ePathshala पाठशाला
A Gateway to All Post Graduate Courses

ePathshala पाठशाला
MHRD Govt. of India
An MHRD Project under its National Mission on Education through ICT (NME-ICT)

Subject: Physics

Production of Courseware
e-Content for Post Graduate Courses

Paper No. : Physics at Nanoscale - I
Module : Properties at Nanoscale

ePathshala पाठशाला
MHRD Govt. of India

Development Team

Principal Investigator	
Paper Coordinator	Prof. Subhasis Ghosh, School of Physical Sciences Jawaharlal Nehru University, New Delhi
Content Writer	Prof. Subhasis Ghosh, School of Physical Sciences Jawaharlal Nehru University, New Delhi
Content Reviewer	

Table of Contents of Chapter 1

Properties at Nanoscale

Properties of materials are size-dependent in the nanorange. Types of properties that often change at nanoscale include:

1. Thermal properties (e. g. melting point)
2. Optical properties (e. g. fluorescence, color etc.)
3. Electrical properties (e. g. conductivity)
4. Magnetic properties (e. g. permeability)
5. Chemical properties (e. g. reactivity, catalysis)
6. Mechanical properties (e. g. adhesion, capillary forces)

1.2.1 Dominance of Electromagnetic forces at Nanoscale

As shown in Table 1, there are four basic forces: gravitational, electromagnetic, strong and weak nuclear forces. The strong and weak nuclear forces are typically short range interactions, and are mostly considered for inter-nuclear interactions, and therefore will be neglected for this discussion. The gravitational force is a long-range attractive force between two masses, and is directly proportional to the masses of the two objects and inversely proportional to the square of the distance between the objects. Because the mass of nanoscale objects is so small, the force of gravity has very little effect on the attraction between objects of this size. Electromagnetic forces may be attractive or repulsive based only on their charge and magnetic properties, and are not affected by the masses. Therefore, magnetic and electrostatic forces are very important in deciding the physical and chemical behavior of materials at the nanoscale.

Table I. *The four basic forces in nature and the length scales at which these forces become significant. Note that all forces exist at all scales, but their magnitude may become negligibly small.*

	Gravitational	Electromagnetic	Weak Nuclear Force	Strong Nuclear Force
Cosmic scale (10^7 m and bigger)	Y	Y*		

Macro-scale (10^{-2} *m* to 10^{6} *m*)	Y	Y**		
Micro-scale (10^{-3} *m* to10^{-7} *m*)	Y	Y		
Nano-scale (10^{-8} *m* to 10^{-9}*m*)		Y		
Atomic scale (10^{-10} *m* and less)			Y	Y

**In places like the sun, where matter is ionized and in rapid motion, electromagnetic forces are dominant.*

***On a human scale, where matter is neither ionized nor moving rapidly, electromagnetism, though important, is not dominant.*

1.2.2 Quantum Mechanics and Nanoscale Physics: Key Concepts

Classical mechanical models explain phenomena at the bulk scale, but break down when dealing with the very small objects and at nanoscale. At the nanoscale, there are many phenomena that cannot be explained by classical mechanics, and therefore quantum mechanics needs to be invoked. Here we cover a few key concepts of quantum mechanics needed to explain the physics at nanoscale.

1.2.2.1 The Wave-Particle Duality of Light and Matter

In 1690, Christian Huygens theorized light as wave, while in 1704, Isaac Newton theorized that light was made of small particles. However, neither a all-particle theory nor a all-wave theory could explain *all* of the phenomena associated with light. The wave picture could explain phenomena such as reflection, interference and polarization, but failed to account for others such as the "*photoelectric effect*". The photoelectric effect was explained by Albert Einstein, and is observed when light falls on the surface of a metal knocking out electrons in the process. This effect can however be completely explained by considering light to be made of particles known as photons and then considering collisions between photons and electrons. Subsequently, scientists began to treat light as both a particle and a wave, and depending on the experiment you perform, you see light behave in one of these two ways. This duality was further extended to matter, and small particles such as electrons. De Broglie came up with a relation for the wavelength of such matter waves, given by, $\lambda = \frac{h}{p}$, where h is plank constant and p is the momentum of the particle ($p = mv$).

1.2.2.2. Uncertainty of Measurement and Schrodinger's Equation

The centerpiece of quantum mechanics is the Heisenberg's uncertainty principle. The uncertainty principle states that one cannot accurately determine both the position, *x* and the momentum, *p* of a particle at the same time because the process of measuring the particle's position disturbs the particle's momentum and vice versa. This also led to the concept of a wave function associated with a particle, which gives a measure of the probability of finding the particle in a given state.

In 1925, physicist Schrodinger analyzed the wave function that electrons would follow if they behaved as waves, and proposed an equation analogous to the classical harmonic wave function and Newton's second law:

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\psi(x,t)$$

This is called the one dimensional Schrodinger's equation. Here$\hbar = h/2\pi$, where h is the Planck's constant, *m* is the electron mass and *V* is the potential energy of the electron. The term $\psi(x,t)$ is the wave function of the electron, such that $|\psi(x,t)|^2$ represents the probability of finding an electron at location *x* and time *t*. In three dimensions, the Schrodinger equation can be written as:

$$i\hbar \frac{\partial \psi(x,y,z,t)}{\partial t} = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2 \psi(x,y,z,t)}{\partial x^2} + \frac{\partial^2 \psi(x,y,z,t)}{\partial y^2} + \frac{\partial^2 \psi(x,y,z,t)}{\partial z^2}\right\} + V(x,y,z,t)\psi(x,y,z,t)$$

In one dimension, if the potential energy *V(x, t)* is only a function of space and does not change with time (in most cases this assumption is valid) and assuming for further simplification

$$\psi(x,t) = \psi(x) * f(t)$$

Substituting this back into the Schrodinger's equation, we get:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi$$

Where, the constant *E* turns out to be the total energy of the particle.

We now consider a few simple solutions to the Schrodinger's equation.

1.2.2.3. Free Electrons

This implies *V(x)* = 0 for all values of *x*. Hence, the Schrodinger's equation can be written as:

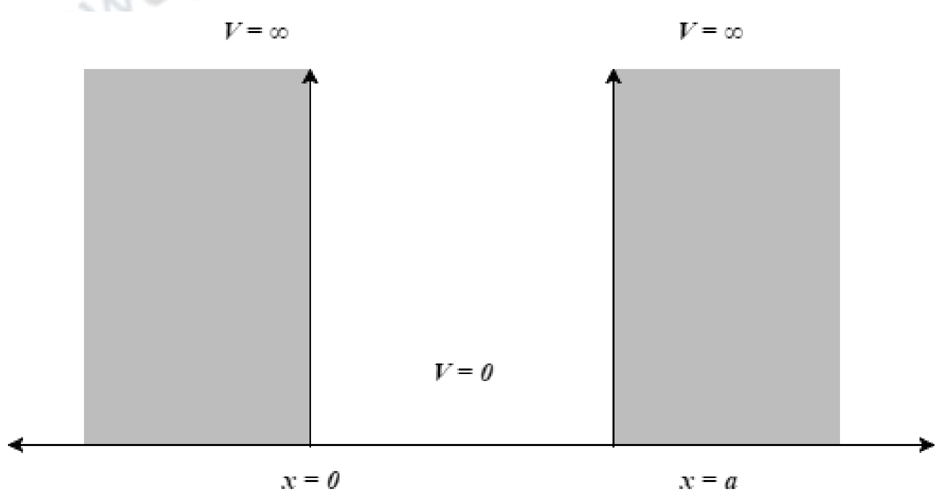
$$\frac{\partial^2\psi}{\partial x^2} + \frac{2mE}{\hbar^2}\psi = 0$$

Because the energy, *E*, must always be positive, we assume $k^2 = 2mE/\hbar^2$. Solving the second order differential equation, we get the general solution:

$$\psi(x) = Aexp(ikx) + Bexp(-ikx)$$

Including the time dependence, we find that the solutions represent travelling waves in the positive and negative x-directions. The energy *E* is equal to $\hbar^2k^2/2m$. Comparing with results from classical mechanics where the kinetic energy is given by $p^2/2m$, we find that the momentum *p* is given by $\hbar k$, which is nothing but de Broglie's equation. If we plot the total energy, *E*, as a function of *k*, we obtain a parabolic relationship. This is also called the dispersion of free electrons.

1.2.2.4 Electrons in potential wells: Infinite well



An infinite potential well has zero potential inside and infinite outside the well, as described by:

$$V(x) = \begin{cases} \infty \; if \; x < 0 \\ 0 \; if \; 0 < x < a \\ \infty \; if \; x \geq a \end{cases}$$

Inside the potential well, the electrons behave as free particle, and outside the potential well, the probability of finding an electron is zero due to the infinitely high barriers. Therefore,

$\Psi(0) = 0$ and $\Psi(a) = 0.$

Within the well, the solutions are given by: $\Psi = Ae^{ikx} + Be^{-ikx}$

As the wave function must be continuous at the boundaries, we get:

$\Psi(0) = A + B = 0 \rightarrow B = -A$ and $\Psi(a) = Ae^{ika} + Ae^{-ika} = 0 \rightarrow B = -A$

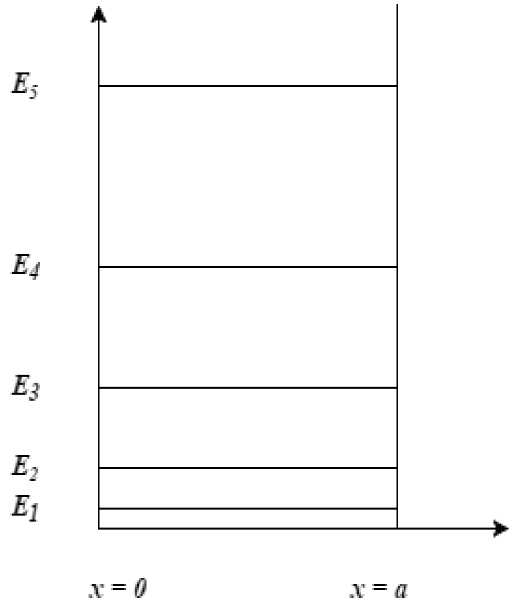
This leads to $2i \; sin(ka) = 0$ and $E = \frac{n^2h^2}{8ma^2}$

And by normalizing the wave function, such that the probability of finding the electron over all space is 1, we get:

$$\Psi(x) = \sqrt{\frac{2}{a}} sin(kx)$$

Here, n=1, 2, 3, 4…., is an integer and we call it the quantum number. From this equation it is clear that the energy of an electron inside an infinite well can only be at some finite and discrete levels as opposed to that of a free electron. The quantization of the energy levels is a direct result of the Schrodinger's equation, and the continuity of the wave function. Unlike classical mechanics, where a particle or object can take on any value of energy, in quantum mechanics the energy of an electron can only have a quantized value. The difference between two adjacent levels is given by:

$$\Delta E = E_{n+1} - E_n = \frac{(2n+1)h^2}{8ma^2}$$



As the size of the potential well '*a*' decreases, the energy level spacing decreases. Therefore, large values of *a*, we can consider the energy levels to be continuous rather than discrete, as the spacing becomes vanishingly small. In other words, when the feature size is large, quantum mechanical predictions agree with classical results. This is also known as Bohr's correspondence principle.

1.2.2.5 Tunneling Across a Barrier

Tunneling is a microscopic phenomenon that suggests the passage of a particle through a potential barrier is allowed even when the particle's total energy is less than the height of the barrier (Figure 1.4). In numerous examples in physics, tunnelling phenomena has been established unambiguously particularly in microscopic world, however the concept of tunnelling is invalid according to classical mechanics. Tunnelling is purely a quantum phenomena and this is manifested in the dominant contribution of quantum effects at nanoscale. The tunnel effect underlies many important processes in different fields of physics, such as atomic, molecular, nuclear, and solid state physics. For example, it is the basis of scanning tunnelling microscope, which can be used to image nanostructures on surfaces. If the particle's energy E is less than V and as the kinetic energy of the particle $p^2/2m = E\text{-}V$ (where m is the mass of the particle) would be negative and the particle's momentum p would be an imaginary quantity. Fixing the particle in a region of space within the barrier makes the particle's momentum indeterminate because of the uncertainty relation. This leads to a nonzero probability of finding the particle in a region that is forbidden from the standpoint of classical mechanics. Hence, there is a definite probability of the particle's passage through the potential barrier. This phenomena is known as tunnel effect. The tunnelling probability increases as the mass of the particle decreases, or the thickness of the potential barrier decreases, or the difference between the particle's energy and the height of the barrier decreases. The probability of passage through the barrier is called the penetration probability which determines the physical characteristics of the tunnel effect at nanoscale.

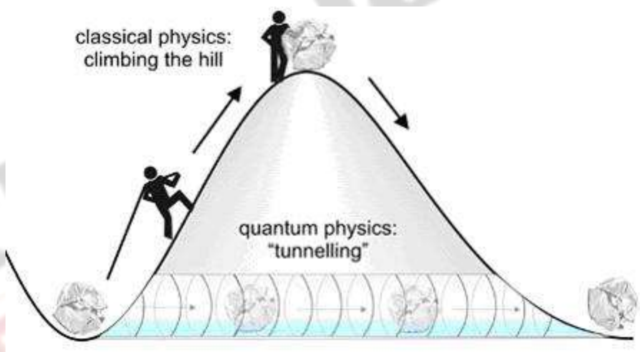


Figure 1.4. *Schematic illustration of quantum tunneling through a barrier. Image taken from http://quantumaniac.com/post/10373804268/quantum-tunneling-according-to-quantum-mechanics.*

1.2.3 Changes in Properties of Matter at Nanoscale

When we look at nanomaterials, there are four important distinctions from bulk materials:

1. Due to the small mass of the particles at nanoscale, gravitational forces are negligible, and instead electromagnetic forces are dominant in determining their behavior.
2. Nanoparticles tend to have a very large surface area to volume ratio.
3. At nanoscale, to describe motion and energy, quantum physics takes over classical physics and concepts such as tunneling, quantum confinement and energy quantization become important.
4. Random (Brownian) molecular motion becomes more important at nanoscale.

As explained above, the results of these effects lead to a very different and interesting physics being studied at the nanoscale. Next we take some examples of changes in the properties of the materials when studied at the nanoscale.