Quantum size effect, electrical conductivity and Quantum transport

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1 Quantum size effect

As we seen in module 5, the nanomaterials have unique properties due to its increases surface to volume ratio and quantum size effect. In this module we will learn about the property change arising due to size effect. When the size of a nanocrystal (i.e. a single crystal nanoparticle) is smaller than the de Broglie wavelength, electrons and holes are spatially confined and electric dipoles are formed, and discrete electronic energy level would be formed in all materials. Similar to a particle in a box, the energy separation between adjacent levels increases with decreasing dimensions.

1.1 Electronic configuration

The electronic configurations of nanomaterials are significantly different from that of their bulk counterpart. These changes arise through systematic transformations in the density of electronic energy levels as a function of the size, and these changes result in strong variations in the optical and electrical properties with size.
1.2 Size effect in metal and semiconductor

In any material, there will be a size below which there is substantial variation of fundamental electrical and optical properties with size, when energy level spacing exceeds the temperature. For a given temperature, this occurs at a very large size (in nanometers) in semiconductors as compared with metals and insulators. The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the interband transition shifting to higher frequencies.

1.3 Required size for size effect

In the case of metals, where the Fermi level lies in the centre of a band and the relevant energy level spacing is very small, the electronic and optical properties more closely resemble those of continuum, even in relatively small sizes (tens or hundreds of atoms). In semiconductors, the Fermi level lies between two bands, so that the edges of the bands are dominating the low-energy optical and electrical behavior. Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10,000 atoms. For insulators, the band gap between two bands is already too big in the bulk form.

The same quantum size effect is also known for metal nanoparticles; however, in order to observe the localization of the energy levels, the size must be well below 2 nm, as the level spacing has to exceed the thermal energy (~26 meV). In a metal, the conduction band is half filled and the density of energy levels is so high that a noticeable separation in energy levels within the conduction band (intraband transition) is only observed when the nanoparticle is made up of ~100 atoms. If the size of metal nanoparticle is made small enough, the continuous density of electronic states is broken up into discrete energy levels. The spacing $\delta$, between energy levels depends on the Fermi energy of the metal, $E_F$, and on the number of electrons in the metal, $N$, as given by:

$$\delta = \frac{4E_f}{3N}$$

(1)

where the Fermi energy $E_F$ is typically of the order of 5 eV in most metals. The discrete electronic energy level in metal nanoparticles has been observed in far-infrared absorption
measurements of gold nanoparticle. When the diameter of nanowires or nanorods reduces below the de Broglie wavelength, size confinement would also play an important role in determining the energy level just as for nanocrystals. For example, the absorption edge of Si nanowires has a significant blue shift with sharp, discrete features and silicon nanowires also have shown relatively strong "band-edge" photoluminescence.

2 Electrical Conductivity

This lecture provides you the various mechanism and effect on the electrical conductivity of nanomaterials

The effects of size on electrical conductivity of nanostructures and nanomaterials are complex, since they are based on distinct mechanisms. These mechanisms can be generally grouped into categories

i) surface scattering including grain boundary scattering
ii) quantized conduction including ballistic conduction
iii) coulomb charging and tunnelling
iv) widening and discrete of band gap
v) change of microstructures.

In addition, increased perfection, such as reduced impurity, structural defects and dislocations, would affect the electrical conductivity of nanostructures and nanomaterials.

2.1 Surface scattering

Electrical conduction in metals or Ohmic conduction can be described by the various electron scattering, and the total resistivity, $\rho_T$, of a metal is a combination of the contribution of individual and independent scattering, known as Matthiessen’s rule:
\[ \rho_T = \rho_{th} + \rho_D \]  

\( \rho_{th} \) is the thermal resistivity and \( \rho_D \) the defect resistivity. Electron collisions with vibrating atoms (phonons) displaced from their equilibrium lattice positions are the source of the thermal or phonon contribution, which increases linearly with temperature. Impurity atoms, defects such as vacancies, and grain boundaries locally disrupt the periodic electric potential of the lattice and effectively cause electron scattering, which is temperature independent. Obviously, the defect resistivity can be further divided into impurity resistivity, lattice defect resistivity, and grain boundary resistivity. Considering individual electrical resistivity directly proportional to the respective mean free path (\( \lambda \)) between collisions, the Matthiessen’s rule can be written as:

\[ \frac{1}{\lambda_T} = \frac{1}{\lambda_{th}} + \frac{1}{\lambda_D} \]

\( \lambda_T \) ranges from several tens to hundreds of nanometres. Reduction in material’s dimensions would have two different effects on electrical resistivity. One is an increase in crystal perfection or reduction of defects, which would result in a reduction in defect scattering and, thus, a reduction in resistivity. However, the defect scattering makes a minor contribution to the total electrical resistivity of metals at room temperature, and thus the reduction of defects has a very small influence on the electrical resistivity, mostly unnoticed experimentally. The other is to create an additional contribution to the total resistivity due to surface scattering, which plays a very important role in determining the total electrical resistivity of nanosized materials. If the mean free electron path, \( \lambda_s \), due to the surface scattering is the smallest, then it will dominate the total electrical resistivity:

\[ \frac{1}{\lambda_T} = \frac{1}{\lambda_{th}} + \frac{1}{\lambda_D} + \frac{1}{\lambda_s} \]  

In nanowires and thin films, the surface scattering of electrons results in reduction of electrical conductivity. When the critical dimension of thin films and nanowires is smaller than the
electron mean-free path, the motion of electrons will be interrupted through collision with the surface. The electrons undergo either elastic or inelastic scattering. In elastic, also known as specular, scattering, the electron reflects in the same way as a photon reflects from a mirror. In this case, the electron does not lose its energy and its momentum or velocity along the direction parallel to the surface is preserved. As a result, the electrical conductivity remains the same as in the bulk and there is no size effect on the conductivity. When scattering is totally inelastic or nonspecular or diffuse, the electron mean-free path is terminated by impinging on the surface. After the collision, the electron trajectory is independent of the impingement direction and the subsequent scattering angle is random. Consequently, the scattered electron loses its velocity along the direction parallel to the surface or the conduction direction, and the electrical conductivity decreases. There will be a size effect on electrical conduction.

2.2 Change of electronic structure

![Diagram showing change in electronic structure of various low dimensional materials](image)

As shown in above Fig. 1, a reduction in characteristic dimension below a critical size, i.e. the electron de Broglie wavelength, would result in a change of electronic structure, leading
to widening and discrete band gap. Such a change generally would also result in a reduced electrical conductivity. Some metal nanowires may undergo a transition to become semiconducting as their diameters are reduced below certain values, and semiconductor nanowires may become insulators. Such a change can be partially attributed to the quantum size effects, i.e. increased electronic energy levels when the dimensions of materials are below a certain size as discussed in the previous section. For example, single crystalline Bi nanowires undergo a metal- to-semiconductor transition at a diameter of ~52 nm and the electrical resistance of Bi nanowires of ~40nm was reported to decrease with decreasing temperature. GaN nanowires of 17.6 nm in diameter was found to be still semiconducting, however, Si nanowires of ~15 nm became insulating.

3 Quantum transport

This lecture provides you the charge carrier transport mechanism and types in low dimensional materials

The commercial mass production of nanodevices has reached 45 nm length scales and the International Technology Roadmap for Semiconductors predicts shrinkage of this scale below 10 nm during the next decade. At these length scales, however, the transport is dominated by quantum mechanics such as interferences, quantum confinement and coherent tunneling. These effects complicate any intuitive explanation of the device properties.

First, consider transport in large, macroscopic systems. In bulk materials and devices, transport has been well described via the Boltzmann transport equation or similar kinetic equation approaches. The validity of this approach is based on the following set of assumptions: (i) scattering processes are local and occur at a single point in space; (ii) the scattering is instantaneous (local) in time; (iii) the scattering is very weak and the fields are low, such that these two quantities form separate perturbations on the equilibrium system; (iv) the time scale is such that only events that are slow compared to the mean free time between collisions are of interest. In short, one is dealing with structures in which the potentials vary slowly on both the
spatial scale of the electron thermal wavelength and the temporal scale of the scattering processes.

Ballistic conduction occurs when the length of conductor is smaller than the electron mean-free path. In this case, the conductance jumps insteps of $G_0 = 2e^2/h = 12.9k\Omega^{-1}$ (see the adjacent figure for the case of FET conductance). Another important aspect of ballistic transport is that no energy is dissipated in the conduction, and there exist no elastic scattering. The latter requires the absence of impurity and defects. When elastic scattering occurs, the transmission coefficients, and thus the electrical conductance will be reduced, which is then no longer precisely quantized. Ballistic conduction of carbon nanotubes was first demonstrated by Frank and his co-workers. Extremely high stable current densities $J > 10^7 A/cm^2$ have been attained.

Coulomb blockade or Coulomb charging occurs when the contact resistance is larger than the resistance of nanostructures and when the total capacitance of the object is so small that adding a single electron requires significant charging energy. Metal or semiconductor nanocrystals of a few nanometers in diameter exhibit quantum effects that give rise to discrete charging of the metal particles. Such a discrete electronic configuration permits one to pick up the electric charge one electron at a time, at specific voltage values. This Coulomb blockade behaviour, also known as "Coulombic staircase" and has originated the proposal that nanoparticles with diameters below 2-3 nm may become basic components of single electron transistors (SETs). To add a single charge to a semiconductor or metal nanoparticle requires energy, since electrons can no longer be dissolved into an effectively infinite bulk material. For a nanoparticle surrounded by a dielectric with a dielectric constant of $\varepsilon_r$, the capacitance of the nanoparticle is dependent on its size as:

$$C(r) = 4\pi \varepsilon_0 \varepsilon_r r$$

(5)
where \( r \) is the radius of the nanoparticle and \( \varepsilon_0 \) is the permittivity of vacuum. The energy required to add a single charge to the particle is given by the charging energy:

\[
E_c = \frac{e^2}{2C(r)}
\]

Tunnelling of single charges onto metal or semiconductor nanoparticles can be seen at temperatures of \( k_B T < E_c \), in the I-V characteristics from devices containing single nanoparticles or from STM measurements of nanoparticles on conductive surfaces. Such Coulomb staircase is also observed in individual single-wall carbon nanotube. It should be noted that equations (5) and (6) clearly indicate that the charging energy is independent of materials. Tunneling involves charge transport through an insulating medium separating two conductors that are extremely closely spaced. It is because the electron wave functions from two conductors overlap inside the insulating material, when its thickness is extremely thin. Under such conditions, electrons are able to tunnel through the dielectric material when an electric field is applied. It should be noted that Coulomb charging and tunneling conduction, strictly speaking, are not material properties. They are system properties. More specifically, they are system properties dependent on the characteristic dimension.

### 3.1 Effect of microstructure

Electrical conductivity may change due to the formation of ordered microstructure, when the size is reduced to a nanometer scale. For example, polymer fibres demonstrated an enhanced electrical conductivity. The enhancement was explained by the ordered arrangement of the polymer chains. Within nanometer fibrils, polymers are aligned parallel to the axis of the fibrils, which results in increased contribution of intramolecular conduction and reduced contribution of intermolecular conduction. Since intermolecular conduction is far smaller than intramolecular conduction, ordered arrangement of polymers with polymer chains aligned parallel to the conduction direction would result in an increased electrical conduction. Depending upon the
values of characteristic lengths as we seen in module 2, in comparison with the system size \( L \), different transport regimes can be distinguished and can be classified as below

### 3.1.1 Classical diffusive transport

For macroscopic dimensions \( L >> l_m \) or \( l_{\Phi} \), the carrier experiences many elastic and inelastic collisions so that the energy and the momentum is relaxed and the average velocity is given by the \( v=\mu F \) with the mobility \( \mu=\frac{e \tau_m}{m^*} \) following in the simplest case from Drude theory. Diffusion occurs due to gradients in the carrier density and the diffusion current density is given by \( eD\nabla n \), where the diffusion constant \( D \) is related to the mobility by the Einstein relation \( eD=\mu kT \).

### 3.1.2 Ballistic transport

If the system size \( L < l_m \), then the charge carriers can moves without scattering except with the surface. The carrier momentum grows due to the accelerating force of the electric field.

### 4 Quiz and Assignment

1. When the size of the material decreases , the band gap energy ________
2. The size of the nanocrystal ______________ than the de-Broglie wavelength, __________ energy levels formed.
3. The Fermi energy of the metal are in the order of ______________
4. The size of the Cadmium Selenide fluorescent quantum dot ____________ covers the entire visible region.
5. The relationship between the crystal size and color
   (a) Smaller crystal size , Shorter wavelength
   (b) Larger crystal size, Shorter wavelength
   (c) Smaller crystal size, Longer wavelength
   (d) Larger crystal size, Longer wavelength
6. What are the types of defects resistivity?
7. The dimension of the nanomaterials reduced to de-Broglie wavelength, the semiconductor nanomaterials changes to ____________
8. Ballistic conduction occurs at length of conductor is smaller than the _______________-
9. Quantum effects mainly occurs at ____________________________
10. This Coulomb blockade behaviour is also called as ____________________

4.1 Solutions

1. Increases.
2. Smaller, Discrete
3. 5eV
4. 2-6 nm
5. Smaller crystal size, Shorter wavelength
6. Defect resistivity can be divided as follows,
   - Impurity resistivity,
   - Lattice defect resistivity
   - Grain boundary resistivity
7. Insulator
8. Electron mean-free path.
9. Metal or Semiconductors Nanocrystal
10. Coulombic staircase

5 References