 \quad d = 9\sqrt{3}K$   
 (V)  $m=9, n=7 \quad d = \sqrt{9^2 + 7^2 + 9 \cdot 7}K$

**Q.3. (a) Mention two microscopy (nanoscopy) techniques that can measure/image the surface topography of nanomaterials.**

answer: Atomic Force Microscopy and Scanning Tunneling microscopy.

**Why are high-energy electrons used in electron microscopy techniques?**

We know that the resolution is given by  $\frac{\lambda}{2n \sin \theta}$ . In order to decrease the wavelength, we know that  $p = \frac{h}{\lambda}$ , so to decrease  $\lambda$ , we need to increase the velocity. Hence, high potential and high-energy electrons are required to ensure that the resolution can be measured accurately. High energy also allows the electrons to penetrate the sample while interfering less with the medium.

**Name a nanoscopy technique whose work environment can be air or liquid, not necessarily vacuum.**

One such technique is **Dynamic Light Scattering (DLS)**.

DLS is a technique that relies upon temporal fluctuations in the light scattered from an ensemble of particles to determine their motion.

- Typically, the motion in colloidal or aerosol systems is random Brownian motion, which is quantified by a size-dependent diffusion coefficient,  $D$ .
- The DLS method measures the decay of the temporal fluctuations in the scattered light, which is related to the particles' diffusion. This diffusion is, in turn, related to their size.

**Mention three intensive properties' that do not remain intensive' in nanomaterials**

Solubility, melting point, color

## **When do size effects begin to appear in materials?**

Size effects begin to appear in materials when the size of the particle reaches the characteristic wavelength, such as the Fermi wavelength, domain length, or diffusion length.

**When the characteristic size (D) (e.g., diameter, thickness, length) of the building blocks of microstructures becomes comparable to or smaller than the length scale (l) of the physical phenomenon (e.g., mean free path length of electrons, phonons, etc.; coherent length, screening length), quantum size effects on the material properties begin to appear.**

## **Why do the surface-interface effects play a great role in determining the material properties in the nanomaterials, unlike bulk materials?**

As the particle size decreases, the fraction of atoms on the surface increases drastically relative to the volume. Properties such as melting point and solubility depend significantly on the surface atoms. Since the number of surface atoms is much higher in nanomaterials (with less coordination number hence more reactive) compared to bulk materials, they become more reactive, leading to changes in various material properties.

Q.4. (a) Define and explain the phenomenon of Ostwald Ripening by using an appropriate thermodynamic expression. [1,3]

$$\mu_P(sol) - \mu_S(sol) = \frac{2\gamma_{SL}}{\rho r}$$

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At this point, **the difference results proportional to the surface area of the particle**, the chemical potential can be expressed in terms of the chemical potential of the molecules in the pure liquid phase and  $\mu^0$  is the chemical potential of the pure liquid phase,  $\rho$  is the universal gas constant, and  $T$  is the Kelvin temperature. Substituting this into the former equation, one gets

$$\mu_i(sol) = \mu^0 + RT \ln(x_i)$$

Chemical potential of the molecules in the solution phase and  $\mu^0$  is the chemical potential of the pure liquid phase,  $\rho$  is the universal gas constant, and  $T$  is the Kelvin temperature. Substituting this into the former equation, one gets

$$\ln\left(\frac{x_P}{x_S}\right) = \frac{1}{\rho RT} \frac{2\gamma_{SL}}{r}$$

In other words, the smaller the particle, the more energetically favorable the dissolution becomes. As a result, molecules that dissolve from smaller particles tend to "prefer" to recondense onto larger particles rather than returning to the smaller ones. This leads to the growth of larger particles over time, both in terms of size and relative number, at the expense of the smaller ones, which tend to shrink and eventually dissolve completely. This process decreases the solute concentration in the solution.

This peculiar time evolution of the particle size distribution is a well-established phenomenon known as **Ostwald ripening**.

(b) What is the effect of Ostwald Ripening on the size distribution (dispersity) of the nanoparticle dispersions? [1]

Smaller particle tend to shrink and ultimately dissolve into the solution while the larger particle tend to grow on the expense of the smaller particle

(c) How does the Cassie-Baxter model differ from the Wenzel model in explaining the superhydrophobicity of a surface?

## 1. Wenzel Model

- **Concept:** The Wenzel model assumes that the liquid fully wets the surface asperities, or rough structures, and the liquid follows the contours of the surface. Essentially, the liquid "invades" the roughness features of the surface.
- **Contact Angle:** In this model, the apparent contact angle ( $\theta_x$ ) is related to the intrinsic contact angle ( $\theta_Y$ ) of the smooth surface and the roughness factor ( $r$ ), where  $\cos \theta_W = r \cos \theta_Y$ .
- The roughness factor  $r$  is defined as the ratio of the actual surface area to the projected area.
- This model is primarily applicable to surfaces where the roughness leads to an increase in surface area and consequently a larger contact angle for hydrophobic surfaces.
- For **hydrophobic surfaces** (where  $\theta_Y > 90^\circ$ ), roughness increases the contact angle, making the surface more hydrophobic.
- For **hydrophilic surfaces** (where  $\theta_Y < 90^\circ$ ), roughness decreases the contact angle, making the surface more hydrophilic.

## 2. Cassie-Baxter Model

- **Concept:** The Cassie-Baxter model explains the behavior of liquid droplets on rough surfaces where the liquid does not fully wet the surface but instead rests on top of the asperities. A key characteristic of this model is that there is an air layer trapped between the liquid and the solid surface, effectively reducing the contact area between the liquid and the surface.
- **Contact Angle:** The apparent contact angle ( $\theta_{CB}$ ) in this model is a composite of the contributions from the solid and the air phases. It is given by:

$$\cos \theta_{CB} = f_1 \cos \theta_Y + f_2 \cos \theta_A$$

Where:

- $f_1$  and  $f_2$  are the area fractions of the solid and air phases, respectively, in contact with the liquid.
- $\theta_Y$  and  $\theta_A$  are the Young's contact angles for the solid and air phases, respectively.

- Since the air phase has a contact angle near  $180^\circ$  (because it doesn't interact with the liquid), the overall contact angle increases with the amount of trapped air on the surface.
- This leads to a **superhydrophobic** effect, with higher contact angles and lower hysteresis compared to the Wenzel model.

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Q.5. (a) Compare the mechanisms responsible for the appearance of colors in the suspensions of

[2]

metal and semiconductor nanoparticles.

1. **Metal Nanoparticles:**

- The color in metal nanoparticle suspensions arises primarily due to **Localized Surface Plasmon Resonance (LSPR)**. This phenomenon occurs when the conduction electrons on the metal surface oscillate collectively in response to incident light, leading to a resonance condition at certain wavelengths.
- The LSPR is strongly dependent on the size, shape, and material of the nanoparticles. Metal nanoparticles such as gold (Au), silver (Ag), and copper (Cu) show vivid colors, which are a result of the interaction between the electromagnetic field of light and the surface electrons of the nanoparticles.

2. **Semiconductor Nanoparticles:**

- For semiconductor nanoparticles, the color is mainly attributed to **quantum size effects**, where the energy levels become discrete (quantized) as the particle size decreases. In semiconductor nanoparticles, the bandgap widens as the particle size decreases, shifting the absorption and emission spectra toward higher energies (bluer light).
- This phenomenon is governed by **quantum confinement**, where electrons are confined in all three dimensions. The color seen in semiconductor nanoparticles is not due to plasmon resonance but to the energy difference between the valence band and conduction band.

(b) Discuss the nanoparticle size effects on the nature of (bandwidth, peak height, peak wavelength, etc., of) the LSPR (localized surface plasmon resonance). [3.5]

. **Bandwidth:**

- As the size of metal nanoparticles decreases, the **LSPR bandwidth** generally increases due to increased scattering and damping effects. Smaller nanoparticles have less efficient coupling of their plasmon modes to the surrounding medium, leading to a broader resonance.

2. **Peak Height:**

- The **LSPR peak height** is inversely related to particle size. Larger nanoparticles produce more intense plasmonic resonance, whereas smaller nanoparticles show lower peak heights due to fewer surface electrons participating in the resonance.

3. **Peak Wavelength:**

- Peak wavelength** shifts depending on particle size. Smaller nanoparticles shift the LSPR absorption peak to shorter wavelengths (blue shift), while larger nanoparticles shift the peak to longer wavelengths (red shift). This is due to the size-dependent changes in the plasmon resonance frequency.

(c) Two colorless, odorless, and transparent solutions are given to you: one containing an aq. protcin solution and the other an aq. solution of the poison, potassium cyanide. How could you distinguish/identify them using the optical property of gold nanoparticles dispersed in water? Use appropriate theoretical relationships to justify your answers.

A **larger red shift** can be observed with increasing cyanide concentration. This shift is due to the strong interaction between the  $\text{CN}^-$  ions and the gold nanoparticle surface, which causes the nanoparticles to aggregate.

**Practical Distinction:** Measure the **LSPR absorption spectrum** of the gold nanoparticles in both solutions. The KCN solution will exhibit a more pronounced red shift, while the protein solution will have a smaller or even no noticeable shift in comparison.

Q.6. (a) Name two methods that can be applied for nanoscale distance measurements. [1]  
(b) Describe how the assembly-disassembly property of functionalized gold nanospheres can be used for the highly sensitive optical detection of trace amounts of sequence-specific DNA strands. [3.5]  
Describe the principles of this sensing method [3.5]  
(c) Discuss the conditions for the maximum enhancement of the local field on a small spherical plasmonic nanoparticle. [2]  
(d) What is “Surface-Enhanced Raman Scattering (SERS)”? Describe its mechanisms. [3.5]

a- atomic force microscopy and other is scanning tuning microscopy

b)-

he gold nanospheres were functionalized in a programmed scheme such that the presence of a DNA strand with the correct sequence would trigger DNA hybridization and the assembly of the gold nanoparticles. This assembly-induced shift allows for the sensing of trace amounts of sequence-specific DNA strands.

- DNA-AuNPs can be assembled into different structures by designing linker DNA with a complementary sequence. The assembly process is marked by a dramatic red-to-blue color change, along with dampening and red shifting of the surface plasmon. After DNA duplex formation, the DNA-AuNP assembly process is reversible.
- By denaturing the interconnecting DNA duplexes within the AuNP assembly, the DNA-AuNPs can be redispersed, and the red color returns.
- This “melting” process can be induced by an increase in temperature or a decrease in salt concentration.

c)

$$E_{loc} = \frac{3\epsilon}{\epsilon + 2\epsilon_m} E_0$$

d)- mechanism so effect increase 10-50 time , surface area increase due to reosenece of particles ,

The enhancement in scattering on roughened noble metal surfaces.

- A discovery was made that the Raman cross-section of a material can be increased by a factor of  $10^7$  or more by the presence of metal colloids or roughened metal surfaces. This effect is called surface-enhanced Raman scattering (SERS). It is now commonly accepted that the enhancement mechanism has two components: electromagnetic (EM), which is related to the surface plasmons, and chemical, which is related to charge transfer between the metal surface and the adsorbed molecule.
- The contribution of the EM enhancement is much larger than that of the charge transfer, which depends on the chemical properties of the molecule.

**Q.7.** (a) Show the full-loop hysteresis curves for ferromagnetic, paramagnetic, and superparamagnetic materials on the same plot. Show all the cardinal points  $M_s$ ,  $M_r$ , and  $H_c$  on the hysteresis curves. Compare the salient features of the plots. [3]

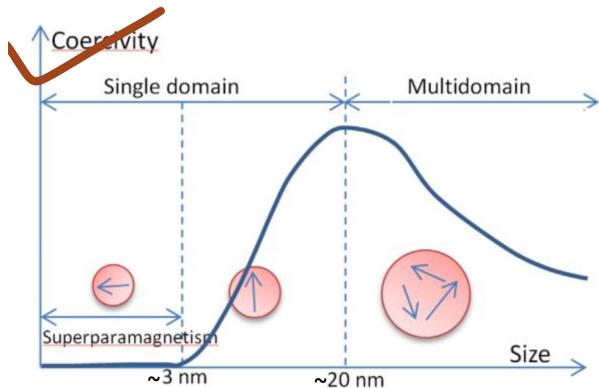
(b) Draw a schematic plot showing the variation of the coercivity of a ferromagnetic particle with its size. Justify the nature of the variation. [3]

(c) Show that a particle acts superparamagnetically on the 100 s experimental timescale if it has a volume smaller than the critical volume,  $V_{sp} = 25kT_B/K$  (the terms have their usual meanings). [4]

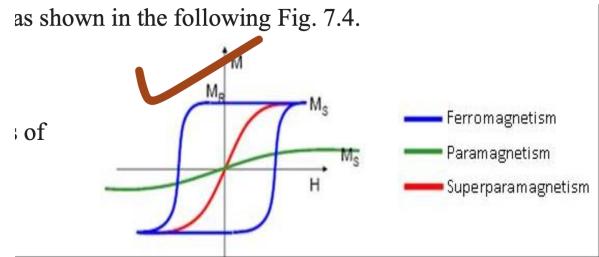
for a measurement time of 100 s, and taking  $f_0$  to be  $10^9$ , one gets

$$\frac{1}{100} = 10^9 \exp\left(-\frac{KV}{kT_B}\right) \quad \text{or} \quad KV \approx 25 kT_B$$

and so, the superparamagnetism will be observed only above a temperature  $T_B = KV/25k$  (note: it is **true for the 100 second *experimental timescale***).



as shown in the following Fig. 7.4.



Q.8. (a) Why is Giant Magnetoresistance (GMR) a quantum mechanical and a nanoscale effect?

[1.5] devices?

**Giant Magnetoresistance (GMR)** is a **quantum mechanical** and **nanoscale** effect because it arises from the behavior of electrons in nanometer-scale materials. At this scale, electron scattering and spin-dependent transport dominate the material's properties.

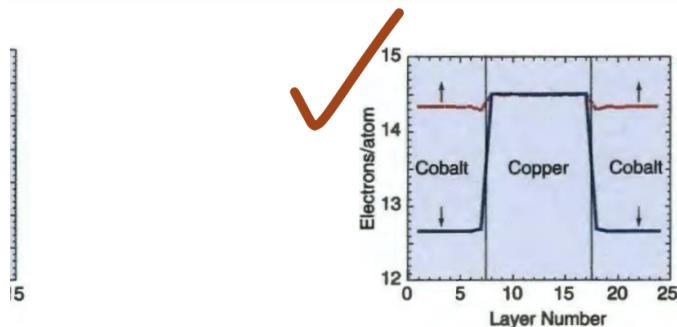
- **Quantum Mechanical:** GMR is based on quantum principles, such as the spin of electrons and the quantum interference of electron waves in thin films. The alignment of electron spins in ferromagnetic layers and their interaction with electron scattering at the interfaces between layers are key factors that determine the resistance.
- **Nanoscale Effect:** GMR occurs in thin-film structures, typically consisting of alternating layers of ferromagnetic and non-magnetic materials at the nanometer scale. The small size of these layers (typically just a few nanometers thick) allows for spin-dependent electron scattering, which is not observed in bulk materials.

(b) How does the construction of a spin valve differ from the magnetic tunneling junction (MTJ) [2.5]

In a **spin valve**, the construction involves two ferromagnetic layers separated by a non-magnetic spacer layer (often made of copper). The magnetization direction of one ferromagnetic layer is pinned by an adjacent antiferromagnetic layer, while the magnetization of the other ferromagnetic layer can be aligned either parallel or antiparallel to the pinned layer. When the magnetization directions are parallel, the resistance is low (a "low resistance state"), and when the magnetizations are antiparallel, the resistance is high (a "high resistance state"). This change in resistance is due to the spin-dependent scattering of electrons at the interface between the ferromagnetic layers.

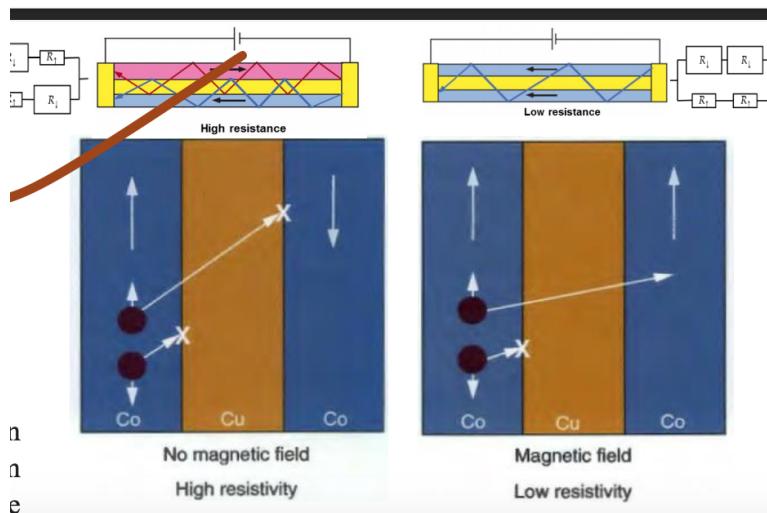
In a **magnetic tunneling junction (MTJ)**, the structure consists of two ferromagnetic layers separated by a thin insulating barrier, typically an oxide (such as aluminum oxide). The magnetization directions of the two ferromagnetic layers can also be parallel or antiparallel. The key difference here is that in an MTJ, electron tunneling occurs through the insulating barrier, and the resistance depends on the relative alignment of the magnetization directions of the ferromagnetic layers. When the magnetizations are parallel, tunneling is more efficient, resulting in low resistance, and when they are antiparallel, tunneling is less efficient, resulting in high resistance. The electron tunneling process in MTJs is governed by the spin polarization of the ferromagnetic layers, which makes MTJs particularly useful for spintronic applications.

(c) Discuss the mechanism (with the help of a schematic diagram) of a GMR device composed of the nanoscale ferromagnetic layers of cobalt separated by the nanoscale nonmagnetic layer of copper.



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Fig. 8. The number of up-spin (red curve) electrons per atom hardly changes between the cobalt and copper layers, but the number of down-spin electrons is much lower for cobalt than for copper.



[4]

(d) Currently, the best technology of 'Read' sensors employ the GMR effect."

Briefly explain

how the GMR effect is used in the 'Reading' head for information retrieval.

he **Giant Magnetoresistance (GMR)** effect is used in 'Read' sensors to retrieve information from magnetic storage devices like hard disk drives (HDDs). Here's a simplified explanation:

1. **Structure:** The GMR sensor in the 'Reading' head is made up of two ferromagnetic layers separated by a non-magnetic spacer layer (like copper). One of the ferromagnetic layers is fixed in place (pinned), while the other is free to rotate.
2. **How it works:** The information on a hard disk is stored as magnetized regions, each with a magnetic direction (north or south). When the GMR read head passes over these regions, the direction of magnetization in the magnetic domains affects the free layer in the GMR sensor.
3. **Change in Resistance:** If the magnetization of the domain aligns with the free layer, the resistance of the GMR sensor is low. If the magnetization is opposite (antiparallel), the resistance is high.
4. **Sensing the Information:** As the head moves over the disk, the change in resistance (from high to low or vice versa) is measured, and this change corresponds to the stored data, allowing the sensor to read the information.

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Q.9. (a) Derive an expression that shows how the density of states (DOS) function depends on the energy of a 1D material.

- For simplicity, let's use a cubical box that has equal length sides  $L$ . In this case, the total energy  $E$  is: 
$$E = \frac{\hbar^2 \pi^2}{2mL^2} [n_x^2 + n_y^2 + n_z^2].$$
- The latter quantity  $[n_x^2 + n_y^2 + n_z^2]$  can be thought of as the square of the length of a vector  $\mathbf{n}$  having three components  $n_x, n_y, n_z$ . Then...  $E = (\hbar^2 \pi^2 / 2mL^2) n^2$  and  $n = (2mL^2 E / \hbar^2 \pi^2)^{1/2}$ .

➤ This kind of analysis for the **1-dimensional (nanowire) case** (with  $n^2=n_z^2$ ) gives

$$\text{➤ } N_{tot} = 2 \times \frac{1}{2} \times (n) = n = \left[ \frac{2mEL^2}{\hbar^2\pi^2} \right]^{\frac{1}{2}} = \left[ \frac{2m}{\hbar^2\pi^2} \right]^{\frac{1}{2}} \cdot L \cdot E^{\frac{1}{2}}$$

➤ We have *multiplied by 2, since each state can be occupied by two electrons of opposite spin.* Also, we have *divided by 2 corresponding to the two directions (positive and negative) of the wire.*

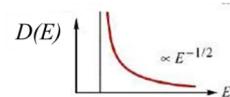
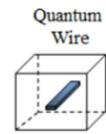
$$\text{➤ } \frac{dN_{tot}}{dE} = \left[ \frac{2m}{\hbar^2\pi^2} \right]^{\frac{1}{2}} \cdot L \cdot \frac{1}{2} \cdot E^{\left(-\frac{1}{2}\right)}$$

$$\text{➤ } \frac{1}{L} \cdot \frac{dN_{tot}}{dE} = \frac{\sqrt{m}}{\hbar\pi\sqrt{2}} \cdot E^{\left(-\frac{1}{2}\right)}$$

➤ The **density  $D(E)$  of states** near energy  $E$  is therefore given as:

$$\text{➤ } D(E)_{1D} = \frac{\sqrt{m}}{\pi\hbar\sqrt{2}} \cdot E^{\left(-\frac{1}{2}\right)}$$

➤ Here the density of states drops as  $E^{(-1/2)}$ , which reflects the growing spacing of states with energy which clearly shows the *widening spacing, and thus lower state density*, as one goes to higher energies.



(b) Show that the quantum of electrical conductance is given by  $e^2/2h$

**Let us consider the conductance of a 1D structure of length,  $L$ .**

Conductance  $G_0$  is defined by a change of current when voltage ( $\Delta V$ ) is applied (also reciprocal of resistance):  $G_0 = 1/R = \Delta I/\Delta V$ .

Current is defined as the rate flow of charge; thus, it is  $\Delta I = \Delta Q/\Delta t$ . Net charge  $\Delta Q$  ( $=Ne$ ), is the number of electrons,  $N$ , times the charge  $e$  of every contributing electron ( $1.602 \cdot 10^{-19}$  C).

In addition, time  $\Delta t$  can be obtained as the velocity of an electron  $v$ , over the distance  $L$  that it travels.

Thus,  $\Delta I = \Delta Q/\Delta t = Ne/\Delta t = Ne/(L/v) = Nev/L$ .

Then  $G_0 = \Delta I/\Delta V = Nev/L\Delta V$ .

The drop in *potential energy* for every electron involved is simply its charge multiplied by the voltage across the sample. Thus,  $\Delta E = e \cdot \Delta V$ , or  $\Delta V = \Delta E/e$ .

Therefore, the conductance,  $G_0 = Ne^2v/L\Delta E$ .

The key to this problem lies in **finding the number of electrons  $N$ , which contribute to the conductance**.

**The number of electrons,  $N$ , which contribute to the conductance in the 1D structure** can be derived from the **DOS**.

In a 1D structure (such as a nanowire),  $N = D(E) \Delta E \cdot L$ , where  $D(E)$  is the density of states which is given by

$$D(E) = \frac{\sqrt{m}}{\sqrt{2}\pi\hbar} \cdot \frac{1}{\sqrt{E}}$$

where  $E$  is the energy in each sub-band and  $m$  is the mass of an electron.

$$\text{Thus, } N = D(E) \Delta E \cdot L = \frac{\sqrt{m}}{\sqrt{2}\pi\hbar} \cdot \frac{1}{\sqrt{E}} \cdot L \cdot \Delta E = \frac{2}{h\nu} \cdot L \cdot \Delta E \quad (\text{since } E = mv^2/2)$$

Thus, the conductance,  $G_0 = Ne^2v/L\Delta E = \left(\frac{2L \cdot \Delta E}{h\nu} e^2 v\right)/L\Delta E = \frac{2e^2}{h} = 7.748 \times 10^{-5}$  S, which is the **quantum of electrical conductance** or **quantum limited conductance**.

(c) If there exists a finite nonzero resistance in a nano-conductor, why does a superconductor have zero resistance?

A superconductor has zero resistance because, at low temperatures, conduction electrons pair up into **Cooper pairs**, which behave like bosons. Unlike individual electrons, these pairs are not subject to the Pauli Exclusion Principle, allowing them to occupy the same quantum state and move freely without scattering. This collective behavior, known as **Bose-Einstein condensation**, enables a superconductor to conduct electricity without energy loss.

- **Thermal motion of the atoms** in the particle can initiate a change of the charge and of the Coulomb energy, so that **electrons may tunnel uncontrolled**.
- **To produce single electron tunneling processes**, the **thermal energy ( $k_B T$ )** of the particle must be much **smaller than the Coulomb energy ( $E_C$ )** in order to keep the electron on the particle.
- Typically,
  - $E_C > k_B T$ .
  - Or,  $e^2/2C > k_B T$
  - Or,  $C > e^2/2k_B T \sim e^2/k_B T$

Q.10. (a) Mention two advantages of a 'single-electron transistor (SET).

The conduction process in Single-Electron Transistors (SETs) involves the movement of individual electrons, requiring only a small amount of energy to operate switches, transistors, or memory elements. This allows SETs to exhibit **very low power dissipation** and achieve **high operational speeds**, making them highly efficient for certain applications.

(b) Discuss the construction and working principles of a typical SET.

[1+3.5]

A Single-Electron Transistor (SET) consists of the following components:

1. **Source and Drain Electrodes:** These are metallic or semiconducting terminals where electrons enter and exit the device.
2. **Quantum Dot (Island):** A nanoscale conductor or semiconductor structure acts as the central region where single electrons are confined.
3. **Tunnel Barriers:** Thin insulating layers separate the quantum dot from the source and drain, allowing electrons to tunnel through due to quantum mechanical effects.
4. **Gate Electrode:** A control electrode coupled capacitively to the quantum dot, allowing precise control over the electron flow by modulating the electrostatic potential.

#### **Working Principle:**

1. Electron transport in SETs relies on **Coulomb Blockade**, which occurs when the addition of a single electron to the quantum dot requires energy greater than

the thermal energy  $k_B T$ . This restricts electron flow unless certain voltage thresholds are met.

2. By applying a voltage to the gate electrode, the electrostatic potential of the quantum dot is modified, aligning energy levels and enabling single-electron tunneling.
3. This precise control over individual electron movement allows SETs to operate as ultra-sensitive switches or transistors.

(c) Calculate the size (radius in nm) of a sphere-shaped Si quantum dot that would produce an observable single electron effect at room temperature (300 K). Given: Dielectric constant of Si = 11.5; Permittivity of vacuum =  $8.85 \times 10^{-12} \text{ F/m}$ ;  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ ;  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ .

The single-electron charging energy  $E_C$  must exceed the thermal energy at room temperature  $k_B T = 300 \text{ K}$ .

Here:

- $e = 1.602 \times 10^{-19} \text{ C}$ ,
- $\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ ,
- $\epsilon_r = 11.5$ ,
- $k_B = 1.38 \times 10^{-23} \text{ J/K}$ .

Setting  $E_C > k_B T$ :

$$\frac{e^2}{4\pi\epsilon_0\epsilon_r r} > k_B T.$$

Rearranging for  $r$ :

$$r < \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}.$$



