



Dr. Avradip Pradhan,  
Assistant Professor,  
Department of Physics,  
Narajole Raj College, Narajole.

## **DSE3T (Nano Materials and Applications)**

### **Topic – Optical Properties (Part – 1)**

#### **Introduction:**

The realization of nano-devices usually requires combining semiconductors with metals, insulators and molecules in a small region of space. The behaviour of these systems strongly depends on the complex repartition of the electric field. Many interesting problems are related to *dielectric properties* e.g. the current-voltage characteristics of a device, the binding energy of a dopant or an exciton, the energy of a carrier in an ultra-small capacitor, the optical properties and many others. Thus, their simulation at the nanometer scale becomes a critical issue for the development of nanotechnologies. Simulation at the macroscopic or even the mesoscopic scale usually relies on the macroscopic electrostatic theory of dielectrics where the latter are described by their bulk macroscopic dielectric constant. One can wonder when this macroscopic approach breaks down as the size of the systems diminishes, since it is no longer valid at the molecular scale. In this e-report, we will briefly review the basic assumptions of the electrostatic theory of macroscopic dielectrics, and we will discuss its validity and its limitations.

#### **Classical Electrostatic Theory of Dielectrics:**

We recapitulate the bases of the macroscopic electrostatic theory of dielectrics, and we see how it is usually implemented to study the Coulomb interaction between charged particles in small systems. The electrostatics of macroscopic conductors and dielectrics is the object of many textbooks. We will concentrate on dielectrics (insulators and semiconductors) where the effect of the confinement is expected to be the largest. However the same effects occur in very small metal clusters. The macroscopic theory is based on quantities defined as averages over small volumes, which however are large enough to average the microscopic fluctuations due to the atomic structure of the material.

For bulk crystalline solids, the averaging volume is the unit cell. If these conditions are realized, one can write the macroscopic electric field as  $\vec{E} = \vec{e}$ ,

**PAPER: C13T (Nano Materials and Applications)**

**TOPIC(s): Optical Properties (Part -1)**



**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
Department of Physics,  
Narajole Raj College, Narajole.

where  $\vec{E}$  is the average of the microscopic field  $\vec{e}$ . In the absence of macroscopic magnetic fields, one can write  $\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0}$ , where  $\rho$  is the mean density of charge in the dielectric.  $\rho$  can be related to the polarization  $\vec{P}$  defined as the dipole moment averaged per unit volume. So,  $\rho = -\nabla \cdot \vec{P}$ . Therefore, we can write  $\nabla \cdot (\epsilon_0 \vec{E} + \vec{P}) = \nabla \cdot \vec{D} = 0$ . Here  $\vec{D} = \epsilon_0 \vec{E} + \vec{P}$  is known as the electric displacement vector. When external charges are introduced in the system, their density  $\rho_{ext}$  must be added to obtain  $\nabla \cdot \vec{D} = \rho_{ext}$ .

To solve these equations, a relation between  $\vec{D}$  and  $\vec{E}$  is required. In many cases, this relation is linear because the external fields are small compared to the internal molecular fields. In isotropic materials,  $\vec{D}$  and  $\vec{E}$  fields are simply proportional to each other, and we can write  $\vec{D} = \epsilon_0 \epsilon_M \vec{E}$ .

Here  $\epsilon_M$  is the *macroscopic dielectric constant* of the material. If we introduce the electrostatic potential  $\phi$  such that  $\vec{E} = -\nabla\phi$ , then we finally obtain  $\nabla \cdot \vec{D} = \nabla \cdot \epsilon_0 \epsilon_M \vec{E} = \rho_{ext}$  or  $\nabla \cdot \epsilon_0 \epsilon_M \nabla\phi = -\rho_{ext}$ . This equation leads to the usual Laplace equation and it remains valid in situations where  $\epsilon_M(\vec{r})$  has a macroscopic space dependence. It can be solved using various numerical approaches, for example using a *Green's function formalism*.

Now we will be mainly interested in the Coulomb interaction between *point charges* in dielectrics. For example, the potential energy or interaction energy between two charges  $q$  and  $q'$  sitting at positions  $\vec{r}$  and  $\vec{r}'$  is  $V(\vec{r}, \vec{r}') = q\phi(\vec{r})$

In the case of a homogeneous bulk material where  $\epsilon_M(\vec{r}) = \epsilon_b$  (constant), we have  $V = V_b(\vec{r}, \vec{r}') = q\phi_b(\vec{r}) = \frac{qq'}{4\pi\epsilon_0\epsilon_b|\vec{r}-\vec{r}'|}$ .

**Self Energy.** When the material is inhomogeneous,  $V$  differs from  $V_b$ . As a result, the Coulomb interactions in heterostructures with large dielectric mismatch can be strongly modified compared to the bulk. Another important consequence is that the electrostatic energy of a charged particle depends on its position  $\vec{r}$ . Indeed, the charge polarizes the dielectrics and induces polarization charges at the surfaces and interfaces of the system. Therefore, there is an interaction between the particle and the polarization charges which depends on

**PAPER: C13T (Nano Materials and Applications)**  
**TOPIC(s): Optical Properties (Part -1)**



**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
Department of Physics,  
Narajole Raj College, Narajole.

the position of the particle with respect to the surfaces and interfaces. The interaction energy is called a *self-energy* because the potential is induced by the own presence of the particle. Using the notations defined above and taking for  $\epsilon_b$  the dielectric constant at the position  $\vec{r}$ , the self-energy can be calculated as  $\Sigma(\vec{r}) = \frac{1}{2} \lim_{\vec{r} \rightarrow \vec{r}'} [V(\vec{r}, \vec{r}') - V_b(\vec{r}, \vec{r}')]$ . Here  $V$  and  $V_b$  are calculated with  $q' = q$ .

### **Coulomb Interactions in a Dielectric Quantum Nanostructures:**

Now we summarize general results concerning Coulomb interactions in dielectric quantum nanostructures, on the basis of macroscopic electrostatics. We describe the *image charge method*, which leads to analytical expressions for the electrostatic potentials and fields. We start with the simplest case of a single charge close to a dielectric interface, and then we consider quantum well.

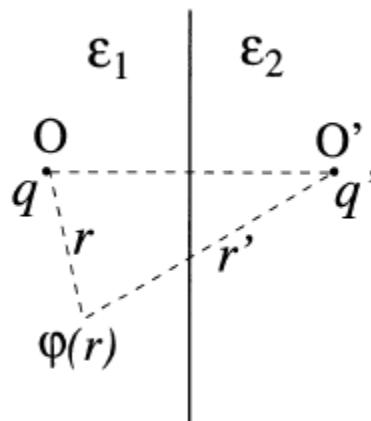


Fig. 1

**For a Planar Dielectric Interface.** We consider the situation of Fig. 1. A charge  $q$  is at point  $O$ , at a distance  $z$  from the planar interface between two dielectrics 1 and 2, with relative dielectric constants  $\epsilon_1$  and  $\epsilon_2$ , respectively. The charge  $q$  is in region 1. The discontinuity of the dielectric constant induces polarization charges at the interface.

Following a well-known approach of image charges, the potential in region 1 can be written as the potential created by two charges in an homogeneous



**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
 Department of Physics,  
 Narajole Raj College, Narajole.

medium of dielectric constant  $\epsilon_1$ : the charge  $q$  and a fictitious charge (image charge)  $q'$  sitting at the point  $O'$ , the image of the point  $O$  with respect to the interface. Thus, we have

$$\phi_1(\vec{r}) = \frac{q}{4\pi\epsilon_0\epsilon_1 r} + \frac{q'}{4\pi\epsilon_0\epsilon_2 r'}$$

where  $r$  and  $r'$  are the respective distances from the points  $O$  and  $O'$ . The potential in region 2 is written as the potential due to a fictitious charge  $q''$  at the point  $O$ , in an homogeneous medium of dielectric constant  $\epsilon_2$ :

$$\phi_2(\vec{r}) = \frac{q''}{4\pi\epsilon_0\epsilon_2 r}$$

Using the boundary conditions on the electric field at the interface, we can obtain  $q' = q \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}$  and  $q'' = q \frac{2\epsilon_2}{\epsilon_1 + \epsilon_2}$ .

From the previously written expressions, the electrostatic self-energy of the charge  $q$  is written as  $\Sigma(z) = \frac{qq'}{16\pi\epsilon_0\epsilon_1 z} = \frac{q^2}{4z} \frac{\epsilon_1 - \epsilon_2}{4\pi\epsilon_0\epsilon_1(\epsilon_1 + \epsilon_2)}$ .

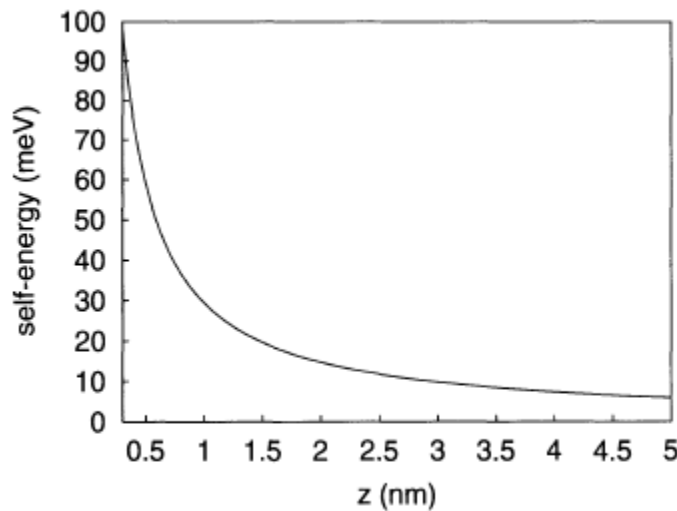


Fig. 2

Fig. 2 shows the self-energy of an electron as function of the distance  $z$ , in the case  $\epsilon_1 = 10$  and  $\epsilon_2 = 1$ . The self-energy is quite substantial at distances in the

nanometer range. Therefore, the electrostatic self-energy of particles cannot be neglected in nanostructures with large dielectric mismatch.

**For a Dielectric Quantum Well.** We consider now the problem of a charge  $q$  located at the point  $(\vec{r}_{\parallel} = 0, z_0)$ , in a semiconductor quantum well.  $L$  is the thickness of the well, and the  $z$  axis is perpendicular to the interfaces. A schematic structure is shown in Fig. 3. The well, with a dielectric constant  $\epsilon_1$ , is sandwiched by barrier layers having a different dielectric constant  $\epsilon_2$ . The potential is calculated using the image charge method. Due to the presence of the two interfaces, there is an infinite series of image charges.

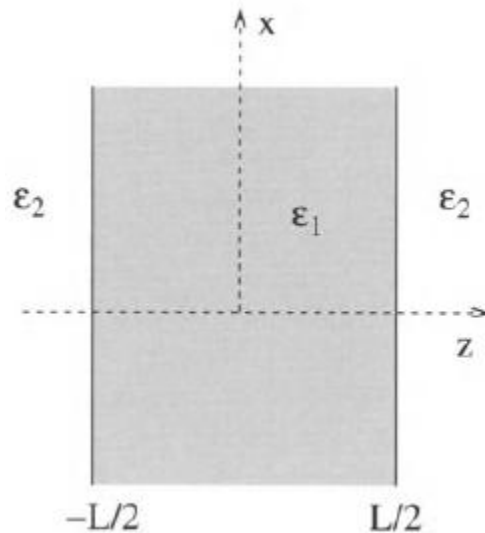


Fig. 3

The potential in the well is given by regarding the whole structure as having a common dielectric constant  $\epsilon_1$ , and by placing image charges  $q_n$  at the positions:  $z_n = nL + (-1)^n z_0$ , with  $n$  as positive or negative integers. The potential in the left-hand-side barrier layer is given by placing image charges  $q'_n$  at  $z_n$ ,  $n = 0, 1, 2 \dots$  and the potential in the right-hand-side barrier layer by placing image charges  $q''_n$  at  $z_n$ ,  $n = 0, -1, -2 \dots$ . In both cases, the whole structure is seen as having a common dielectric constant  $\epsilon_2$ . From the boundary conditions, we obtain  $q_n = q\gamma^{|n|}$  where  $\gamma = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}$  and  $q'_n = q''_n = q_n \frac{2\epsilon_2}{\epsilon_1 + \epsilon_2}$ .



**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
Department of Physics,  
Narajole Raj College, Narajole.

So, the potential in the well, at a position  $(\vec{r}_{\parallel}, z)$ , is given by

$$\phi(\vec{r}_{\parallel}, z) = \frac{1}{4\pi\epsilon_0\epsilon_1} \sum_{-\infty}^{\infty} \frac{q_n}{\sqrt{r_{\parallel}^2 + (z-z_n)^2}}$$

In a limiting case, when  $r_{\parallel} \gg \frac{\epsilon_1}{\epsilon_2} L$ , we can write  $\phi(\vec{r}_{\parallel}, z) \approx \frac{q}{4\pi\epsilon_0\epsilon_2 r_{\parallel}}$ .

Thus, if the semiconductor quantum well is sandwiched between insulators or semiconductors with a small dielectric constant  $\epsilon_2$ , the long-range Coulomb interactions are strongly enhanced compared to the bulk case. This effect is due to the penetration of the electric field into the barrier with a small dielectric constant. This effect has important consequences, such as the enhancement of the exciton binding energy etc.

But the self-energy of a charge  $q$  located at the point  $(\vec{r}_{\parallel}, z)$  does not depend on

$$\vec{r}_{\parallel}. \Sigma(z) = \frac{1}{2} \sum_{-\infty}^{\infty} \frac{q q_n}{4\pi\epsilon_0\epsilon_1 |z-z_n|}$$

### **Dielectric Constant for Nanostructures:**

It can be shown that the dielectric properties of a system are described by  $\epsilon^{-1}(\vec{r}, \vec{r}')$ . From this, in a bulk semiconductor, we can deduce directly the macroscopic dielectric constant  $\epsilon_M(\vec{q})$  (with  $\vec{q}$  described in momentum space) which contains most of the useful information on the *dielectric screening*. We can wonder if this macroscopic treatment is possible in semiconductor nanostructures and if it remains meaningful. Here we explain why macroscopic quantities for nanostructures cannot be deduced from  $\epsilon^{-1}(\vec{r}, \vec{r}')$  as simply as in the bulk case. We show that a physically meaningful macroscopic dielectric constant must be derived taking into account explicitly the polarization charges at the surfaces or interfaces. Using this prescription, we demonstrate that the macroscopic response is the bulk one a few Fermi wavelengths away from the surface and that the bulk response function  $\epsilon_M(\vec{q})$  provides most of the needed information even for very small nanostructures.

**Surface Polarization Charges.** The dielectric function  $\epsilon^{-1}(\vec{r}, \vec{r}')$  provides full information on the screening properties in a system. It relates the screened electrostatic potential to the bare one. From this, in a bulk material, one can

**PAPER: C13T (Nano Materials and Applications)**

TOPIC(s): Optical Properties (Part -1)





**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
Department of Physics,  
Narajole Raj College, Narajole.

directly define the macroscopic dielectric function  $\epsilon_M(\vec{q})$ . But, in a nanostructure, such a direct relation does not exist, due to the presence of polarization charges at the surfaces.

To illustrate this point, let us consider the macroscopic limit of a dielectric sphere (radius  $R$ ) of dielectric constant  $\epsilon_{in}$  embedded in vacuum. If we put a charge at the centre, the macroscopic potential  $\phi(\vec{r})$  can be calculated using the correct boundary conditions. From this, the *potential screening function* can be derived as  $\epsilon_{scr}(r) = \frac{\phi_b(\vec{r})}{\phi(\vec{r})} = \frac{1}{\epsilon_{in}^{-1} + (1 - \epsilon_{in}^{-1})\frac{r}{R}}$  inside the cluster of radius  $R$ . This is completely different from the macroscopic dielectric constant  $\epsilon_{in}$ .  $\epsilon_{scr}(r)$  is much smaller than  $\epsilon_{in}$  on the average when  $\epsilon_{in}$  is large (e.g.  $\epsilon_{scr}(r) \sim 2$  for  $r = \frac{R}{2}$ ). This difference corresponds to the fact that a charge  $1 - \epsilon_{in}^{-1}$  is repelled onto the surface of the finite cluster.

Therefore, a physically meaningful definition of a dielectric constant in a nanostructure must incorporate the effect of the polarization charges at the surfaces. We will show in the following microscopic calculation results of the dielectric screening in quantum wells. A dielectric constant  $\epsilon(\vec{r})$  can be calculated at each position  $\vec{r}$  in the nanostructure by imposing that the macroscopic relation between the screened field  $\vec{E}$  and the bare one  $\vec{E}_b$  is verified.

**Dielectric Screening in Quantum Wells.** We consider here the case of Si thin layers with (001) oriented planes submitted to a bare electric field  $E_b(z)$  which is uniform inside and is vanishing abruptly between the terminating Si-H planes ( $E_b$  is perpendicular to the surfaces). We present the results of tight binding calculations [200]. Fig. 4 gives the screened electric field along the layer. The most striking feature of these curves is that the local dielectric constant  $\epsilon(z)$  defined here as  $\frac{E_b}{E}$  keeps its bulk value to a high accuracy except between the last two planes.

It is also interesting to compare these results to the dielectric response of the bulk silicon to the same perturbation. For that purpose, we define  $E_b$  as

**PAPER: C13T (Nano Materials and Applications)**  
**TOPIC(s): Optical Properties (Part -1)**

$$E_b = E_0 \text{ if } \frac{d}{2} + 2nd > z > -\frac{d}{2} + 2nd$$

$$= -E_0 \text{ otherwise}$$

where  $d$  is the width of the layer,  $E_0$  is a constant and  $n$  is a positive or negative integer. In the figure, ratio between the bare electric field  $E_b$  and the screened one  $E$  in Si layers submitted to a constant electric field perpendicular to the surfaces is shown, with tight binding results (blank square) and continuous model (straight line) using the bulk dielectric constant. The electric field and the potential are periodic functions which can be written in Fourier series. Then, screening each Fourier component by the bulk  $\epsilon_M(\vec{q})$  calculated in tight binding, we obtain the results shown in Fig. 4. The agreement with the tight binding calculation is striking even near the surfaces where however the oscillatory behaviour depends on the nature of the boundary conditions. This is a proof that bulk screening appropriately describes the situation even for very small thicknesses (5 silicon planes).

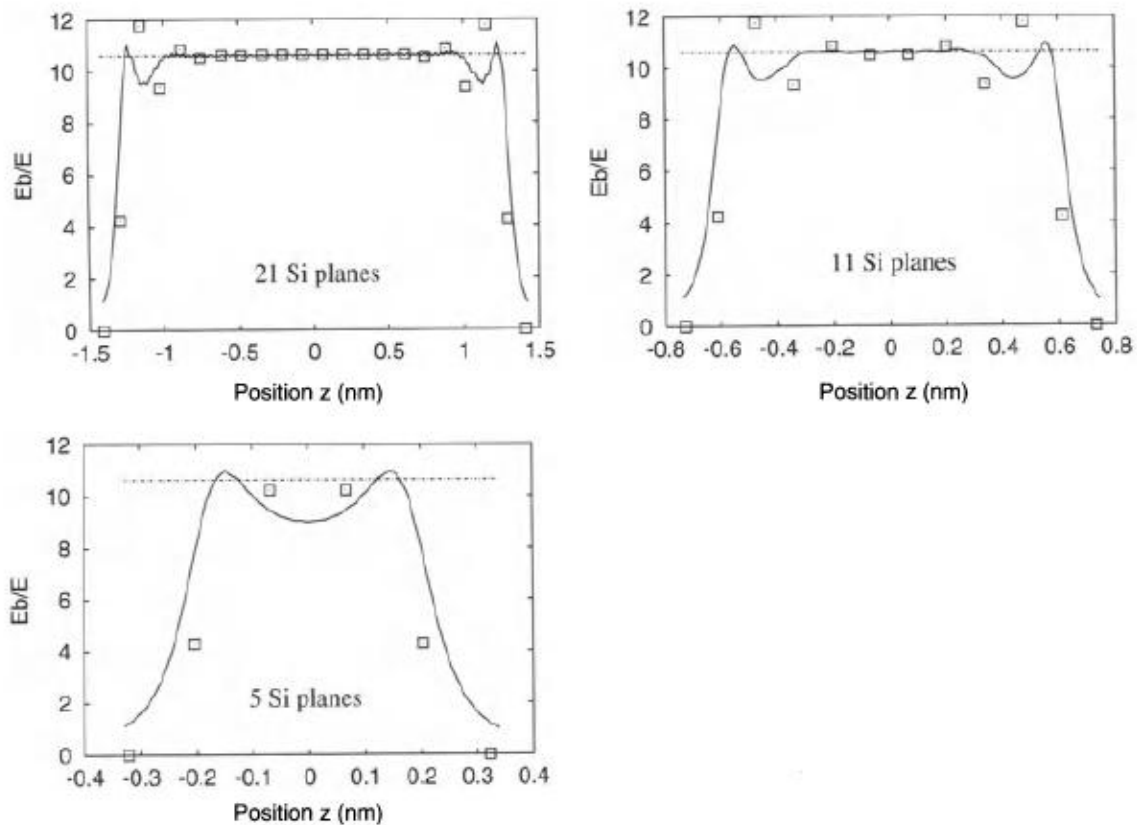


Fig. 4



### Charging of a Nanostructure:

**For a Quantum Dot.** One interesting question concerns the self-energy of particles and Coulomb charging effects in nanostructures.

We consider a spherical quantum dot of radius  $R$  and of macroscopic dielectric constant  $\epsilon_{in}$ . We will argue that the best value for  $\epsilon_{in}$  is the bulk macroscopic dielectric constant  $\epsilon_M$  in that case. In the case of a strong confinement, we can obtain a fairly good estimation of the self-energy  $\Sigma$  of an electron or a hole ( $q = \pm e$ ) injected in the quantum dot, in a first-order perturbation theory. In the limit of an infinite potential barrier, the one-particle state is well-given by the effective mass solution

$$\phi(\vec{r}) = \frac{1}{\sqrt{2\pi R}} \frac{\sin(\frac{\pi r}{R})}{r}$$

In the usual situation when the quantum dot is embedded in an oxide matrix or in a semiconductor with a large gap, the self-energy becomes

$$\Sigma = \frac{1}{2} \left( \frac{1}{\epsilon_{out}} - \frac{1}{\epsilon_{in}} \right) \frac{e^2}{4\pi\epsilon_0 R} + \delta\Sigma$$

where  $\delta\Sigma$  is the correction term.

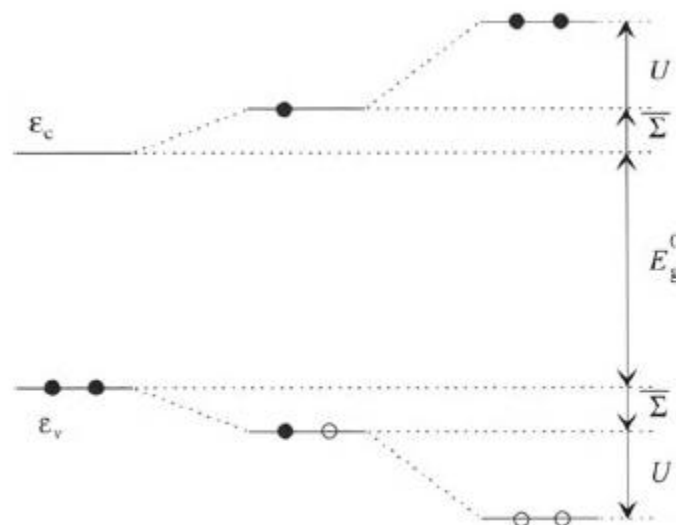


Fig. 5



**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
 Department of Physics,  
 Narajole Raj College, Narajole.

$\Sigma$  gives the shift in energy of the extra electron (hole) in the lowest conduction (highest valence) state (Fig. 5). The injection of a second electron (hole) leads to an additional upwards (downwards) shift  $U$  given by the screened repulsion with the other electron (hole) (Fig. 5). Here  $U$  is known as the *charging energy* of the system. With the same approximations as for  $\Sigma$ ,  $U$  can be obtained as

$$U \approx \left( \frac{1}{\epsilon_{out}} + \frac{0.79}{\epsilon_{in}} \right) \frac{e^2}{4\pi\epsilon_0 R}$$

In many situations, the surrounding of the quantum dots is not a homogeneous dielectric medium. Then, Poisson's and Schrödinger equations must be solved self-consistently to calculate the charging energy  $U$ . However,  $U$  must be necessarily between two bounds, corresponding to  $\epsilon_{out} = 1$  and  $\epsilon_{out} \rightarrow \infty$ . We get two bounds as  $\frac{0.79}{\epsilon_{in}} \frac{e^2}{4\pi\epsilon_0 R} < U < \left( 1 + \frac{0.79}{\epsilon_{in}} \right) \frac{e^2}{4\pi\epsilon_0 R}$ .

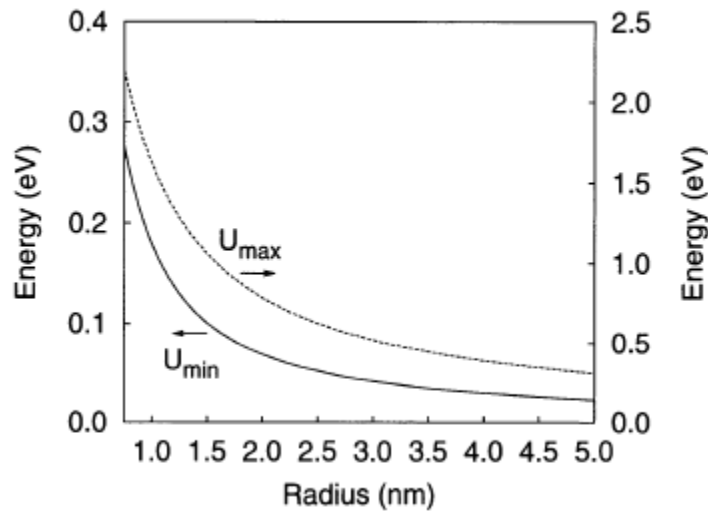


Fig. 6

Fig. 6 shows the evolution of these two bounds for  $U$  in a Si nanocrystal, as function of its diameter. We see that the values of  $U$  can be very large when  $\epsilon_{out} = 1$ , such that the injection of more than one carrier becomes difficult.



**Dr. Avradip Pradhan,**  
**Assistant Professor,**  
Department of Physics,  
Narajole Raj College, Narajole.

In the case of a metallic nanostructure  $\epsilon_{in} \rightarrow \infty$ , and one gets  $U = \frac{e^2}{C}$  and  $\Sigma = \frac{U}{2}$  as it must be for the charging of a metallic sphere of self-capacitance  $C = 4\pi\epsilon_0\epsilon_{out}R$ . This capacitive model is often extended to the case of semiconductor quantum dots, even if it is not perfectly justified.

This concludes part 1 of this e-report.

The discussion will be continuing in the part 2 of this e-report.

### **Reference:**

**Nanostructures: Theory and Modeling, C. Delerue & M. Lannoo,  
Springer**

(All the figures have been collected from the above mentioned reference)