Chapter 2

Theoretical aspects in low-dimensional systems

2.1. Introduction

In low-dimensional system the motion of microscopic degree-of-freedom (electrons, phonons, photons etc.) is restricted. The motion of electrons in nanostructure is governed by effective potentials, which confine the electrons in one, two, or three directions. These confinements bring about plentiful quantum effects, which are useful in designing electronic structures and tailoring physical properties.

The workhorse of low-dimensional system is semiconductor ‘nanostructure’. Semiconductor nanorods, nanocrystals or nanoparticles are a special class of materials whose crystals are composed of periodic groups of II-VI, III-V or IV-VI materials. The most notable and interesting property of semiconductor nanorods is the distinct large magnitude change in optical, physical, magnetic properties as a function of particle size. The quantum-size effect leads to an increase in band gap with a decrease in particle size.

2.2. Particle size effects

2.2.1. Quantum confinement effect

In small nanocrystals, the electronic energy levels are not continuous as in the bulk but are discrete (finite density of states), because of the confinement of the electronic wavefunction to the physical dimensions of particles, this phenomenon is known as quantum confinement. It is caused by localization of electrons and holes in a confined space resulting in observable quantization of the energy levels of the electrons and holes. The confinement is all about keeping electrons and holes trapped in a small area. Quantum confinement comes in several forms which include two dimensional confinements, which is only restricted in one dimension, and the result is a quantum well. One dimensional confinement occurs in nanowires and zero-dimensional confinement is found only in quantum dot. In nature zero-
dimensional confinement is found in atoms. Quantum confinement is essentially important for one thing, it leads to new electronic properties in semiconductor devices.

In semiconductors, an electron-hole pair is created when an electron leaves the valence band and enters the conduction band due to excitation. An exciton is created when a weak attraction force (Coulombic force) between the hole and electron exists. It may be bound or moving in a crystal conveying energy. Excitons have a natural physical separation that varies from semiconductor to semiconductor. The average separation distance is termed as exciton Bohr radius. In bulk, the dimensions of the semiconductor crystal are much larger than the excitonic Bohr Radius. The energy levels of a bulk semiconductor are very close together such that they are described as continuous, meaning that there is almost no energy difference between. Since the band-gap of the bulk semiconductor is fixed, the transitions result in fixed emission frequencies. However, if the sizes of a semiconductor particle are comparable or small enough that they approach the size of the material’s bulk exciton Bohr Radius, the continuum states are broken down into discrete states [107] and can no longer be treated as continuous, meaning that there is a small and finite separation between energy levels. This results a large effective band gap and leads to an optical transition which is blue-shifted from that of bulk materials [107,108].

![Image of one-dimensional nanostructures](image)

**Figure 3:** Schematic diagram of one-dimensional nanostructures. In both x and y directions, electrons are confined but they move freely in z-direction.
The density of states for one dimension quantum mechanical system nanostructures:

\[ g(E) dE = \left( \frac{a}{\pi \sqrt{2m/\hbar}} \right) \frac{1}{\sqrt{E}} dE \]  

(2)

**Figure 4**: Density of states vs. Energy for one dimensional quantum mechanical system.

### 2.2.2. Surface effects

Nanoscale materials, including thin films, quantum dots, nanorods, nanowires, nanobelts, etc. are all structurally unique because they have a relatively high surface area to volume ratio. This increase in surface area to volume ratio is important for nanomaterials because wide and unexpected variations in mechanical and other physical properties, such as thermal, electrical and optical, have been found to scale in some proportion to increase in surface area to volume ratio. The critical impact of this is that standard continuum relations, which do not account for size-dependence or the discrete nature of atomistic surfaces, are no longer valid at the nanometer length scale.

There are two distinct effects due to nanoscale free surfaces. The first effect is that of surface stress. Surface stresses exist in nanomaterials due to the fact that atoms lying at the material surfaces have a different bonding configuration as compared to bulk atoms.
Surface elasticity is another effect that occurs due to the lack of bonding neighbors for surface atoms. Because surface atoms have a different bonding environment than atoms that lie within the material bulk, the elastic properties (stiffness) of surfaces differ from those of bulk material and the effects of the difference between surface and bulk elastic properties become magnified as the surface area to volume ratio increases with decreasing structural dimension.

Surface stress and surface elasticity lead to many new physics and phenomena in nanomaterials that are not well-understood, and thus not predictable or as yet controllable.

### 2.2.3. Quantized conductance

When the length scale of an electrical conductor is reduced to less than the electron mean free path, the scattering of electrons will predominantly take place at the boundary of the conductor. The conductivity of a nanowire is expected to be much less than that of the corresponding bulk material since there is scattering from the wire boundaries, when the wire width is below the free electron mean free path of the bulk material. The conductivity can undergo a quantization in energy. These phenomena are succinctly described by a formula, originally proposed by Rolf Landauer in 1957, for the conductance $G$ (reciprocal of the resistance) of a mesoscopic system. Landauer’s formula is simply $G = |t|^2 e^2/h$, where $t$ is the quantum transmission amplitude for an electron to propagate through the system ($|t|^2$ is the transmission probability). The conductance quantum is the quantized unit of conductance. It is defined by $2e^2/h$ and equals 77.48 microsiemens.

**Figure 5**: Conductance vs. diameter of the particle.

\[
G = NG_0
\]

where $N=0, 1, 2, 3, \ldots$

and $G_0 = 2e^2/h = 77$ mS