Basic Science of Nanomaterials: Quantum Phenomena

➢ Earlier we have used the surface energy concept to calculate changes in the melting point and other classical properties of nanoparticles.

❑ **Learning Objectives**

▪ Understand the physical basis of mesoscopic behavior in nanoscale semiconducting and magnetic particles.

▪ Describe how the particle-in-a-box equation applies to electrons in quantum wells.

▪ Use the Brus formula to calculate the band gap energy of nanoscale semiconductor particles.

▪ Describe the methods used to make semiconducting and metal nanocrystals of uniform size.

▪ Explain the origin of the localized surface plasmon resonance effect in metal nanoparticles.

▪ Describe the emerging analytical and biomedical applications of metal nanoparticles.

- Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. In this section we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.

- The special properties of nanomaterials do not derive from different laws of physics, which are the same for objects large and small. For example, Newton's second law (F=ma), Coulomb's law ($E=q_1q_2/4\pi\varepsilon_0r$), and the laws of energy and momentum conservation are the same for buckyballs (C_{60}) and full-size soccer balls.

- Nevertheless, the physics of electrons, atoms, and photons naturally produce **characteristic length scales**. For example, the mean free path of an electron in a good metal is about 40 nm. The Bohr radius of an electron or hole in doped Si is about 4 nm, and that the coherence length of Cooper pairs in semiconductors is somewhere between a few nm and 1 μm. *When objects become small relative to these characteristic lengths, their physical properties change in interesting ways.*

➢ Materials that exist at the relevant length scale are called mesoscopic (meso = "between," scopic = "size") meaning that they cross over from one kind of behavior - the bulk behavior of large objects - to another.

➢ This ***length scale is different for different kinds of properties***, but for many properties like light emission, electronic conduction, and magnetic behavior, etc. it happens between 1 and 100 nm.

➢ We illustrate this point with a few examples later.

Electron Collisions and Length Scales

There are *two types of collisions* to consider.

➢ First, an electron can collide with an object such that there is no change in energy. (Think of a ball bouncing off a fixed surface.) This type of collision is called an *elastic collision*, and typically, collisions between electrons and fixed impurities are elastic.

➢ In the second type of collision, the energy of the electron changes (although total energy is conserved). This type of collision is called an *inelastic collision* and typically results from collisions between electrons and phonons (quantized lattice vibrations), or between electrons and electrons. Considering the preceding discussion, we'll define several length scales.

• L is the system length, in this case, the length of the conductor in question.
• L_m (or l) is the mean free path defined previously. However, now we want to be explicit and define this to be the length that the electron can travel before having an *elastic collision*.
• $L\varphi$, is the length over which an electron can travel before having an *inelastic collision*. *This is also called the* **phase-coherence length** *since it is the length over which an electron wavefunction retains its coherence* (i.e., retains its phase memory). Over the phase-coherence length, the phase of the wavefunction evolves smoothly.

➢ *We see that elastic collisions do not disrupt phase coherence, but that inelastic collisions destroy phase coherence.* These inelastic collisions are called *dephasing events*. Among other things, these dephasing events will destroy interference effects, including electrons interfering with themselves. *$L\varphi$ is usually on the order of* **tens to hundreds of nanometers** *at low temperatures.*

➢ As is typical of nanosystems, thermal effects play an important role in phase coherence. This is obviously the case for electron-phonon collisions since phonon energy will be greater at higher temperatures; in the classical model, the lattice vibrates more at higher temperatures. Furthermore, due to thermal energy, at nonzero temperatures, an electron should be represented by a wave-packet, the energies of which will vary on the order of $k_B T$. *As T increases, obviously, the spread of energies will increase, along with their associated phase differences, eventually leading to thermal decoherence even in the absence of particle scattering.*

➢ Decoherence of any kind is one of the reasons for systems exhibit classical behavior and is one of the most problematic issues facing the development of *quantum computers*. That is, **the computation must be finished before the quantum state decoheres** (with some exceptions), and, at present, this time is quite short.

For simplicity, we will divide electron transport into two regimes:

- For $L >> L_\varphi$, L_m (l), we have ***classical transport***, which is the familiar macroscopic case previously described. Ohm's law applies, and momentum and phase relaxation occur frequently as charges move through the system. Because of this, we cannot solve Schrodinger's equation over the whole conductor length L. It is fortunate that semiclassical or even classical models generally work well in this case.

- For $L << L_\varphi$, L_m (l), we have ***ballistic*** transport which is our main interest here. Ballistic transport occurs over very small length scales and is obviously coherent; the electron doesn't "hit" anything as it travels through the material, and, therefore, there is no momentum or phase relaxation. Thus, in a ballistic material, the electron's wavefunction can be obtained from Schrodinger's equation. One practical application of ballistic transport is to ultra-short-channel semiconducting FETs or carbon nanotube transistors. Short interconnects may exhibit ballistic transport properties, although material processing issues are important.

Table 9.3. Delocalization and confinement dimensionalities of quantum nanostructures

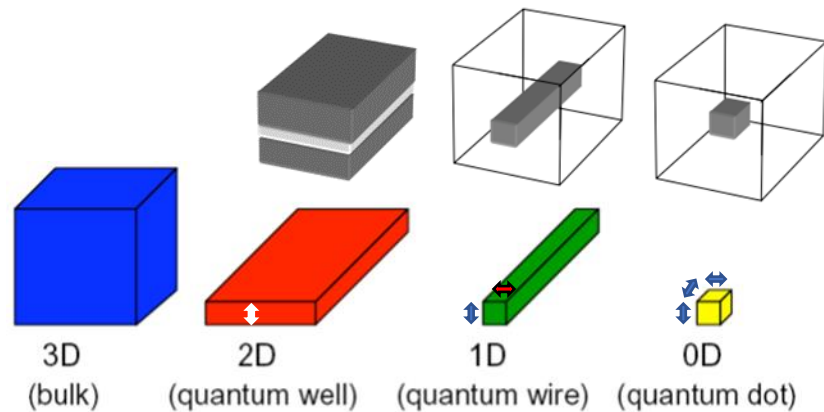| Quantum Structure	Delocalization Dimensions	Confinement Dimensions
Bulk conductor	3 (x, y, z)	0
Quantum well	2 (x, y)	1 (z)
Quantum wire	1 (z)	2 (x, y)
Quantum dot	0	3 (x, y, z)

Fig. 2.2. Three-dimensional (3D) bulk and two (2D), one (1D) and zero-dimensional (0D) nanostructures. Arrows show the confined dimensions.
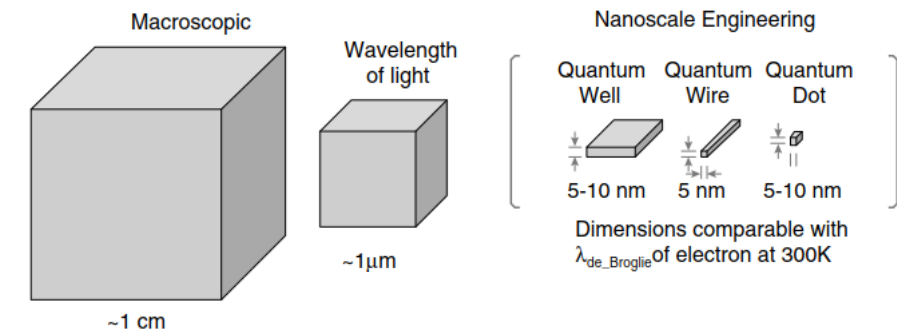
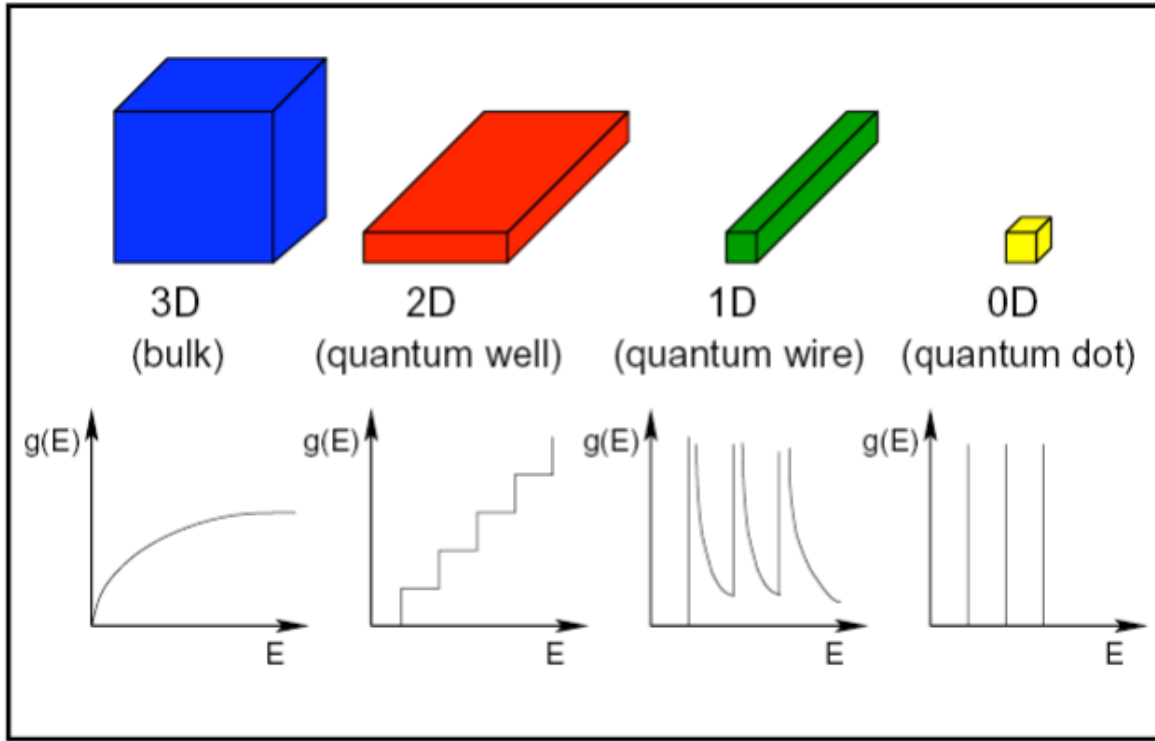**FIGURE 4.62** Comparison of dimension from macroscopic to nanoscale structures.

Figure 3: *Density of states for a free electron gas in various dimensions (general trend).*

➤ For 0D nanomaterials, the excited electrons are completely confined in all three dimensions, and they behave analogously to atomic/molecular clusters with discrete states that are well separated in energy (Figure 3, extreme right).

➤ For **1D nanomaterials**, the excited electrons experience no confinement along the length of the material, and the density of states is **quasi-discrete** with respect to increasing excitation energy (Figure 3).

➤ Finally, for **2D nanomaterials**, the density of states shows a **quasi-continuous *step-like*** increase with increasing excitation energy (Figure 3).

➤ The transformation of the electronic density of states (DOS, *g(E)*) of valence and conduction bands in metals and semiconductors from continuous to discrete to an individual in bulk to quantum-confined matter….

Electron Density of States (DOS)

We know that for single atoms there are distinct energy states that the electrons can occupy.

When millions of atoms come together to form a bulk lattice, *due to inter-atomic interactions several closely placed energy states are now available* for an excited electron to reside only if the exciting energy is at least enough to reach the lowest of the allowed excited state as shown schematically in Figure 5.2.

The availability of allowed states for an excited electron with respect to energy (per unit volume, area or length) of the material) is called the 'density of states' *and for most* bulk crystals, *there are enough available states to form a* **continuum** *called conduction band (CB). The corresponding ground states merge to form the valence band (VB).* In other words, ***the density of states is smooth and continuous for bulk crystals*** (Fig. 3).
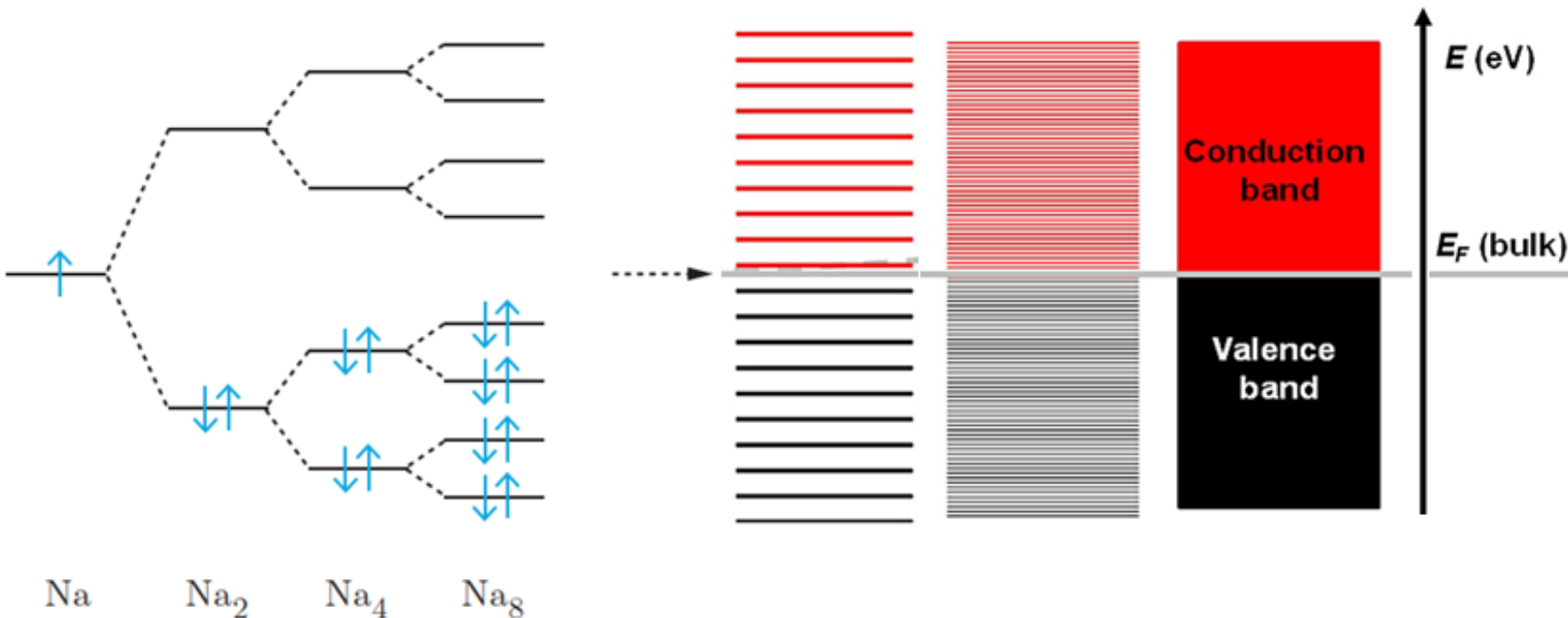

Figure 5.2: Illustration of electron distributions among the energy levels in progressively increasing sizes of clusters of a metal (Na), showing the formation of the valence band (VB) and the conduction band (CB) and the position of the Fermi Level.

❑ The gap between the energy levels can be calculated by:

$$\delta \approx \frac{E_f}{N} \qquad (1)$$

where E_f is the Fermi energy, N is number of atoms. For quantized electronic energy

$$\delta \geq k_B T \qquad (2)$$

➢ Substituting E_f = 5.5 eV (for gold), N ~220 atoms (*Ref: Kumar, S. Synthesis, Characterization and Application of Water-Soluble Gold and Silver Nanoclusters. Dissertations* **2013**.)…..

➢ Nanoparticle volume and number of gold atoms are related as

$$N = (59 \text{ nm}^{-3}) \cdot V \qquad (3)$$

which gives ~2 nm is the particle size below which quantization of energy levels occurs *and above this*, collective plasmon modes become active.

✓ *The energy levels become a continuum above this size* and hence free electrons are available on the metal surface.

➢ N can also roughly be expressed in terms of particle diameter, d as $\delta \approx \frac{E_f}{d^3}.$ ……………(4)

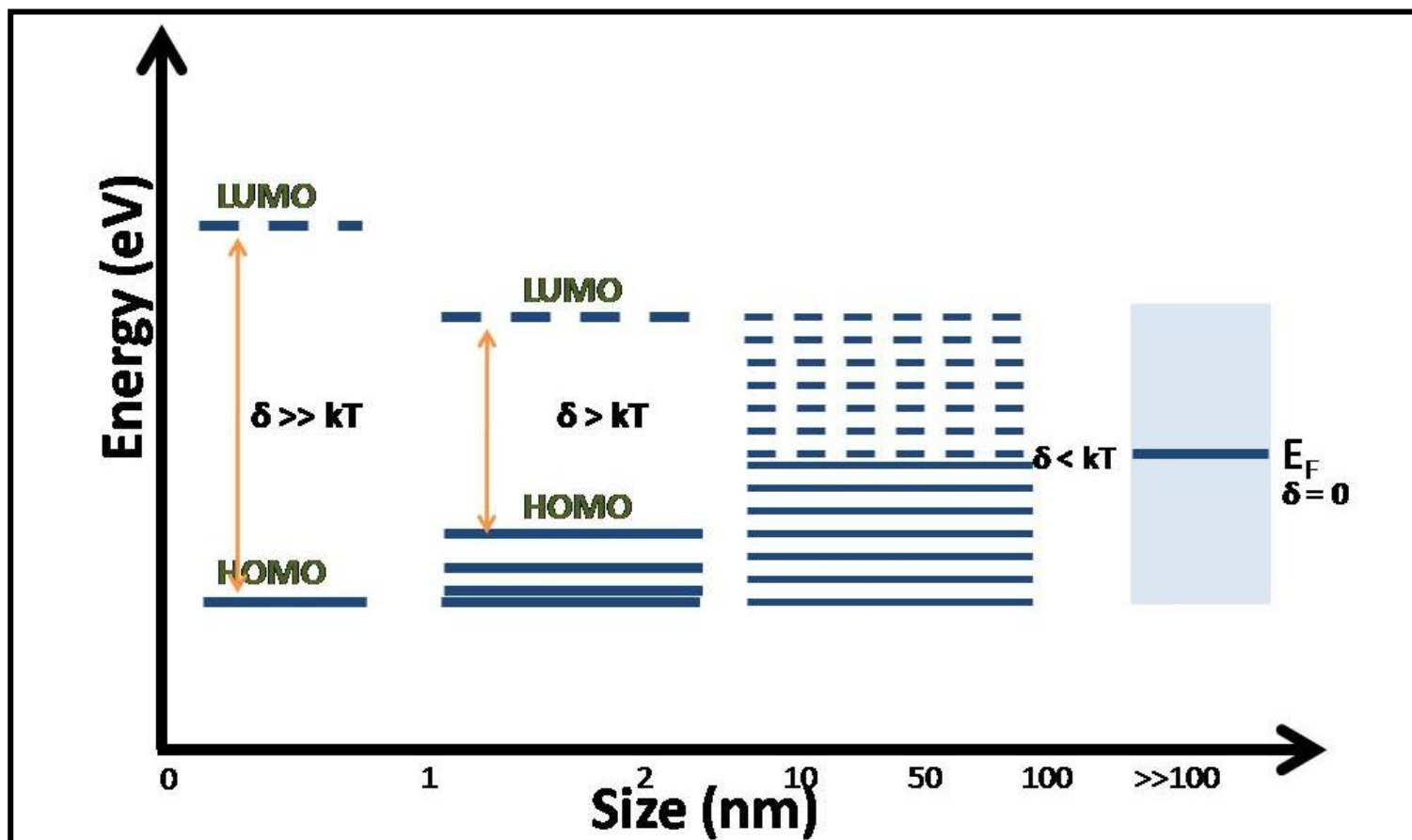The electronic energy gap variation with nanoparticle size is depicted in Figure 1.5.

Figure…. Band gap and density of states change with the nanoparticle size. Reproduced with permission from (*Ref: Roduner, E. Size Matters: Why Nanomaterials Are Different. Chem. Soc. Rev.* **2006**, *35 (7), 583–592.*)

➢ *The energy gaps measured were between 10 and 70 meV for clusters below 1 nm for Pd, Ag, Cd, and Au, observing a closing of the gap for clusters above this size.*

➢ This crossover point (**metallicity-no metallicity**) is of *extreme interest allowing us* to test the accuracy of theoretical predictions of finite Fermi systems and to develop interesting technological applications, like the use of *metal clusters as tunable quantum dots (QDs).*

❖ *Note that as the clusters grow*,

  ➢ the energies of the lowest orbital continue to decrease and hence the spread of available energies increases;

  ➢ **the** **separation** **of the energies** **de**creases *or the* **"density** **of energy states"** **in**creases;

  ➢ *the electrons all occupy lowered energy states leading to a more and more stable system;* and

  ➢ *the difference in energy between the highest occupied orbital and the lowest unoccupied orbital approaches zero.*

➢ **In the** *limit of very large clusters*, **the density of states is very high, and the electrons occupy** *a nearly continuous range of energies*.

❖ However, *when we have* **a very small crystal (nanocrystal)**, *due to lack of enough atoms, the availability of* **energy states for electrons become discrete** *and far apart.*

❖ For *quantum confined* nanocrystals, *the bandgap and* **the density of states** *becomes* **sensitively dependent on the size** **of the** **nanocrystal (along the confined direction).** *The band gap energy and the separation between available states for an excited electron in a nanocrystal become larger with decreasing size.*

➢ If the band gap between the VB and CB is comparable to the thermal energy at room temperature, the material will act as a **conductor** since there will be some electrons in the conduction band.

➢ *If the band gap is much greater than the thermal energy but less than **a few electron volts*** (1 eV = 1.602×10^{-19} J), then it is possible to populate the conduction band by applying a small voltage to the material and the material will conduct electrons in response to the applied electric field. These materials are called ***semiconductors***.

➢ ***If the band gap is much greater than several electron volts***, the material will not conduct electrons even with a significant applied voltage. These materials are ***insulators***.

Free electron gas model of metals: *Metal to Insulator Transition*

The following figure shows the discrete energy states to the band formation in Li atoms. A 1-mg sample of Li would contain nearly 10^{20} atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.
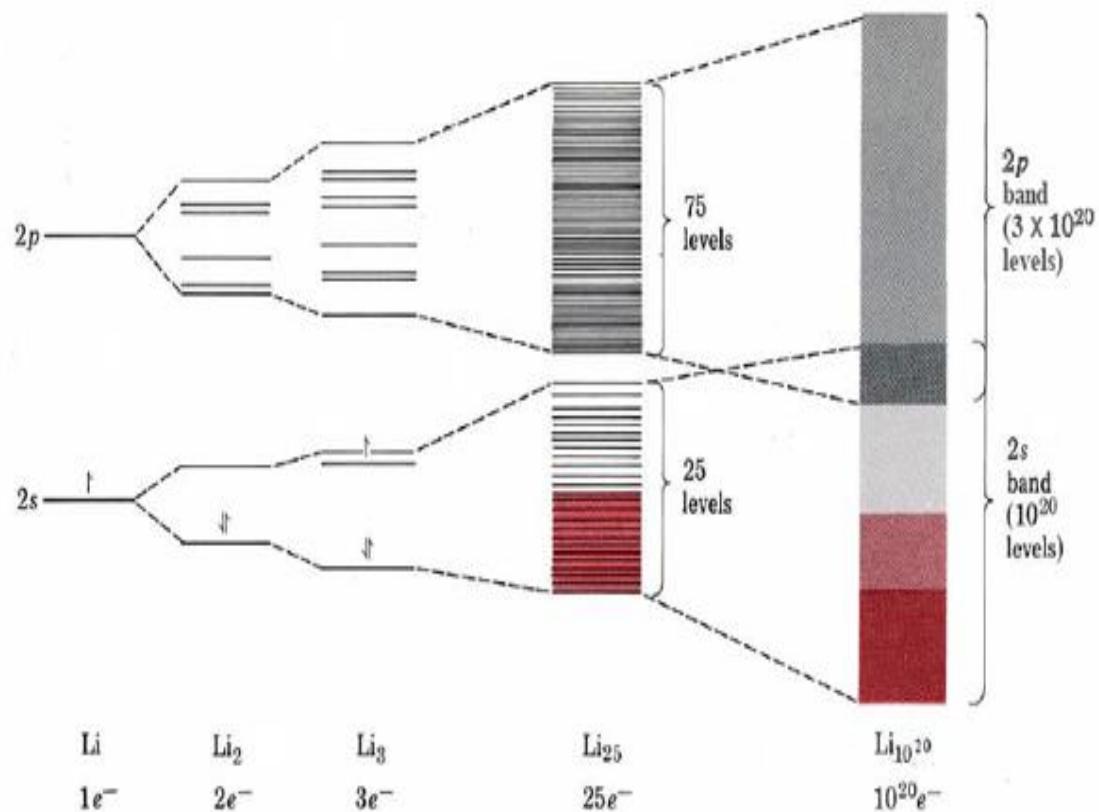

Figure 22.2.1: Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1-mg sample of Li would contain nearly 10^{20} atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.

Free electron gas model of metals: *Metal to Insulator Transition*

We have seen above that *when metal particles become small and their size approaches the Fermi wavelength*, the continuous energy bands break up into discrete energy levels, being *the adjacent energy levels separated by the so-called* **Kubo gap** as $\delta \sim E_F/N$, predicted to depend on the number of atoms, N.
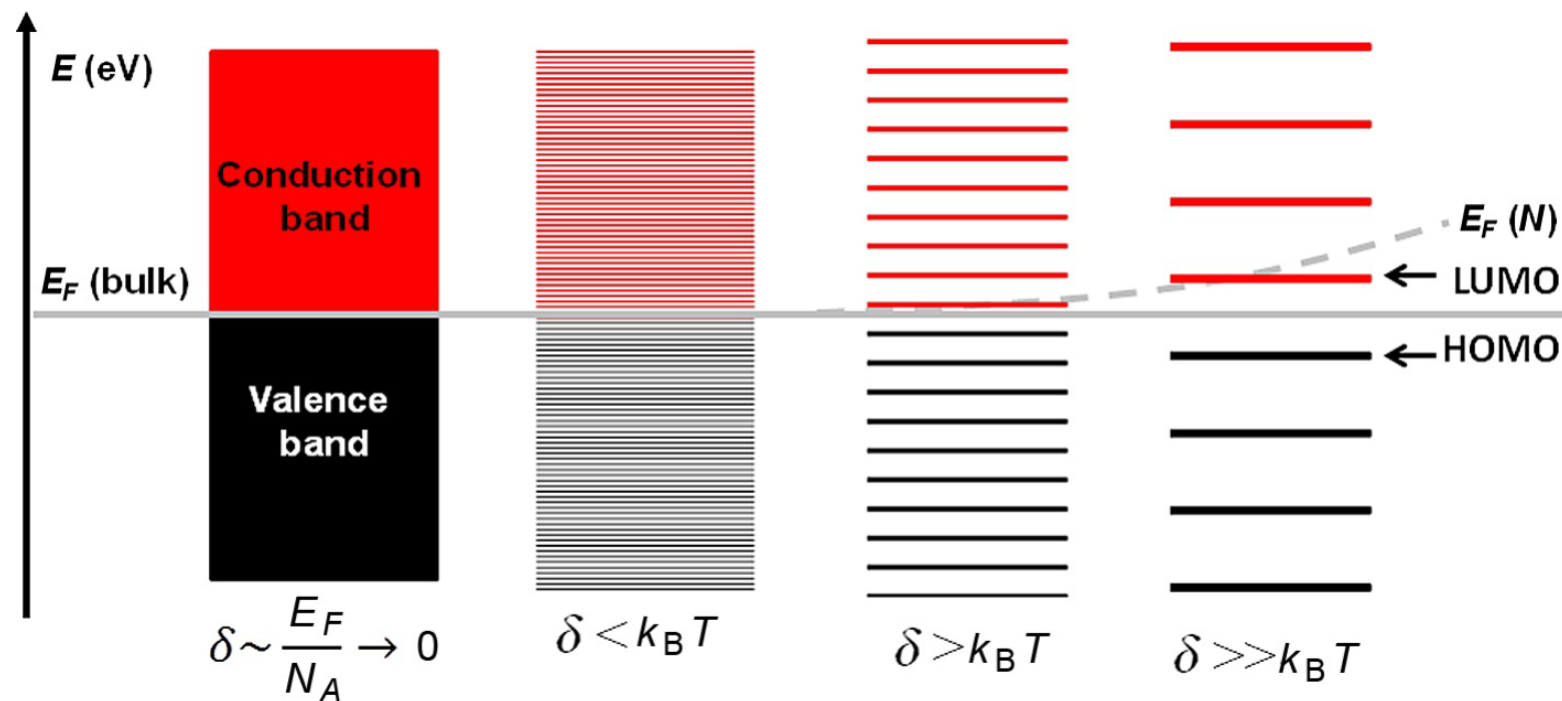

FIGURE 4.9 Confinement in multiple electron systems leads to the size-induced discretization of energy levels from bulk to cluster range, which results in an increasing of energy gaps.

➢ This discretization of DOS directly affects the *electrical conductivity in small particles*, as far as the classical criterion based on a continuity of available states in the conduction band is no longer affordable.

➢ Therefore, Dicenzo and Wertheim conceived a new criterion to define metallicity by stating that ***if the gaps are sufficiently small and the partially filled band is located close to the Fermi level, a small external excitation (electrical or thermal) can promote electrons to produce current flow***.

➢ However, for nanoclusters, *the energy gap δ becomes large and metallicity is suppressed, because $\delta > k_B T$. In this case, electrons can only produce* **electronic transitions** *and conductivity is suppressed*.

➢ Figure 4.9 illustrates the **so-called size-induced metal-to-insulator transition** *produced by the opening of the energy gap for decreasing sizes*, where the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are indicated below and above, respectively, of the Fermi energy level.

➢ **The appearance of the HOMO-LUMO gap is one of the main effects of confinement in small metallic particles**, confirmed by scanning tunneling microscopy.

The Electron Density of States (DOS) Function for Low Dimensional Systems

❑ Electronic properties of bulk metals:

✓ the solid composed of a positively charged background (core ions composed by the nuclei and the core localized electrons) bound to a gas of delocalized valence electrons.

✓ *The **inner electrons** remain localized inside the core ions forming **thin bands**, while **the valence electrons** strongly overlap forming a structure of wide energy bands whose density of states (DOS) increases proportionally to the number of atoms (valence electrons) becoming almost a continuous magnitude for bulk materials.*

➢ *However, the electronic density of states (DOS) strongly varies with the dimensionality of the nanostructure.*

✓ The density of states of *quantum confined nanocrystals* has characteristic shapes for 2D, 1D and 0D nanomaterials, and *the differences are due to the degrees of confinement of the electrons* (Fig. 3 below).

➤ In band theory, the breadth of a band is directly related to the strength of interactions among nearest neighbors. For atoms/molecules, this interaction is weak, which corresponds to a narrow band. However, as additional atoms are added to the solid, stronger interactions will ensue, resulting in a greater DOS near the Fermi level. Hence, the insulating properties of very small nanoclusters are due to the small number of neighboring atoms, which are held together primarily by *nonmetallic interactions* (e.g., van der Waal forces).

➤ *As nanocluster size increases, the atomic s, p, and d orbitals from many constituent atoms will broaden into bands, forming an energy continuum.*

➤ As the nanocluster size decreases, the energy continuum of the bulk metal is transformed into discrete energy levels, especially at band edges as shown in Figure 8.3. The **electrical properties** such as *electrical conductivity, dielectric constant, internal charge characteristics, etc.* **change drastically** when materials are **in nanoscale regime**.
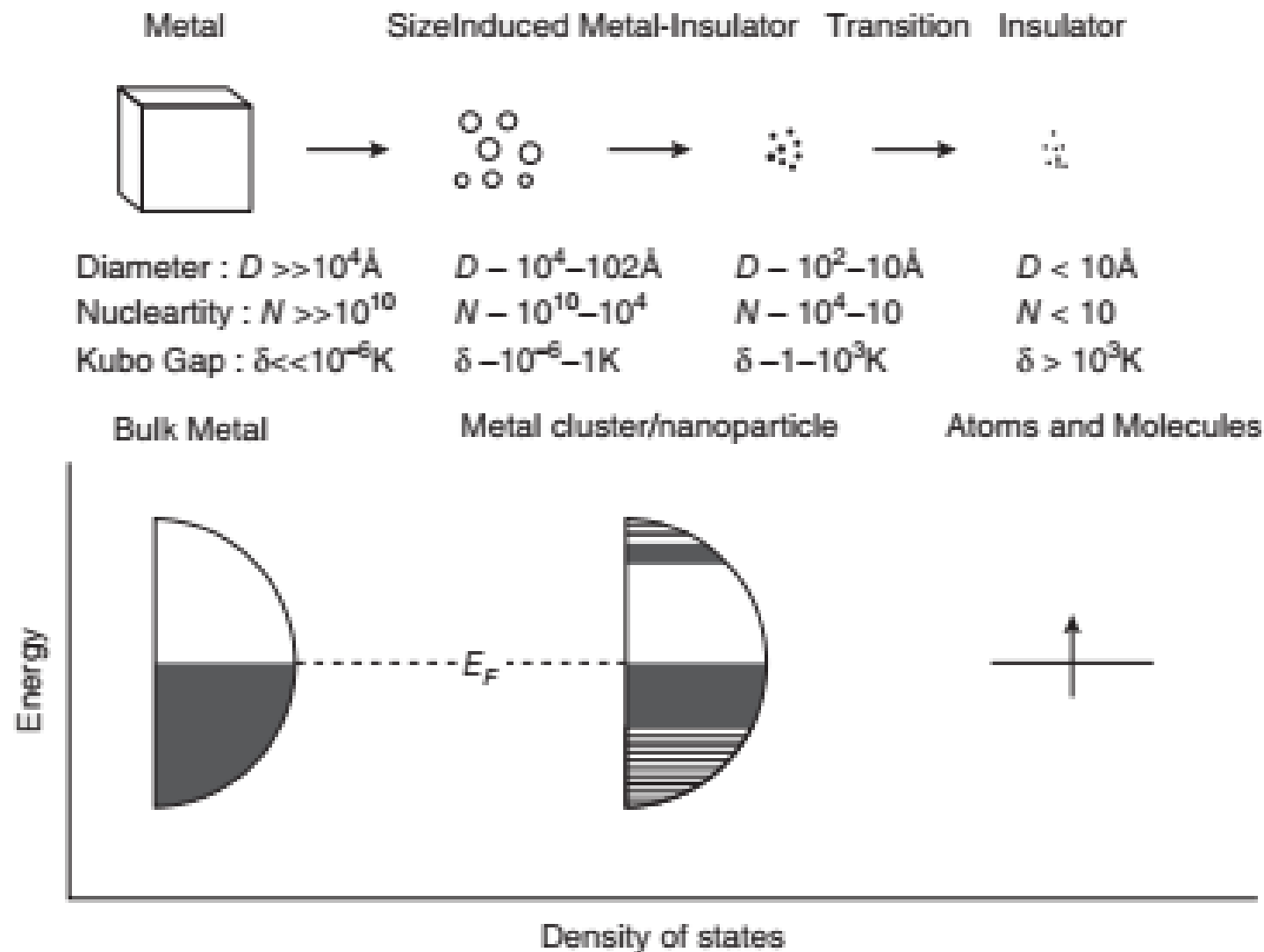
Figure 8.12 Schematic of the density of states exhibited by bulk metal relative to increasingly smaller nanoclusters. The approximate diameter (D), nuclearity (N), and Kubo gap (δ) for each size regime are indicated.

- We know electrons are Fermions. Two Fermions cannot occupy the same state!

- How do *electrons get distributed* within *bands*?

- How many electrons per band?

- What makes metal a metal and semiconductor a semiconductor?

- All crystalline materials have energy bands and band gaps. It's the filling of those bands that defines whether the material will be a metal, a semiconductor or an insulator….

- In order to find out how bands get filled with electrons we need to consider two important concepts:

- Density of states (D.O.S) – How many states per unit energy can our crystal provide?

- Electron Distribution Function – Given the Fermionic nature of electrons how can we distribute them among the available states?

- Let's first consider a Density of States function.

❑ Density of States (DOS) Calculation

❖ How do would you calculate the DOS? What is its significance?

The density of states, denoted by *D(E)*, refers to the number of quantum states per unit energy. *D(E) is the number of allowed states with energies between E and E+dE, in an **element of length or area or volume** (depending on the dimensionality).* In other words, ***the density of states, D(E), indicates how densely packed quantum states in a particular system.***

➤ *D(E)* is defined more precisely by the mathematical derivative *D(E) = dN/dE*, corresponding to the expression *dN = D(E)dE*.

➤ This means that the number of electrons *dN* with an energy *E* within the narrow range of energy $dE = E_2 - E_1$ is proportional to the density of states at that value of energy.

➤ First, let us calculate the resulting formula for *D(E)* for the **3D delocalized (bulk)** electrons.
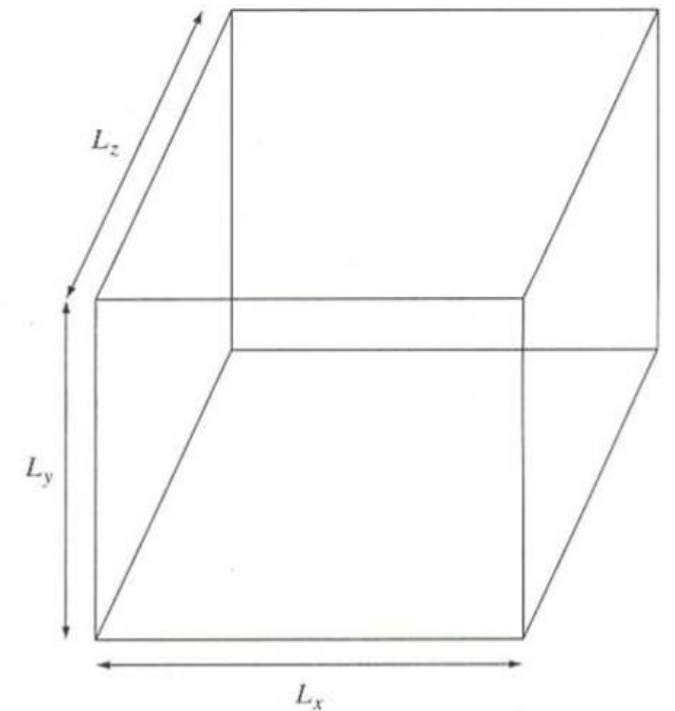

Figure 4.15 An effectively three-dimensional region of space; $L_{x,y,z} \gg \lambda_e$.

➢ In the preceding discussion, we used the de Broglie wavelength as the important "size scale" of the electron; that is, a region of space having length L is "large" if $L >> \lambda_e$, and "small" if $L \leq \lambda_e$.

➢ While this is true, the ***de Broglie wavelength depends on the energy of the electron and the most important energy is the Fermi energy***. The ***de Broglie wavelength at the Fermi energy is called the Fermi wavelength*** and is denoted by the symbol λ_F.

➢ Therefore, for a space to be sufficiently "**large**" so that the energy levels of the electron form an approximately continuous set, we usually require L_x, L_y, $L_z >> \lambda_F$.

➢ If we assume that the electrons (of mass m) are **confined** by the hard wall boundaries (of dimensions as shown in the Figure), then by solving the Schrödinger wave equation for a particle in a 3D box, the energy levels are given by:

$$E = \frac{\hbar^2}{2m}[\left(\frac{n_x\pi}{L_x}\right)^2 + \left(\frac{n_y\pi}{L_y}\right)^2 + \left(\frac{n_z\pi}{L_z}\right)^2]$$

➢ Since n_x, n_y, n_z are integers, and $L_{x,y,z}$ are very large (for bulk system), the ratios n_x/L_x, n_y/L_y, and n_z/L_z vary *almost continuously* from very small values to very large values of energy.

❑ Density of States (DOS) Calculation: *Dimensionality*

❖ *Key points:* When a large number of neighboring orbitals overlap, bands are formed. However, the natures of these bands, their energy patterns, and their densities of states are very different in different dimensions.

➢ *For the calculation of the density of electronic states* and what determines the energy range into which orbitals of *a given band will split,* first, let's recall the energy expression for the 1 and 2- dimensional electron in a box case, and let's generalize it to three dimensions. The general result is

➢ $$E = \sum_j \frac{\hbar^2}{2m} \left[\left(\frac{n_j \pi}{L_j} \right)^2 \right]$$

➢ where the sum over j runs over the number of dimensions (1, 2, or 3), and L_j is the length of the box along the *j*-th direction. We see here that the energy level spacing grows as n^2. Whereas there is only one state for a given energy in the 1D case, in the 3D case the degeneracy of states grows with energy.

➢ For one dimension, one observes a pattern of energy levels that grows with increasing n, and whose spacing between neighboring energy levels also grows as a result of which *the state density decreases with increasing n.*

➤ However, in 2 and 3 dimensions, the pattern of energy level spacing displays a qualitatively different character, especially at high quantum number.

➤ Consider first the **3-dimensional case** and, for simplicity, let's use a box that has equal length sides L. In this case, the total energy E is $\hbar^2\pi^2/2mL^2$ **times** $(n_x^2 + n_y^2 + n_z^2)$.

➤ The latter quantity can be thought of as the square of the length of a vector R having three components n_x, n_y, n_z. Now think of three Cartesian axes labeled n_x, n_y, and n_z and view a sphere of radius R in this space.

➤ The volume of the 1/8 th sphere having *positive values* of n_x, n_y, and n_z and having radius R is $1/8 \times (4\pi R^3/3)$. Because each cube having unit length along the n_x, n_y, and n_z axes corresponds to a single quantum wave function and its energy, the total number $N_{tot}(E)$ of quantum states with positive n_x, n_y, and n_z and with energy between zero and $E=(\hbar^2\pi^2/2mL^2)R^2$ is

$$N_{tot} = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) = \frac{1}{8}\left(\frac{4}{3}\pi\left[\frac{2mEL^2}{\hbar^2\pi^2}\right]^{3/2}\right)$$

➤ The number of quantum states with energies between E and E+dE is $dN_{tot}dE/dE$, which gives the density $\Omega(E)$ of states near energy E:

$$\Omega(E) = \frac{dN_{tot}}{dE} = \frac{1}{8}\left(\frac{4}{3}\pi\left[\frac{2mEL^2}{\hbar^2\pi^2}\right]^{3/2}\frac{3}{2}\sqrt{E}\right).$$

➤ Notice that this state density increases as E increases. This means that, in the 3-dimensional case, the number of quantum states per unit energy grows; in other words, the spacing between neighboring state energies decreases, very unlike the 1-dimensioal case where the spacing between neighboring states grows as n and thus E grows.

➤ This growth in state density in the 3-dimensional case is a result of the degeneracies and near-degeneracies that occur. For example, the states with n_x, n_y, n_z = 2,1,1 and 1, 1, 2, and 1, 2, 1 are degenerate, and those with n_x, n_y, n_z = 5, 3, 1 or 5, 1, 3 or 1, 3, 5 or 1, 5, 3 or 3, 1, 5 or 3, 5, 1 are degenerate and nearly degenerate to those having quantum numbers 4, 4, 1 or 1, 4, 4, or 4, 1, 4.

➤ We obtain the density of states as number of states per unit energy per unit volume from $\Omega(E)/L^3$.

➤ In the **2-dimensional case**, degeneracies also occur and cause the density of states to possess an E-dependence that differs from the 1- or 3-dimensional case. In this situation, we think of states having energy $E=(\hbar^2\pi^2/2mL^2)R^2$, but with $R^2=n_x^2+n_y^2$.

➤ The total number of states having energy between zero and E is $N_{\text{total}} = 4\pi R^2 = 4\pi E\left(\dfrac{2mL^2}{\hbar^2\pi^2}\right)$

➢ So, the density of states between E and E+dE is

$$\Omega(E) = \frac{dN_{\text{total}}}{dE} = 4\pi \left(\frac{2mL^2}{\hbar^2 \pi^2} \right)$$

➢ That is, in this 2-dimensional case, the *number of states per unit energy is constant* for high E values (where the analysis above applies best).

➢ This kind of analysis for the **1-dimensional case** gives $\quad N_{\text{total}} = R = \sqrt{\dfrac{2mEL^2}{\hbar^2 \pi^2}}$

➢ so, the state density between E and E+dE is: $\quad \Omega(E) = \dfrac{1}{2}\sqrt{\dfrac{2mL^2}{\hbar^2 \pi^2}}\dfrac{1}{2}E^{-1/2}$

➢ 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.

➢ If we normalize to the length (L) of the box, Ω(E)/L (=...???), we obtain the density of states as number of states per unit energy per unit length.

➢ These findings about densities of states in 1-, 2-, and 3- dimensions are important because, in various problems one encounters in studying electronic states of extended systems such as solids, chains, and surfaces, one needs to know how the number of states available at a given total energy E varies with E.

➢ A similar situation occurs when describing the translational states of an electron or a photo ejected from an atom or molecule into the vacuum; here the 3-dimensional density of states applies.

➢ Clearly, the state density depends upon the dimensionality of the problem, and this fact is what I want the students reading this text to keep in mind.
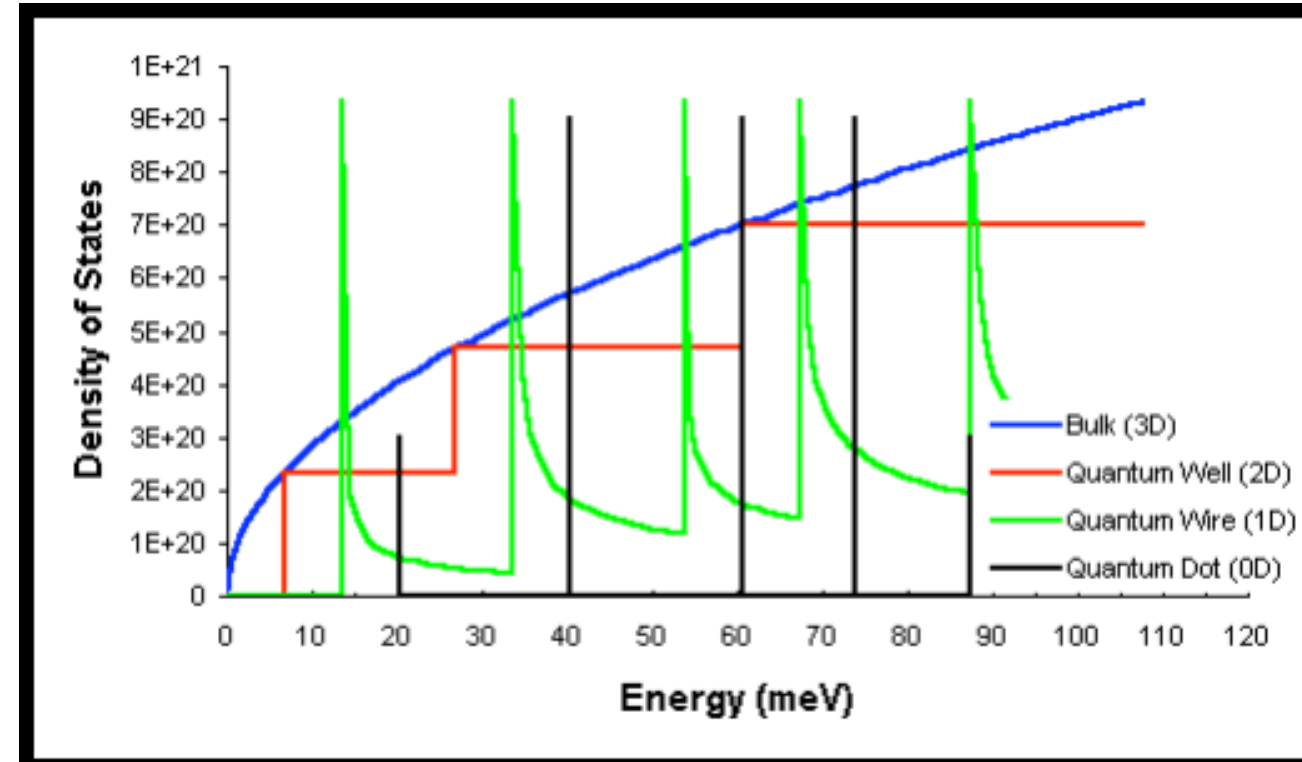
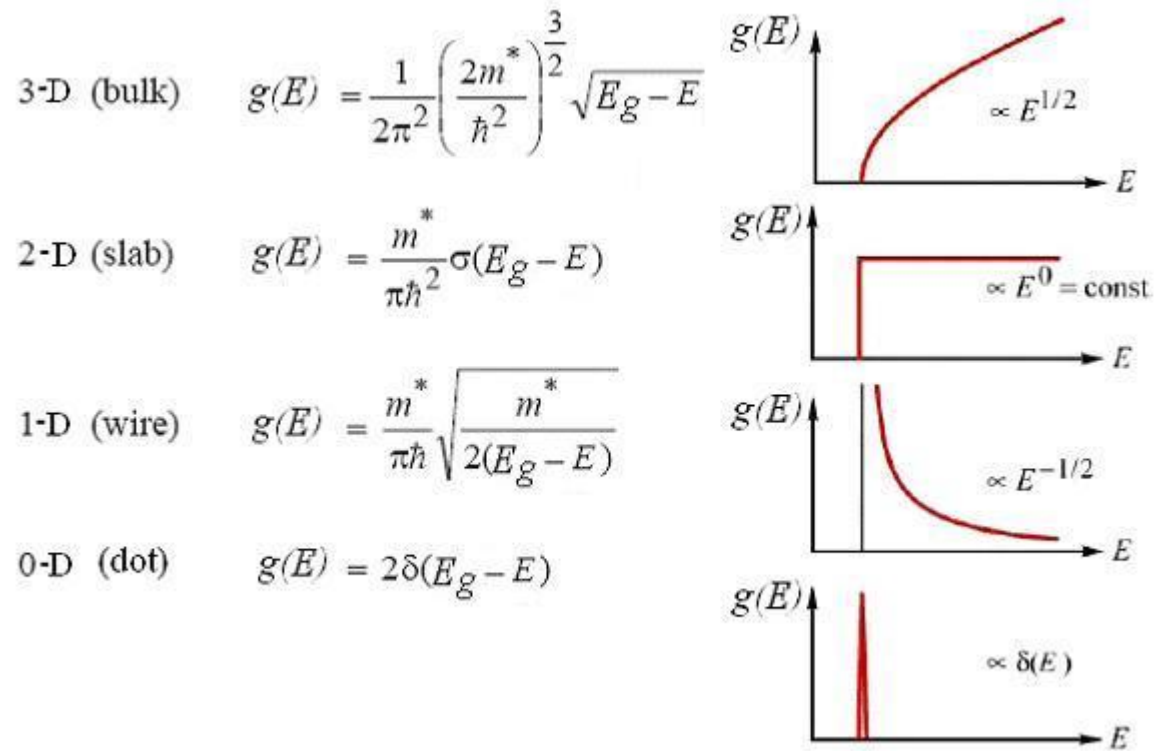|			
3-D (bulk)	$g(E) = \dfrac{1}{2\pi^2}\left(\dfrac{2m^*}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E_g - E}$		
2-D (slab)	$g(E) = \dfrac{m^*}{\pi\hbar^2}\sigma(E_g - E)$		
1-D (wire)	$g(E) = \dfrac{m^*}{\pi\hbar}\sqrt{\dfrac{m^*}{2(E_g - E)}}$		
0-D (dot)	$g(E) = 2\delta(E_g - E)$		

Figure… Density of states D(E) plotted as a function of the energy E for conduction electrons delocalized in one (Q-wire), two (Q-well), and three (bulk) dimensions and confined in all three dimensions.

Electrical Properties

➤ There are *three categories of materials based on their electrical properties*, namely **conductors, semiconductors, and insulators**. The energy separation between the *valence band* and the *conduction band* is called band gap, E_g.

➤ *The ability to fill the conduction band with electrons and the energy of the band gap determine whether a material is a conductor, a semiconductor or an insulator.* In conducting materials such as metals the valence band and the conducting band overlap, so that the value of E_g is small: thermal energy is enough to stimulate electrons to move to the conduction band. In semiconductors, the band gap is of few electron volts. If an applied voltage exceeds the band gap energy, electron jump from the valence band to the conduction band, thereby forming electron–hole pairs called ***excitons***. Insulators have large band gaps that require an enormous amount of voltage to overcome the threshold. This is why these materials do not conduct electricity.

➤ **As the size of a particle is brought down in the nanometer regime, the quantum confinement effect causes the band gap to increase, thus a metal becomes semiconductors and finally an insulator on decreasing its size.**
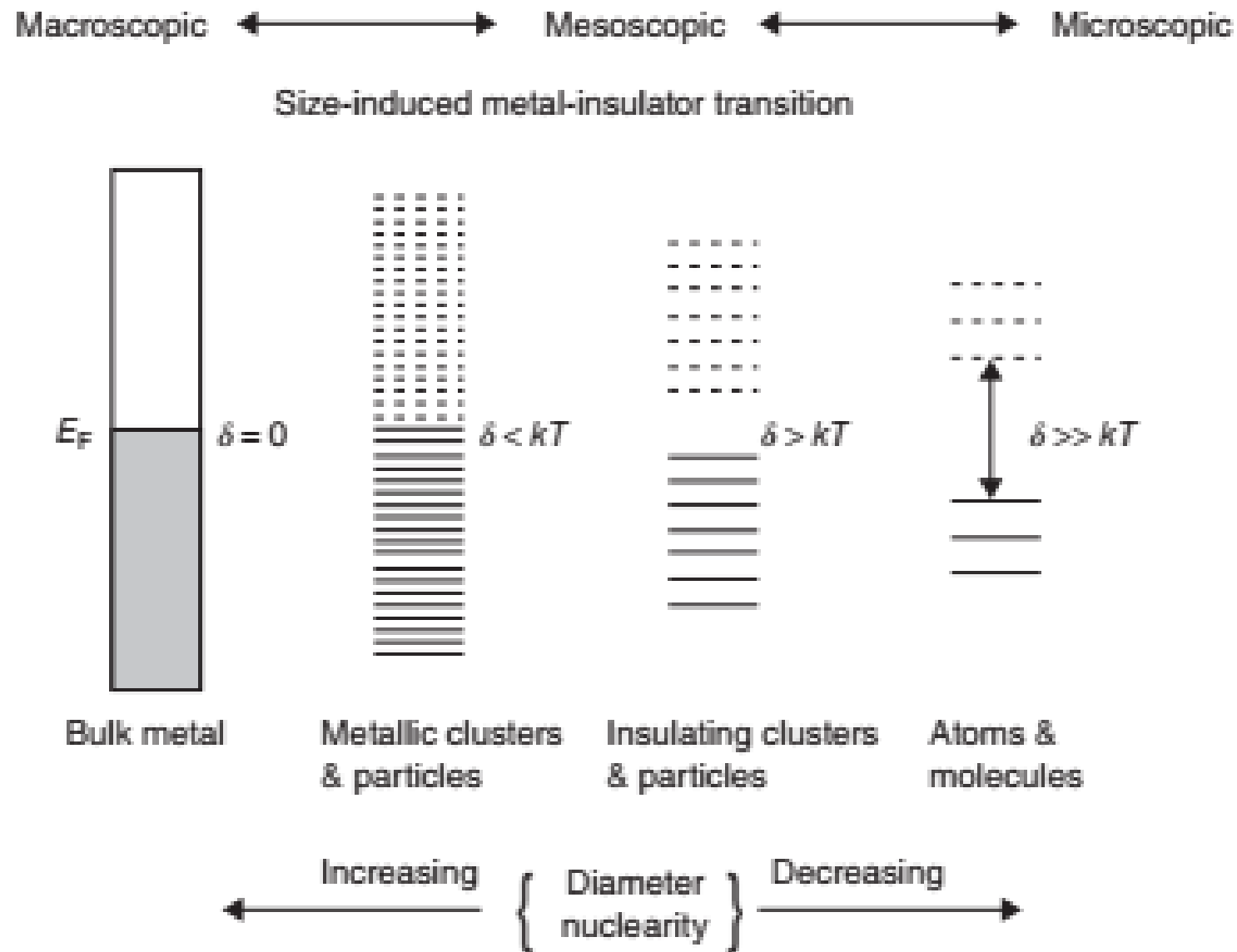
Macroscopic ◄─────► Mesoscopic ◄─────► Microscopic

Size-induced metal-insulator transition

E_F $\delta = 0$ $\delta < kT$ $\delta > kT$ $\delta \gg kT$

Bulk metal   Metallic clusters   Insulating clusters   Atoms &
              & particles   & particles   molecules

◄───── Increasing ───── { Diameter / nuclearity } ───── Decreasing ─────►

Figure 8.3 Evolution of the band gap and the density of states as the number of atoms in a system increase.

For the smallest of metallic nanoclusters with dimensions ca. <2 nm, the absorption of surface plasmons disappears.

Since so few atoms comprise discrete nanoclusters of this size, the spacing between adjacent energy levels (referred to as the Kubo gap, δ) becomes comparable to the thermal energy, k_BT – especially at lower temperatures and smaller nanocluster diameters. *This results in a shift in conductive properties of the nanoclusters from metallic to semiconducting and insulating, with decreasing size* (Figure 8.3).

Electrical properties of some nanomaterials are related to their unique structures and some nanomaterials exhibit electrical properties that are absolutely exceptional. *For instance, carbon nanotubes can be conductors or semiconductors depending on their nanostructure.*

ELECTRICAL CONDUCTANCE in NANOMATERIALS

Some nanomaterials exhibit remarkable electron transport properties, which are strongly dependent on their nanocrystalline structure. ***In particular, 1D nanomaterials (carbon nanotubes, titania nanotubes, silica nanowires, polymeric nanowires, and nanofibers) are the most attractive materials due to their different electrical conductance, which can be monitored by the change in electrical conductance of the fabricated electrode***. Electron transport properties of such nanomaterials are very important for electrical and electronic applications, as well as for *understanding the unique 1D carrier transport mechanism.*

It has been noticed that the wire length and diameter, wire surface condition, chemical composition, crystal structure and its quality, crystallographic orientation along the wire axis, and so on are all important parameters *that influence the electron transport mechanism of nanowires.*

Because of the high surface-to-volume ratio and novel electron transport properties of these nanostructures, their electronic conductance is strongly influenced by minor surface perturbations (such as those associated with the binding of macromolecules).

Such 1D material thus offers the prospect of rapid (real-time) and sensitive label-free bioelectronics detection, and massive redundancy in nanosensor arrays.

In particular, carbon nanotubes are the most exciting 1D nanomaterial that has generated considerable interest due to their unique structure-dependent electronic and mechanical properties. The direct electron transfer ability of carbon nanotubes is another important factor that has been exploited in the fabrication of efficient electrochemical biosensing devices. *Carbon nanotubes enhanced the performance of bioelectronic devices partly due to the high enzyme loading and partly because of the better electrical communication ability of the nanotubes.*

Two scattering mechanisms participate in any metal: (1) **scattering by lattice defects** (foreign atoms, vacancies, interstitial positions, grain boundaries, dislocation, stacking disorders, etc.), and (2) **scattering at thermal vibrations of the lattice**, called **phonons**.

The first contribution is more or less independent of temperature, the second is independent of lattice defects.

The rule of Matthiessen, $\rho = \rho_s + \rho_T(T)$, says that the *specific resistance* of a metal ρ consists of the temperature-independent part of the lattice defects ρ_s and the temperature-dependent part of the lattice vibrations ρ_T. *At elevated temperature ρ_T increases linearly with the temperature. This linear increase of the specific resistance is a typical property of bulk metals.* At low temperatures, the phonon contribution to the resistance disappears by the 5th power of temperature.

A collective motion of electrons (current I) in a bulk metal is induced by applying a voltage V. Ohm's Law describes the linear relation between ρ and I by $V = R \cdot I$ (where R = resistance of the material).

All relations described above depend on the existence of a band structure, that is, the presence of freely mobile electrons in the lattice. As already discussed, **the band structure begins to change if the dimension of a metal particle becomes small enough**. ***Discrete energy levels finally dominate* and,** *as a consequence,* ***Ohm's law is no longer valid***.

How does the current–voltage behavior change if we approach a ***nanoscale metal particle?***

We observe ***"Quantum transport"***.

Quantum transport in small devices and materials has been studied extensively. Only a brief account is presented below including discussion on *ballistic conduction, tunneling conduction, and Coulomb charging*.

QUANTUM RESISTANCE AND QUANTUM CONDUCTANCE

Conductance—*The Influence of Wire Radius*

The concept of conductance is used to explain the manner in which electrical current flows through a material.

The original theory of conductance was developed in 1900 by Paul Drude. This theory states that a conductor must have free electrons to contribute to the flow of current.

These free electrons move though the conductors like gas. They have a mean velocity of zero because of the random direction of the movement, while the mean speed is quite high. When an electric field is placed on the conductor, the cloud of electrons will move from high potential to low potential. *Along the path of travel, the electrons move and collide with lattice ions and then move again.* **This collision and acceleration pattern are what limit the flow of current and creates conductor resistance.** The movement of the electrons is referred to as the *drift velocity*.

In the next section we will examine what happens when wire length L becomes extremely small relative to the mean free path, resulting in an interesting phenomenon that is not encountered in the world of macroscopic conductors. However, before considering this case, it is worthwhile to make *some comments about the influence of wire cross-section size on conductivity.*

In the classical Drude model of metal conduction the resistance of a wire is given by:

$R = L/\sigma A$

where A = cross-sectional area of a homogeneous rectangular solid and length L.

For example, assuming a copper ($\sigma = 5.9 \times 10^7$ S/m) wire having radius $a = 10$ mm, $R = L/\sigma A$ $= L/[(5.9 \times 10^7 \text{ S/m})(2\pi a L)] = 5.395 \times 10^{-5}$ ohms/m.

Thus, one would need approximately 18,536 m of wire to amount to a resistance of one ohm, which is why we can often ignore wire resistance in electrical circuits.

However, if $a = 10$ μm, $R = 53.95$ ohms/m, amounting to 1 ohm in only 1.85 cm.

If $a = 10$ nm, the resistance is huge, $R = 5.395 \times 10^7$ ohms/m.

However, it is important to note that for wires having radius values on the order of the mean free path or less, the conductivity value is changed from the case of bulk material.

In the 1–20 nm radius range, the conductivity of the wire certainly will differ appreciably from the bulk value, and generally the conductivity significantly decreases as a is reduced.

This is due to several effects, such as scattering from the wire's surface and from grain boundaries, not to mention the difficulty in fabricating high-quality, defect-free metals at small size scales.

Thus, **as a very rough rule of thumb, one can use the bulk value of conductivity for many good conductors when the radius value is above approximately a = 80 – 100 am**.

Below this point, down to radius values of perhaps 5–10 nm (*but above metallic **quantum** wire dimensions*), *one may **expect to need to use a size-dependent value of conductivity**,* perhaps based on measurement.

At very low wire cross-sectional dimensions, a quantum wire model that accounts for transverse quantization would be necessary.

In the **classical Drude model** of metal conduction the **conductance** $G \equiv 1/R = A/\rho L$, measured in Siemens S, **decreases** uniformly **as the cross-section A of the wire decreases**.

In **quantum mechanics**, *the* **conductance of a metallic wire is** *not a continuous function* *of area A, but changes in steps, or* **G $=2e^2n/h$** *= (7.75×10^{-5})n Siemens, where n is an integer and each step corresponds to a "conductance channel".*

We obtain the classical conductance over a continuous range from 0 to ∞ by connecting these channels, each with a conductance $G_0 = 2e^2/h$, in combinations of series and parallel circuits.

Ballistic Transport

As **the length L of a conduction path** becomes very small, do the above formulas continue to hold?

One may guess that **they do not**, since, for one thing, conductivity is a bulk parameter, and is derived assuming a large number of electrons (the electron gas model) and a large number of collisions between electrons and phonons, impurities, imperfections, etc.

In particular, if L is reduced to become much less than the mean free path L_m (l), one would expect that *no collisions would take place*, rendering the collision-based model useless. This indeed occurs, and in this section, we consider the case when $L << L_m$ (or l).

It has been possible only recently to experimentally investigate resistance at the nanoscale. Much progress has been made in understanding the underlying physics of nanoscale and mesoscopic transport. The overarching idea is that **at very small length scales**, electron transport occurs **ballistically**.

It can be appreciated that ballistic transport will be important in many future nanoscopic devices.

Ballistic conduction occurs when the length of the conductor is smaller than the electron mean-free path.

In this case, each *transverse* waveguide mode or conducting channel contributes $G_0 = 2e^2/h = 12.9$ kΩ^{-1} to the total conductance.

Another important aspect of ballistic transport is that no energy is dissipated in the conduction, and *there exists no elastic scattering.*

The latter requires the absence of impurities 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.
The conductance of arc-produced multi-wall carbon nanotubes is one unit of the conductance quantum G_o, and no heat dissipation is observed. Extremely high stable current densities, $J > 10^7$ A/cm^2 have been attained.

A. Conductivity of Metallic (1-D) Nanowires

In order to understand what the conductance steps actually are and why they occur at the integer multiples of $2e^2/h$ we need to refer to a simplified explanation of this complicated phenomenon:

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

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

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

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

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

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 $\Delta V = \Delta E/e$.

From the above equations, we can infer that the conductance, $G = Ne^2v/L\Delta E$, **is dependent on the number of electrons, their charge, velocity, and drop in potential energy, as well as the length of the wire.**

However, 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), $N = D(E)\Delta E.L$, 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.

Thus, $N = D(E)\Delta E.L = \dfrac{\sqrt{m}}{\sqrt{2}.\pi\,\hbar} \cdot \dfrac{1}{\sqrt{E}} \cdot L \cdot \Delta E = \dfrac{2}{hv} \cdot L \cdot \Delta E$ *(since E=mv²/2)*

Thus, the conductance, $G = Ne^2v/L\Delta E = = \dfrac{2e^2}{h} = 7.748 \times 10^{-5}$ S, which is the *quantum of electrical conductance.* It is important to note how in this derivation *nothing is mentioned about the material properties* of the conductor or *its dimensions*, therefore **G is a truly fundamental unit**.

Wires in which the inequality $l\ (L_m) >> L$ applies are defined ballistic conductors (rather than diffusive conductors) and their conductance can increase (decrease) only in units of G (as conduction channels are added or removed), in other words, their conductance is quantized.

Consequently, the two-terminal resistance is calculated to be 12.906 kΩ for such a 1D structure.

As can be observed, an ideal 1D structure has a *finite resistance*. This is called a **resistance quantum** (the inverse of **conductance quantum**).

Such resistance can also be experimentally measured. At the end of the 1980s, the University of Cambridge and Delft groups reported the measurements of steps in the conductance of a quasi-1D configuration in a field effect transistor structure by means of the voltage applied at the gate as shown in Figs. 3 and 6.6 below.

Similarly, we can obtain the equation defining current, I, as: $I = 2e^2 \Delta V / h$.

Interestingly, the above two Eqns. show that **in a 1D structure, the current only depends on the voltage across it via fundamental constants**.
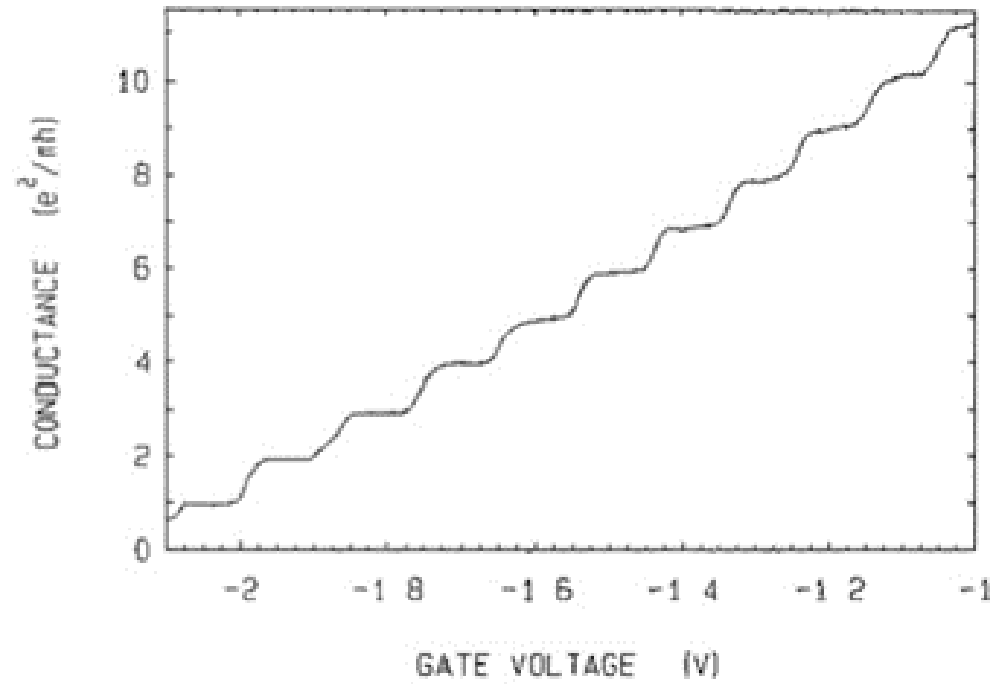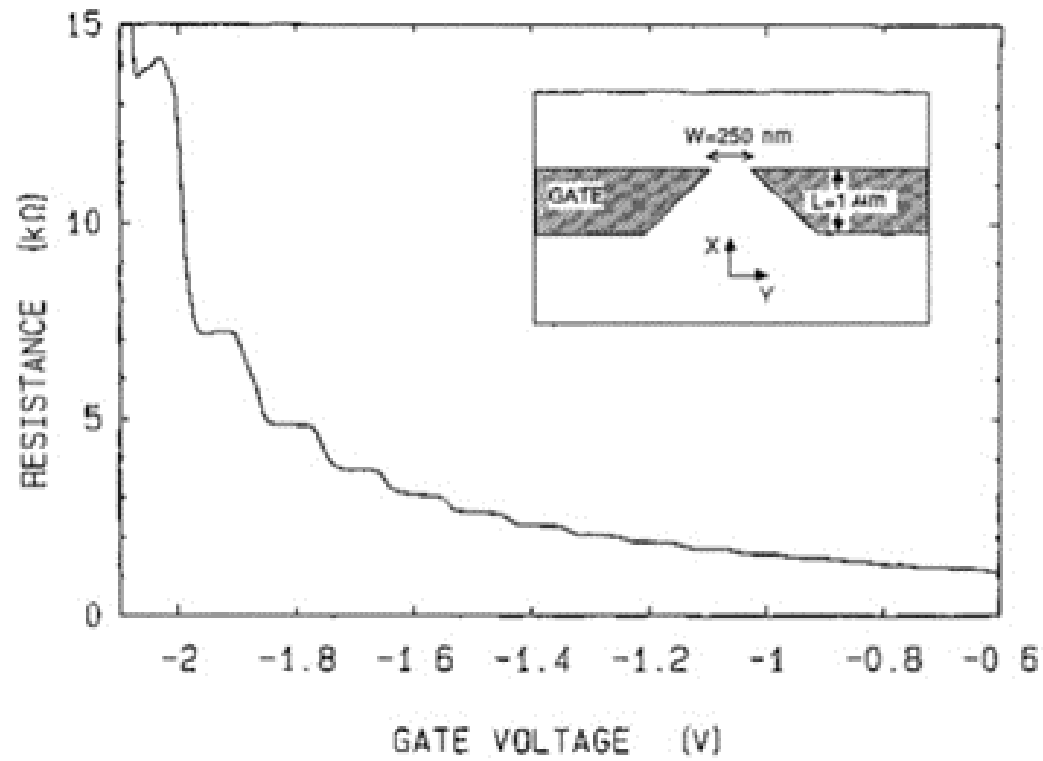
Figure 3: **Left**: Resistance of the point contacts as a function of gate voltage at 0.6 K. Inset: Point-contact layout.

Right: Point-contact conductance obtained from resistance after subtraction of the lead resistance. *The conductance shows plateaus at multiples of $2e^2/h$.*

All the above assumptions are for near-zero Kelvin temperatures. The quantization of conductance is readily shown in low-temperature experiments. *At higher temperatures, a thermal effect also appeared which smoothed out the step shape*.

Notice that as temperature increases, the *observed quantization tends to vanish*. This is due to thermal energy $k_B T$ becoming comparable to the sub-band energy spacing. For instance, **at room temperature (T = 293 K), $k_B T$ = 0.025 eV**. For a rectangular cross-section wire with infinite confining potential (hard-wall model), we have

$$E_{n_y n_z} = \frac{\hbar^2}{2m} \left[\left(\frac{n_y \pi}{L_y} \right)^2 + \left(\frac{n_z \pi}{L_z} \right)^2 \right].$$

Assuming $L_y = L_z = 10$ nm, then with n_y, n_z = 1, 1 and n_y, n_z = 1, 2 we have, $E_{1,1}$ =0.0075 eV and $E_{1,2}$ = 0.0188 eV, such that ΔE = 0.0113 eV, which is less than $k_B T$. Therefore, the sub-band quantization becomes "washed out."

However, if $L_y = L_z = 1$ nm, then E_{11} = 0.75 eV and E_{12} = 1.88 eV, such that ΔE = **1.13 eV**, which is much **greater than $k_B T$**. *In this case, the conductance quantization will be quite evident at room temperature.*

The temperature dependence of the conductance quantization of a quantum point contact is shown in Fig. 6.6 where quantization disappears quickly with increasing temperature due to the large size of the point contacts (around 250 nm).

Therefore, **either temperature must be very low,** or **cross sections must be very small, for quantum effects to be noticed**. Even for low temperatures, for paths longer than a few hundred nanometers, defects are likely to be present that destroy quantization.
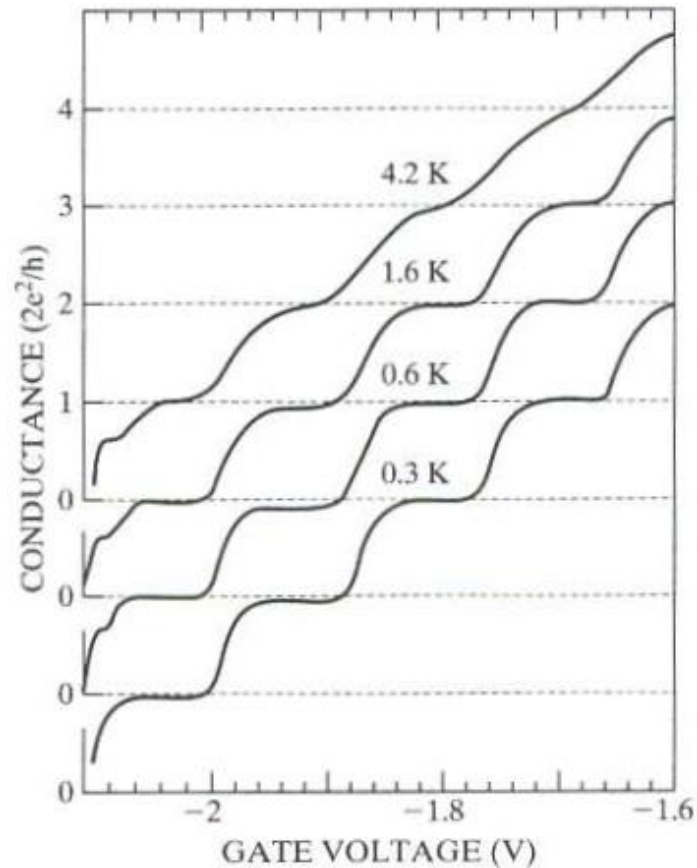

Fig. 6.6 Conductance quantization of a quantum point contact in units of $2e^2/h$. As the gate voltage defining the constriction is made less negative, the width of the point contact increases continuously, but the number of propagating modes at the Fermi level increases stepwise. The resulting conductance steps are smeared out when the thermal energy becomes comparable to the energy separation of the modes.

Temperature dependence of quantized conductance for a quantum point contact. The two-dimensional electron gas has a Fermi wavelength of 40 nm and the width of the point contact is around 250 nm. (Based on Fig. 6 from "Quantum Ballistic and Adiabatic Electron Transport Studied with Quantum Point Contacts." Phys. Rev. B 43 (1991): 12431. © 1991. American Physical Society.)

Since the invention of the first transistor, electronic devices kept decreasing in size to improve performance and power consumption.

If technology continues to progress at the present pace, the devices will become so small that they will no longer be governed by the diffusive conduction model used today.

Instead, nano-machines will obey the quantum laws of nature, which are quite foreign to modern industry.

Therefore, it is becoming increasingly important to investigate quantized conductance and behavior of matter at the atomic scale in order to build reliable circuitry.

Usually, quantum contacts are made using sophisticated techniques and state-of-the art equipment. However, recently it was shown that quantum contacts can also be shown by gently vibrating two thin wires.

Effects of Quantum Conductance

➢ **The resistance created by quantum conductance can cause** *a number of undesired effects* **with respect to nanotechnology.** These effects can be demonstrated with an example.

➢ Consider *a microprocessor designer who wishes to use* **molecular transistors** *in a new design*. The design, in theory, calls for *the flow of current across a carbon-carbon bond*. Let us take a look at some numbers that will bring this example to light.

➢ Let us take a look at the *carbon-carbon* (**C = C**) bond. This **C = C** bond has a bond energy of more than 606.68 kJ/**mol**. If we divide this number by Avogadro's constant, we will obtain the energy per bond:

$$\text{(606.68 kJ/mol)}/(6.022 \cdot 10^{23} \text{ bonds/mol}) = \mathbf{1.0074 \cdot 10^{-18} \text{ J/bond}}.$$

Remember the following relations:

1A = 1C/1s

$e- = 1.602 \cdot 10^{-19}$ C

1 amp = $6.242 \cdot 10^{18}$ $e-$/s

$V=IR$

$V=1J/1C$

$R=1027.3\Omega$

➢ Say, *the design parameters call for this transistor to operate at 3 GHz clock speed.* Current flow is measured in amperes and one ampere equates to $6.242 \cdot 10^{18}$ electrons passing a cross-sectional area per second. Now consider the following equations.

➢ If this hypothetical processor is to work at 3 GHz it would need *at least one electron to flow* for each transition. This means at least $3 \cdot 10^{9}$ electrons must flow per second at maximum.

➤ The *current* *flowing* is:

$$(3\times10^9 \text{ e-/s}) \times (1.602\times10^{-19} \text{ C}) = 4.806\times10^{-10} \text{ A}$$

➤ From Ohm's Law:

$$V = 4.8062\times10^{-10} \text{ A} \times 1027.3 \text{ } \Omega = 4.9374\times10^{-7} \text{ V}$$

➤ Now we will calculate the **total charge** by multiplying the charge of an electron by the total number of electrons.

$$1.602\times10^{-19} \text{ C/e-} \times (3\times10^9 \text{ e-}) = 4.806\times10^{-10} \text{ C}$$

➤ Using the solutions from above equations, we will now calculate the **energy generated**.

$$J = V\times C = 4.9374\times10^{-7} \text{ V} \times 4.806\times10^{-10} \text{ C} = \mathbf{2.3729\cdot10^{-16} \text{ J}}$$

➤ From a comparison of the energy of the electrons (2.3729×10^{-16} J) and the C=C bond energy (1.0074×10^{-18} J/bond), we see that at **3 GHz** *the current required is two orders of magnitude high* that **the bond would break** when *the transistor works with this clock speed*.

➤ This *problem could be overcome* with a different molecule, but *its effect is evident in the current state of nanotechnology*.

➢ ***The effects of quantum conductance show a clear obstacle in nanotechnology*** and must be overcome by new thinking and new designs if the current state of the art is to continue expanding in accordance with Moore's Law.

➢ *The International Technology Roadmap for Semiconductors shows that single electron transistors and molecular transistors have a theoretical maximum circuit speed of* **one gigahertz.**

➢ *This is much slower than the current state of the art.*

➢ **Their size**, however, allows them to be **packed in tightly enough to create multiple core systems** *that are superior to what is currently available.*

❑ Quantum Resistance & Superconductivity

➢ In the previous section, **we showed that the resistance between two atoms has a finite nonzero value.**

➢ However, **superconductors have shown zero resistance *and unimpeded conductance.*** This creates an interesting question.

➢ *Why does a superconductor have zero resistance and hence zero resistivity?*

➢ For that answer, *we will take a look at BCS theory. BCS theory was developed by John Bardeen, Leon Cooper and John Schrieffer in 1948.*

➢ In essence, *the theory states that superconductivity is a* **macroscopic effect** of the **Bose condensation of a pair of electrons.**

➢ In superconducting solids, the conduction electrons condense (at low temperatures) into Cooper pairs with the characteristic size given by the coherence length ξ. *These electrons will take on the properties of a* **boson**.

➢ Recall that the **bosons** *are* **full integer spin particles** *and are* **not fermions (*half-integer spin particles*).**

➢ This property excludes them from the restriction set down by the Pauli Exclusion Principle. According to Pauli Exclusion Principle, only two electrons could be promoted to the conduction band. We assumed that *electrons could not have the same quantum state which dictated the need for slight energy changes for electrons to move from state to state*. However, *bosons do not have this restriction* and *would be able to move about freely without the need for an external potential* to push them along.

➢ Superconductivity in quantum wires depends on whether the normal resistance R_N of the wire is lower (superconducting) or higher (normal conducting) than the quantum resistance $R_q = h/2e^2 \approx 6.5/k\Omega$ for Cooper pairs. This has been demonstrated for MoGe quantum wires of diameters of ~15 nm and lengths of ~150 nm with a coherence length (size of Cooper pairs) ξ = 8 nm, where the normal resistance R_N increases with decreasing diameter so that superconductivity disappears at diameters below 14 nm. This normal conducting behavior at small diameters is ascribed to quantum phase slip tunneling. A non-zero low-temperature resistance has also been observed for an 11 nm diameter wire (R_N = 9kΩ) of Al which is a bulk superconductor.

B. Current–Voltage Behavior of a Zero-Dimensional (0-D) Metal Particle

❖ *Key points*: How does the *current–voltage behavior change if we approach a zero-dimensional metal particle*? A "staircase" kind of current–voltage (I–V) plot is obtained due to repeated tunneling of single electrons, as shown later. This is observed when **Coulomb blockade** or **Coulomb charging** occurs.

➢ A very important aspect to consider is the connection of the quantum dot to the "outside world," or, alternatively, the interaction of a quantum dot with the outside world.

➢ In the second case, we often want to "interrogate" the dot remotely. For example, we may want the dot to glow (i.e., emit photons) when illuminated with radiation, in order to be used as a marker, for, say, locating a cancer cell to which the dot is attached. We may even want the dot to cause sufficient heating of the cell to kill it, which has, in fact, already been used in the treatment of skin cancer.

➢ Here, we want to consider the first scenario, where we "connect" a quantum dot to wires *via tunnel junctions*, in order *to form an electronic device such as a **transistor***.

➢ Not only is this a practical issue, but also, as it turns out, it is one that leads to interesting phenomena and useful applications.

➢ In particular, *we want to study a method of "communicating" with a nanoscopic object by bringing electrical leads in close proximity to, but not making contact with the object*.

➢ This is depicted schematically in Fig. 6.1. which shows a quantum dot separated from two leads by an insulating region (surrounding the Q-dot).
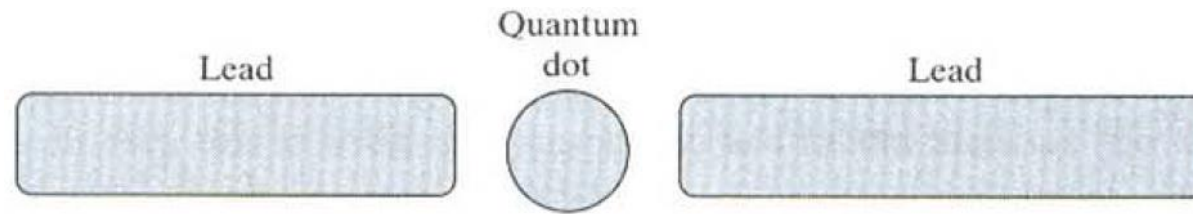

Figure 6.1 Nano-object coupled to external leads.

➢ *Although the leads do not contact the object, d.c. electrical current can pass through the system if the gap between the leads and the dot is sufficiently small, despite the fact that the gap is modeled as a perfect insulator.*

➢ Indeed, the connection between the object and the outside world (i.e., the leads) is by a process known as **quantum tunneling**, or simply **tunneling**.

➢ Note there are two tunnel junctions between the dot and leads.

➤*It should be noted that "**tunneling**" is the penetration of an electron into an energy region that is classically forbidden.* In classical physics, the probability of finding the object on other side of the barrier is zero. In quantum physics, on the other hand, a particle with energy less than that required to jump the barrier has a finite probability of being found on the other side of the barrier mainly due to the tunneling effect.

➤*In order to have tunnel effect, the thickness of the barrier (i.e., energy potential) must be comparable to the wavelength of the particle;* in other words, electron (or quantum) tunneling is attained when a particle (an electron) with lower kinetic energy is able to exist on the other side of an energy barrier with higher potential energy, thus defying a fundamental law of classical physics. Therefore, this effect is observed only at a nanometer level.

Figure 8.1 Schematic representation of tunneling.
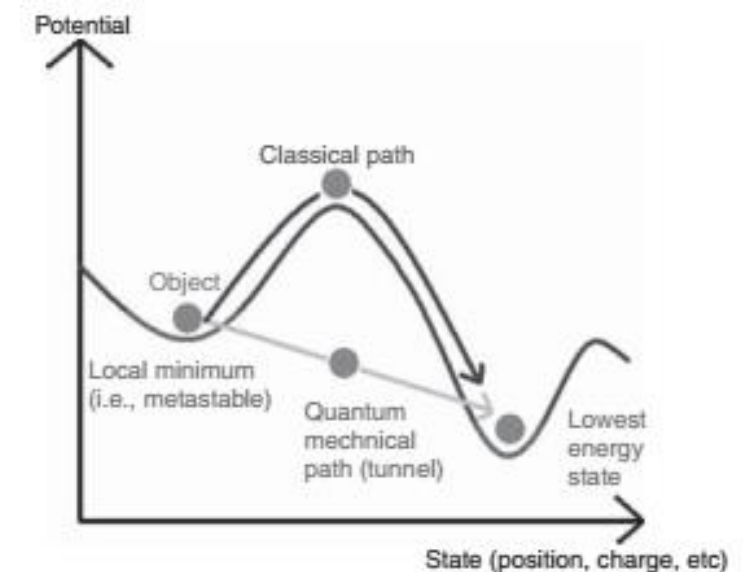
❑ **Let us understand the Coulomb blockade or Coulomb charging phenomenon.**

❖ **Background**

➢ A capacitor is a (macroscopic) device that stores electrical charge. The basic structure of a capacitor is shown at the right. When a voltage is applied to such a device, it develops a charge ($\pm$ Q) on the two plates that is proportional to the voltage: $\boldsymbol{Q = CV,}$ where Q is the charge on the conductors ($+Q$ on one conductor and $-Q$ on the other), $\boldsymbol{C}$ **is the capacitance**, and $\boldsymbol{V}$ **is the d.c. voltage** between the conductors.

$$C = \frac{\varepsilon_0 \varepsilon_r \cdot A \, (\boldsymbol{Area})}{d \, (\boldsymbol{distance})}$$

➢ where ε_0 = 8.854×10^{-12} F/m (farads/meter) = vacuum permittivity and ε_r = relative permittivity of the dielectric (known as the dielectric constant).

➢ The magnitude of the capacitance C is determined by the permittivity ε and the dimensions of the dielectric layer, A and d.
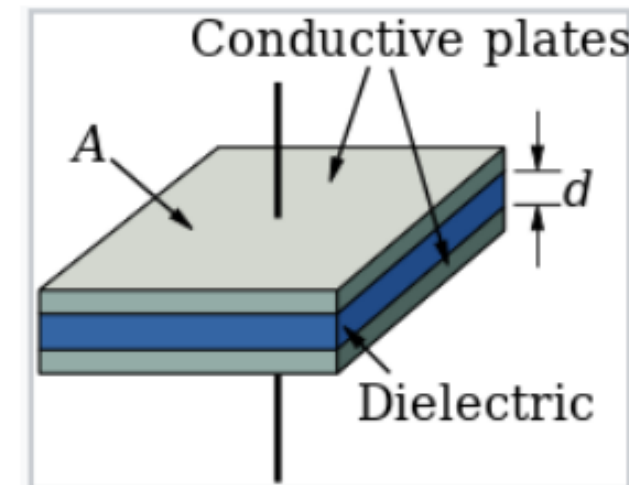
➢ We can also calculate the work done in charging the capacitor up (i.e., the energy stored by charging the capacitor) by integrating the voltage times the charge:

$$E = int_0^Q V(q)dq = \int_0^Q \frac{q}{C}dq = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2 = \frac{1}{2}VQ$$

➢ The electrostatic energy stored in a capacitor is **E** is the energy required to separate the charges initially upon applying the potential across the conductors (i.e., the work that must be done by a source to establish the charge configuration on the capacitor surfaces).

➢ Now it is interesting to ask, what happens to *a capacitor when we make it very small*? This is of particular interest in a device called a *single electron transistor.*

➢ The ***capacitance values for several parallel-plate capacitors*** are given in Table 7.1, where we assume a vacuum between the capacitor plates ($\varepsilon = \varepsilon_0$).

TABLE 7.1 Properties associated with several different Capacitors. The last column = the change in *energy due to the transfer of a single electron through the capacitor*. For these small capacitance values, the prefixes femto, (f), 10^{-15} and atto (a), 10^{-18} are useful.

	A (nm²)	d (nm)	C (F)	ΔE (eV)
nanocapacitor	5^2	2	1.1×10^{-19}	0.73
nanocapacitor	80^2	1	5.7×10^{-17}	0.0014
mm capacitor	$(5\times10^6)^2$	2×10^6	1.1×10^{-13}	7.3×10^{-7}
μ capacitor	$(5\times10^3)^2$	2	1.1×10^{-13}	7.3×10^{-7}

➢ The first two capacitors have very small nanoscale dimensions, the third capacitor listed in the table is completely macroscopic, and the last one has micron plate size and nanoscopic thickness.

➢ As can be seen, *the nanoscale capacitors have extremely small values of capacitance*.

➢ ***For nanoscale dimensions***, *the **small values of capacitance** lead to the interesting observation that **the transfer of a single electron** results in **an appreciable energy change.***

➢ For example, for the **nanoscale capacitor** having $C = 1.1 \times 10^{-19}$ F, the transfer of a single electron ($\Delta Q = q_e$) yields a change in energy ΔE that **is an appreciable fraction of an electron volt**.

➢ On the other hand, for the *macroscopic capacitor* ($C = 1.1 \times 10^{-13}$ F), the *change in energy due to the transfer of a single electron is negligible*.

➢ *For nanoscale capacitors, it is this sensitivity to the transfer of an extremely small amount of charge that allows for the possibility of so-called single-electron precision devices*.

❑ **Coulomb blockade or Coulomb charging: This effect is unique to the nanoscale**

❖ *Metal or semiconductor nanocrystals of a few nanometers in diameter exhibit quantum effects that give rise to the discrete charging of the nanoparticles*.

➢ 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*** behavior, also known as the "***Coulombic staircase***", originated the proposal that nanoparticles with diameters below 2–3 nm may become basic components of *single electron transistors (SETs)*.

➤ *Coulomb Blockade or Coulomb Charging* occurs **when the contact resistance is larger** than the resistance of nanostructures in question and **when the total capacitance of the object is so small** that adding a single electron requires significant charging energy.

➤ The **principle** and **application** of this property are discussed below.

➤ *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.

➤ If an electron is transferred to the particle, its Coulomb energy E_C increases. The energy required to add a single charge to the particle is given by the charging energy:

➤ $E_C = \dfrac{e^2}{2\,C}$ where e is the electronic charge and C is the capacitance of the nanoparticle.

➤ For a **spherical nanoparticle** surrounded by a dielectric with a dielectric constant of ε_r, the capacitance of the nanoparticle is dependent on its size as:

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

where r is the radius of the spherical nanoparticle and ε_0 is the permittivity of vacuum.

➤ Since *energy is given by (charge×voltage), $E_C = QV$ or $V = E_C/Q$*, tunneling current will only flow when a sufficiently large voltage $V > (e/2C)$ exists across the capacitor.

➢ In other words, **electron transfer is energetically forbidden for voltages $V < (e/2C)$.**

➢ *This regime of zero tunnel current despite a finite voltage across the junction is called the* ***Coulomb blockade***.

➢ *This **critical voltage, equal to e/2C**, needed to transfer an electron onto the island, is called the **Coulomb gap voltage**.*

➢ The current–voltage characteristic for an ideal quantum dot shows no current up to

$$V = \pm\, e/2C \quad \text{(Coulomb Blockade voltage)}$$

➢ If this value is reached, an electron can be transferred.
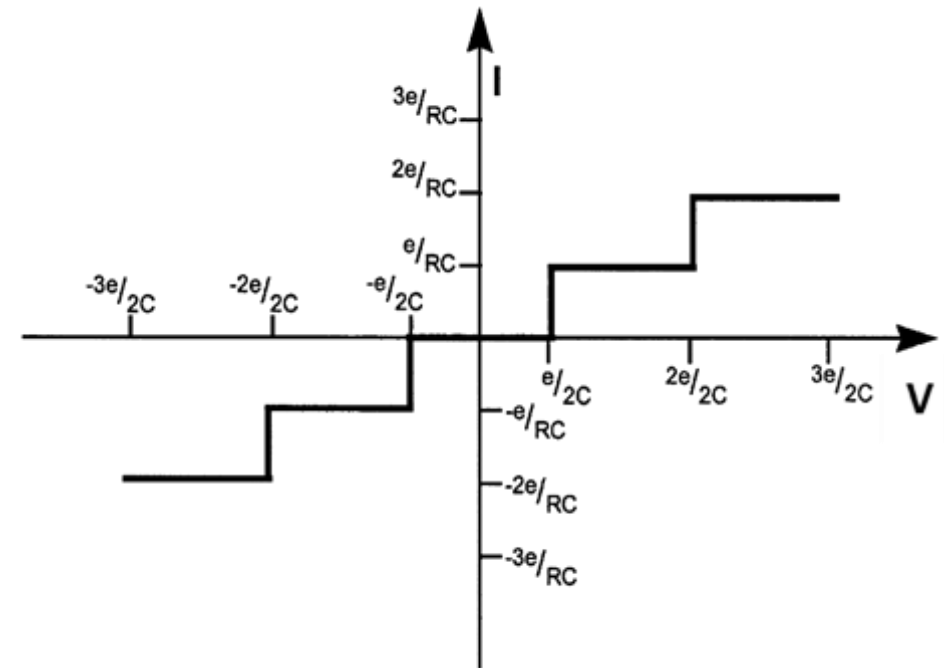

FIGURE 2.13. Current-Voltage (I-V) characteristic
of ideal single electron transport.

➢ Following this, an electron tunneling process occurs if the Coulomb energy of the quantum dot is compensated by an external voltage of $V = \pm ne/2C$.

➢ An idealized "staircase", resulting from the repeated tunneling of single electrons, is shown in Figure 2.13. The step width ΔV to $e/(2C)$ and the height ΔI corresponds to $e/(RC)$ (note: $Q = CV$. Therefore, $V = e/C$ for a single electron transfer and $I = V/R = e/RC$).

➢ It thus becomes possible to *charge and to discharge a quantum dot in a quantized manner,* which is a condition for use of such particles *in future generations of computers.*

➢ The Coulomb blockade is a direct result of the additional Coulomb energy, $e^2/2C$.

➢ For nanoscale systems with small values of capacitance, the transfer of a single electron results in an appreciable energy change, unlike their macroscopic counterparts.

➢ From the above equations, we can see that **the charging energy gives rise to a barrier to a current flow known as Coulomb blockade** and **the charging energy depends on the capacitance and the particle size.**

➢ Tunneling 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 a **Coulomb staircase** is also observed in individual single-wall carbon nanotubes.

➢ *The above equations clearly indicate that the charging energy is independent of materials*.

➢ Let us consider one example. In the small yet macroscopic capacitor considered in Table 7.1 where C = 1.1×10^{-13} F, we only need V > 0.73 µV for tunneling to occur. For the nanoscale capacitor with C = 5.7×10^{-17} F, we need V > 1.4 mV to have tunneling, and for the nanoscale capacitor with C = 1.1×10^{-19} F, V > 0.73 V is required.

➢ **Note that regardless of the voltage, capacitor plate separation *d* must be adequately small such that tunneling can take place**, *which is the difference between the first two capacitors* in Table 7.1. Thus, *Coulomb blockade is not evident in macro-sized circuits because the charging energy is so low but may be observed in nanometer scale circuits.*

❏ *Single-Electron Transistors (SET)*

➢ When a gate electrode is added to such a double tunnel junction structure Fig. 1.14, the chemical potential of the nanoparticle as well as the voltage of current flow can be modulated. ***Such a three-terminal device known as a single-electron transistor* has received great attention as an exploratory device structure.

a. *Construction and Operation of a SET*

➢ To construct a SET, single Q-dots have to be placed in between the source and drain. This is a big challenge! In principle individual particles have to be positioned between two electrodes to which an increasing/decreasing voltage can be applied.

➢ However, to observe electronic details, direct contact between electrodes and metal particles has to be avoided. Instead, two capacitances (non-conducting materials) between electrodes and object are used.

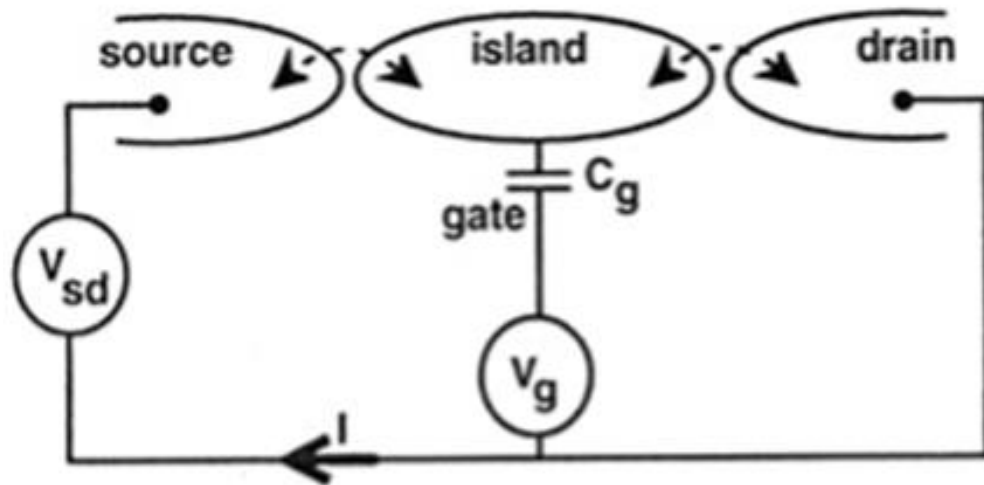➢ The adjoining Figure illustrates the schematic SET device.

Fig. 1.14 Schematics of a quantum dot (island) connected to three terminals: source, drain, and gate. The terminals and the island are separated by thin insulating layers.
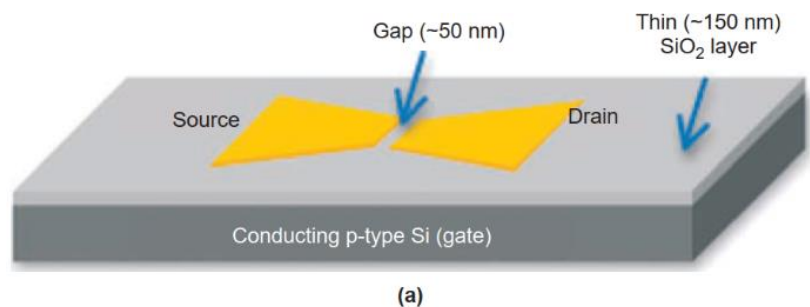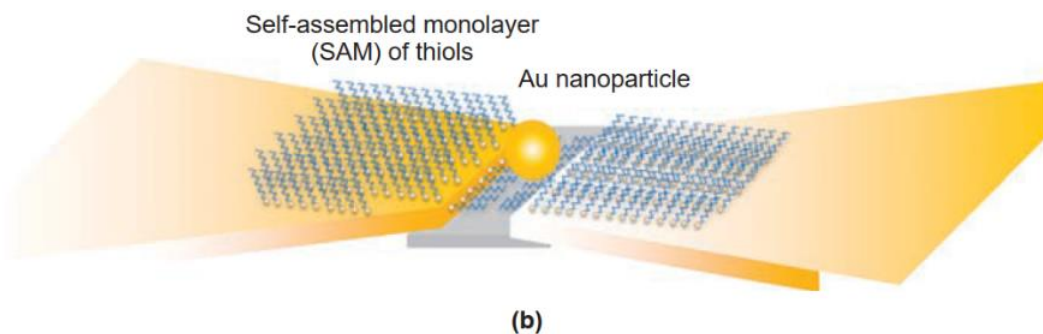

Fig. 5.12 Synthesis of single-nanoparticle SET. Synthesis of SET with the channel consisting of a single Au nanoparticle following the method of Hong et al.

(a) The source and gate electrodes are patterned onto an oxide-coated conducting Si substrate which forms the gate electrode.

(b) The electrode structure is coated with a self-assembled monolayer (SAM) of thiols (1,8-octanedithiol in this case). This layer forms the insulating tunnel junctions. Au colloid is then deposited onto the electrodes and Au nanoparticles are attracted to the gap by dielectrophoresis.

➢ The key point is that the charge passes through the Q-dot (island) in quantized units.

➢ An entirely *classical* model for electron-electron interaction is based on the *electrostatic capacitive charging energy, E_C*. The interaction arises from the fact, that for every additional charge *dq* which is transported to a conductor, work has to be done against the field of already present charges residing on the conductor. Charging an island with capacitance C with an electron of charge *e* requires $E_C = e^2/2C$.

➢ For an electron to hop onto the island, its energy must equal the Coulomb energy $e^2/2C$.

➢ When both the gate and bias voltages are zero, electrons do not have enough energy to enter the island and current does not flow.

➢ As the bias voltage between the source and drain is increased, an electron can pass through the island when the energy in the system reaches the Coulomb charging energy. This effect is known as the *Coulomb blockade*, and the critical voltage needed to transfer an electron onto the island, equal to *e/2C*, is called the **Coulomb gap voltage**.

➢ The current–voltage characteristic for an ideal quantum dot shows no current up to $V = \pm e/2C$ (Coulomb Blockade).

➢ Now imagine that the bias voltage (V_{sd}) is kept below the Coulomb gap voltage. If the gate voltage is increased, the energy of the initial system (with no electrons on the island) gradually *increases*, while the energy of the system with one excess electron on the island gradually *decreases*. At the gate voltage corresponding to the point of maximum slope on the Coulomb staircase, both of these configurations equally qualify as the lowest energy states of the system. This lifts the Coulomb blockade, allowing electrons to tunnel into and out of the island.

➢ The effect is illustrated in Fig. 5.11, which shows the energy states of a nanoparticle connected to source and drain electrodes via thin insulating barriers with a gate electrode in close proximity. The diagram has the rather odd but revealing structure of energy diagrams such as this in that energy is plotted vertically and distance horizontally.
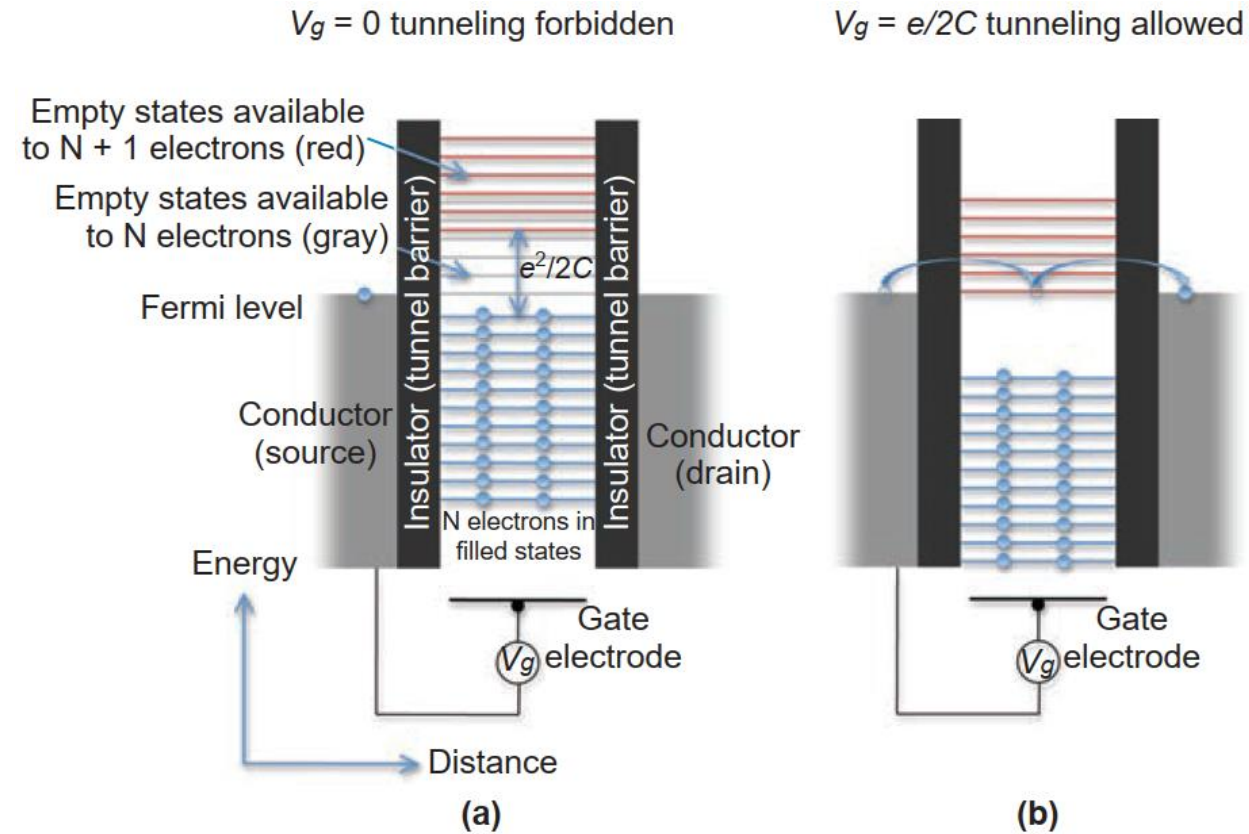
Fig. 5.11 Coulomb Blockade in a nanoparticle FET. (a) Energy level diagram of nanoparticle with discrete states due to the quantum size effect connected to source and drain electrodes via thin insulating tunnel barriers and a gate electrode in close proximity. The highest filled state of the particle approximately aligns with the highest filled electron level of the continuum in the source and drain electrodes (the Fermi level). The gray empty states are available to the N electron population of the nanoparticle but not to N + 1 electrons. If an extra electron was forced onto the particle the extra energy due to charge ($e^2/2C$) would shift the available empty states to the red ones so tunneling from the source onto the particle is forbidden. If a voltage e/2C is applied to the gate electrode the lowest red state is pulled down into line with the Fermi level and if a bias is applied between the source and drain a single electron can tunnel onto the particle and off again. The device thus acts as an FET with the gate controlling whether tunneling conductance is allowed (one electron at a time), or not. To conduct two electrons at a time would require a further increase in the gate voltage.

The nanoparticle contains N electrons and as shown in the figure the electron energy levels are discrete because the quantum size effect has become important. There are two electrons, one for each of the two allowed electron spins, in each quantum state. The top filled state will approximately align with the Fermi level—that is, the highest filled state of the continuum of states—of the electrodes. For the N electrons in the nanoparticle there are empty states (shown in gray) continuing up in energy from the highest filled state; however, these are not available to an electron from outside the particle. If we were somehow to force the nanoparticle to accept an extra electron to give it a population of $N + 1$, its negative charge would increase the energy of the particle by an amount $e^2/2C$. *For any macroscopic object this term would be insignificant, but the capacitance of the particle is so small that the energy is significant compared to the normal energy level spacing. Thus, for a particle containing N + 1 electrons the empty energy levels available are actually the ones shown in red in Fig. 5.11, which are shifted upwards by the capacitance energy.* This means that the process of quantum mechanical tunneling is forbidden to electrons from the source electrode. Applying a voltage of $e/2C$ to the gate electrode (Fig. 5.11b) brings the lowest red state into line with the source electrode and applying a bias voltage between the source and drain will enable a single electron to hop onto the nanoparticle and then off. At this gate voltage, there would only be one electron at a time allowed onto the particle because if two appeared on it at the same time, the capacitance energy would be increased, and the gate voltage would have to be increased further to bring the forbidden states back into line. The device can also be made to conduct by applying a sufficiently large source-drain voltage so that the Fermi level of the source is lifted to the empty states of the nanoparticle with N + 1 electrons. *This is not, however, the normal mode of operation for a transistor which we want to "switch on" only when the gate voltage is applied.* In summary, the gate voltage controls whether or not the nanoparticle conducts, one electron at a time, via quantum mechanical tunneling. **It therefore acts as a single-electron FET; and if it can be realized, a whole new generation of electronics based on nanoparticles and quantum mechanics will be created.**

The Coulomb blockade is lifted when the gate capacitance is charged with exactly minus half an electron. If we further increase the gate voltage so that the gate capacitor becomes charged with -e, the island again has only one stable configuration separated from the next-lowest-energy states by the Coulomb energy. The Coulomb blockade is set up again, but the island now contains a single excess electron. The conductance of the SET transistor therefore oscillates between minima for gate charges that are integer multiples of e, and maxima for half-integer multiples of e.

If a voltage V_g is applied to the gate capacitor Cg (Fig. 1.14a) a charge is induced on the island which leads to the so-called *Coulomb oscillations* of the source-drain conductance *as a function of* V_g *at a fixed source-drain voltage*, V_{sd} (Fig. 1.14b). In the valleys between the oscillations, the number of electrons on the dots is fixed to the integer N with zero conductance (Coulomb blockade). Between the two stable configurations N and $N+1$ a "charge degeneracy" (see Fig. 1.14b) appears where the number of electrons can alternate between N and $N+1$. This produces a current flow and results in the observed current peaks.

An ***alternative measurement*** with ***fixed gate voltage*** V_g and ***varying source-drain voltage*** (*like the Coulomb Charging experiment shown above*) shows nonlinear current–voltage characteristics exhibiting a Coulomb staircase (see Fig. 1.15). A new current step occurs at a threshold voltage $e/2C$ at which an extra electron is energetically allowed to enter the island. This threshold voltage is periodic in the gate voltage (see Fig. 1.15) in accordance with the Coulomb oscillations of Fig. 1.14(b).
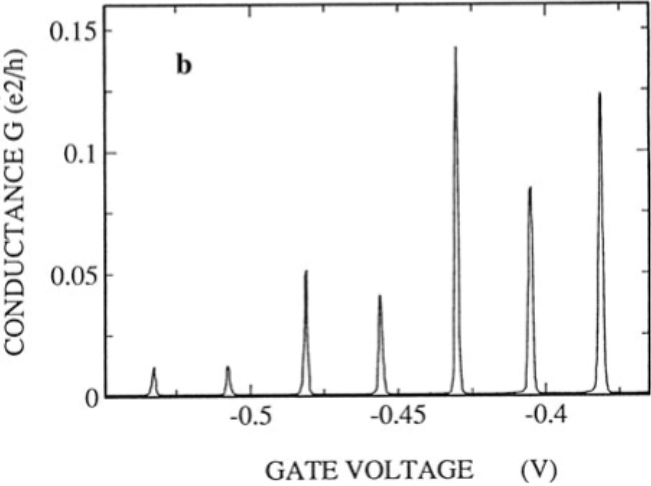

Fig. 1.14 (b) Coulomb oscillations for illustrating the effect of single electronic charges on the macroscopic conductance I/V$_{sd}$. The period in the gate voltage is about e/Cg.

The island is very susceptible to surrounding impurities or stray charges. In order to prevent suppress of coulomb blockade by stray charges or ions it is surrounded by insulators, which means that the charge on it must be quantized in units of e, but the gate is a metallic electrode connected to a plentiful supply of electrons. The charge on the gate capacitor merely represents a displacement of electrons relative to a background of positive ions.
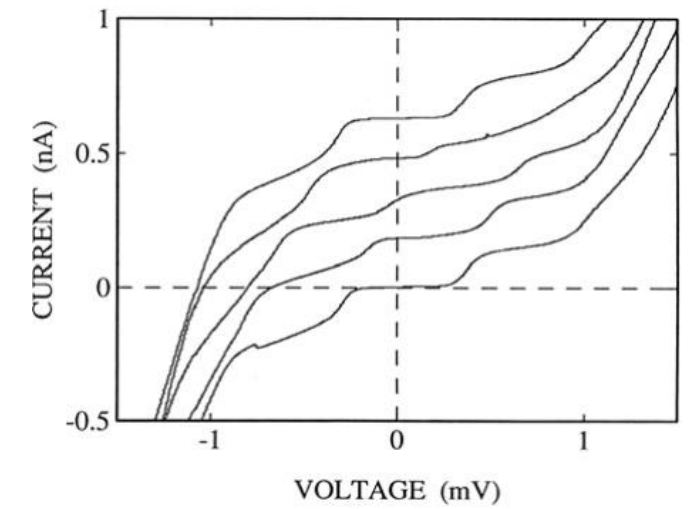

Fig. 1.15 Coulomb staircases in the $I-V_{sd}$ characteristics of a GaAs/AlGaAs heterostructure.

The different curves which are shifted vertically for clarity ($I = 0$ occurs at $V_{sd} = 0$) are taken for five different gate voltages to illustrate the periodicity in accordance with the oscillations in Fig. 1.14(b).

b. Conditions for Coulomb Blockade (single electron charging)

➢ The SE tunneling can be detected when the resistance R_T of the tunneling barriers is sufficiently high at low temperatures when the **energies fluctuations** are small.

➢ The related Heisenberg uncertainty of energy $\delta E = h/\tau = h/(R_T C)$ leads to unexpected tunneling if it exceeds the Coulomb energy. This is quantum mechanically described by the **quantum Hall resistance R_{QH}** and the capacity of the particle (quantum dot):

$$E_{C,QH} = \frac{h}{R_{QH}C} \tag{2.5}$$

➢ Thus, a second condition for SET effects is $R_{QH} \ll R_T$.

i) Minimum Tunnel Resistance for Single Electron Charging

The formulation of the Coulomb blockade model is only valid, if electron states are localized on islands. In a classical picture it is clear that an electron is either on an island or not. That is, the localization is implicit assumed in a classical treatment. Clearly, if the tunnel barriers are not present, or are insufficiently opaque, one cannot speak of charging an island or localizing electrons on a quantum dot, because nothing will constrain an electron to be confined within a certain volume.

➢ With an additional charge, a voltage $V = e/C$ is produced, leading to a tunneling current $I = V/R_T = e/(R_TC)$ (where R_T = tunnel resistance). The resulting additional charge on the particle has a mean lifetime $\Delta t \approx R_TC$.

➢ A qualitative argument is to consider the Heisenberg Energy Uncertainty of an electron

$$\Delta E \Delta t > h/4\pi$$

where the energy gap associated with a single electron and the characteristic time for charge fluctuations is the time constant for charging capacitance C through tunnel resistor R_T is

$$\Delta E = e^2/2C \text{ and } \Delta t \approx R_T C$$

➢ Combining these two, it can be estimated that ***the condition for the tunnel resistance:***

$$R_T > h/2\pi e^2 = 25813 \ \Omega \approx 25 \text{ k } \Omega$$

➢ In other words, the tunnel resistance $\approx$ 25 k Ω should be much higher than the ***resistance quantum***. *Experimental tests have also shown this to be a necessary condition for observing single electron charging effects.*

ii) *Requirement on temperature/voltage*

Temperature plays an important role in Coulomb blockade phenomena.

Thermal motion of the atoms in the particle can initiate a change of the charge and of the Coulomb energy, so that further 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,

$C > e^2/2k_B T \sim e^2/k_B T$

Put simply, if the above relationship is not satisfied there is too much thermal energy available to the electron to be held back by the charging energy E of the capacitor.

For the nanoscale capacitor considered previously (C = 1.1 x 10^{-19} F), T $\ll$ 16,91 1 K, which is obviously the typical situation. Therefore, we should be able to observe Coulomb blockade for this capacitor at any practical temperature.

However, **for the macroscale capacitor (C = 1.1 x 10^{-13} F), T $\ll$ 0.017 K,** which is difficult to achieve. (This, of course, *explains why Coulomb blockade is not seen in macroscale electronics at room temperature*.)

For the somewhat larger nanoscale capacitor (C = 5.7 x 10^{-17} F), T $\ll$ 32.6 K. These conditions can be met by small dots with low C values and weak tunneling coupling. For a quantum dot sphere with a 1 μm diameter the value $E_C \approx 3$ meV is found which can be easily resolved at low temperatures. Thus for devices larger than about 5-6 nm, individual electron charging events are washed out at room temperature by thermal fluctuations.

The main point is that if the junction capacitance is sufficiently small, room-temperature Coulomb blockade can be observed; otherwise, **low temperatures must be used.**

To observe the Coulomb blockade, and SET oscillations, one has to protect the very small tunnel junctions against the shunting influence of the environment. This can be done by surrounding it with thin film resistors. The special (and simplest) case of the two junction one dimensional array leads us to the device called the single electron transistor.

c. Towards room temperature

To integrate SET into ICs they must be able to perform at room temperature. To observe coulomb blockade effect, one need temperature of a few hundred milli Kelvin to maintain the thermal energy of the electrons below the Coulomb energy of the device. Most early devices had Coulomb energies of a few hundred microelectronvolts because they were fabricated using conventional electron-beam lithography, and the size and capacitance of the island were relatively large.

For a SET transistor to work at room temperature the capacitance of the island must be less than 10^{-17} F and therefore its size must be smaller than 10 nm.

In 1998, a paper was published by Lei Zhuang and Lingjie Guo of the University of Minnesota, and Stephen Chou of Princeton University in the US that they fabricated a SET transistor in a similar way to a field-effect transistor with a channel just 16 nm wide which operates at room temperature. The fabrication process generated variations in the channel that act as tunnel junctions defining several different islands, and the behavior of the device is dominated by the smallest island. This is a step towards the realization of SETs at room temperature.

➢ The single-island SET is sensitive to even fractional changes in the background or 'offset' charge near the island, e.g. if this changes by $e/2$, the Coulomb blockade may be overcome, and this is undesirable for reliable circuit operation.

➢ A solution may be to use SETs with multiple tunnel junctions (MTJ) and islands, where the Coulomb gap is the sum of the Coulomb gaps of all the islands. Any fluctuation in the offset charge overcomes the Coulomb blockade in only one of the islands, reducing the total Coulomb gap voltage by only a fraction. This makes the MTJ SET much less sensitive to offset charge and of greater practical significance.

➢ Various structures have been made in which electrons are confined to small volumes in metals or semiconductors. Perhaps not surprisingly, there is a deep analogy between such confined electrons and atoms. Such regions are referred to as 'quantum dots', 'artificial atoms' or 'solid state atoms'. Such quantum dots form the heart of the SET gates.

➢ In effect, the gate can act as a switch, as in a conventional field-effect transistor. Single-electron transistors are being researched as ultra-sensitive electrometers and singlemolecule chemical sensors, since a tiny change in the electrostatic environment of the dot can switch the device on or off.

a. Why use SET ??.

How can a nanoscale capacitor like this act as a transistor, which functions as a switch in an electrical circuit?

The semiconductor transistor has been one of the most remarkable inventions of all time. It has become the main component of all modern electronics. In conventional microelectronics, the most common trandistor in today's microchips is the metal-oxide-semiconductor field-effect transistor (MOSFET).

In conventional microelectronics, currents are typically on the order of 1 µA to 1 mA, corresponding to the movement of $6.25 \times 10^6 - 6.25 \times 10^9$ electrons per microsecond. This occurs through a device perhaps 100 nm in length. Even considering devices at the upper limit of optical lithography, perhaps on the order of 10^5 electrons are involved in performing, for example, digital operation. In keeping with ever decreasing device sizes, the miniaturization trend has been very rapid.

Like magnetic recording, the microelectronics industry has achieved amazing feats of miniaturization and modern computer chips contain more than 500 million FETs, which compares with 3500 on the Intel 8008 microprocessor manufactured in 1972. The increase in the number of transistors is achieved by reductions in the feature size patterned onto the chips. The width of the channel on an FET in a modern chip is less than 50 nm, and the number of electrons applied to the gate is just thousands. The roadmap of the microelectronics industry refers to devices with gate lengths of ~13 nm, below which the quantum size effect will start to affect circuit behavior.

To keep up with the pace of large-scale integration, the idea of single electron transistors (SETs) has been conceived. The *most outstanding property of SETs is the possibility to switch the device from the insulating to the conducting state by adding only one electron to the gate electrode*, whereas a common MOSFET needs about 1000–10,000 electrons.

In addition, the switching time of SETs is mainly determined by the RC-time constants of the constrictions that can be made very small. Therefore, it is generally assumed that single-electron devices have the potential to **be much faster** than conventional MOSFETs. Moreover, **it consumes less power for operation**. A major problem today is that the transistors cannot be packed very closely due to the heat they generate. Since *dissipation can be highly suppressed* in these novel devices, they might be especially suited for future applications in single electronics.

Recent advances in integrated circuit technology have led to a reduction in the size of electronic devices into the nanometer scale. Metal-oxide-semiconductor field effect transistors (MOSFETs) with gate lengths of a few tens of nanometers have now been fabricated, raising the possibility of large increases in the number of transistors on a chip.

However, if the minimum feature size is reduced below 10 nm, quantum mechanical effects such as tunneling affect device performance significantly.

The scaling-down of devices also leads to a reduction in the number of electrons available for digital switching operations. Ultimately, only a few electrons may be available for switching and statistical fluctuations in the average number of electrons would prevent the definition of clear digital states. The Coulomb blockade or single-electron charging effect, which allows for the precise control of small numbers of electrons, provides an alternative operating principle for nanometer-scale devices. In addition, the reduction in the number of electrons in a switching transition greatly reduces circuit power dissipation, raising the possibility of even higher levels of circuit integration.

Although most single-electron devices are at an early stage of development, especially in the area of manufacturability, they offer the potential benefits of ultralarge-scale integration, with device dimensions on the order of nanometers. Since SET conduction process involves single electrons, and as a result, they require only a small amount of energy to operate a switch, transistor, or memory element.

They also may exhibit very low power dissipation and high speed. All of these positive attributes arise from the need to move only single electrons, or small groups of electrons, through devices.

All these phenomena can be utilized to produce radically different types of components for electronic, optoelectronic, and information processing applications.

❑ THERMAL CONDUCTANCE QUANTUM

➢ In nanosystems the classical picture of a diffusive heat flow mechanism is often not applicable because the phonons or electrons that carry heat have mean free paths similar to or larger than the nanoscale feature size. This is a challenge for heat removal in microelectronic devices which already involve features with sizes of the order of the mean free path.

➢ The thermal conductance $\kappa(Vg)$ of electrons in a semiconductor quantum wire at low temperatures shows a quantized behavior in dependence of a gate voltage V_g (Fig. 1.10). This originates from the plateaus in the electrical conductance $G(V_g)$ quantized in units of $G_o = 2e^2/h$.

➢ *The thermal conductance of any electrically insulating structure that exhibits ballistic phonon transport is a positive integer multiple of g_0.* The thermal **conductance quantum** was first measured in 2000. These measurements employed suspended silicon nitride nanostructures that exhibited a constant thermal conductance of 16 g_0 at temperatures below approximately 0.6 kelvin.

➢ For ballistic electrical conductors, the electron contribution to the thermal conductance is also quantized as a result of the electrical conductance quantum and the Wiedemann–Franz law, which has been quantitatively measured at both cryogenic (~20 mK) and room temperature (~300K).

➢ The thermal conductance quantum, also called as *quantized thermal conductance*, maybe understood from the Wiedemann–Franz relation which applies in the case of when the charge and energy are transported by electrons. Wiedemann-Franz law states that the ratio of the electronic contribution of the thermal conductivity (κ) to the electrical conductivity (G_o) of a metal is proportional to the temperature (T).

➢ $\kappa / G_o = LT$

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

➢ $L = (\pi^2/3) (k_B/e)^2 = 2.44 \times 10^{-8} \, W \, \Omega \, K^{-2}$.

➢ In the regime with quantized electric conductance, one may have

➢ $G_o = ne^2/h$,

➢ where n is an integer, called as TKNN (Thouless – Kohmoto – Nightingale - den Nijs) number.

➢ Then $\kappa = L\,T\,G_o = (\pi^2 k_B^2/3e^2)\cdot(ne^2/h)\cdot T = (\pi^2 k_B^2/3h)\cdot n\cdot T = g_0\,n,$

➢ where g_0 is the **thermal conductance quantum** that describes the rate at which heat is transported through a single ballistic phonon channel of temperature T. It is given by:

➢ $g_0 \approx (9.464 \times 10^{-13}\ W/K^2)\,T.$

➢ From this relation it is expected that the electrical conductance plateaus in units of G_O are matched by a thermal conductance quantized in units of $L_o T G_o = \pi^2 k_B^2 2T/3h = (1.89\cdot 10^{-12}\ W/K^2)T$. This is in agreement with the data in Fig. 1.10 for $G > G_o$.

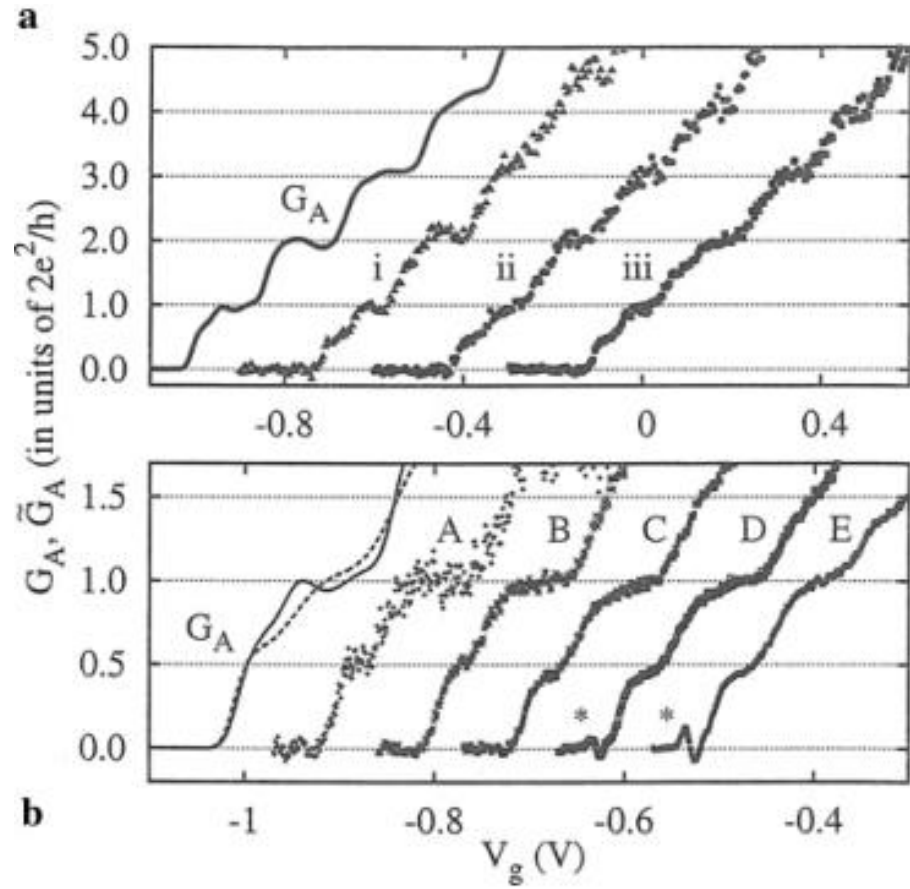Fig. 1.10 (a) Quantized step-like behavior of the thermal conductance $G^{\sim}_A$(i, ii, iii) and of the electrical conductance G_A of a semiconductor quantum wire at 0.27 K obeying the Wiedemann–Franz relation. (b) Close-up of (a) with a half plateau $\kappa = L_o T(G_o/2)$ for $G < G_o$. (Reprinted with permission. © 2006 American Physical Society)

The ratio of the thermal conductances $\kappa_{el}/\kappa_{phon}$ of electrons and phonons increases rapidly when the temperature is lowered.

What happens, however, to the thermal conductivity of systems that are effectively one dimensional, such as a single-wall carbon nanotube (SWNT), a nanowire, or a DNA molecule?

By analytical calculations it is estimated that the thermal conductivity diverges with a one-third power law as the length of a 1D system increases. This would be a very promising feature to use in the application of SWNTs, such as the design of components that dissipate heat efficiently in nanocircuits.

It should be mentioned here that for the investigation of heat conductivity in confined dimensions extremely sensitive calorimeters are developed with a low-temperature heat capacity of $c \approx 10^3 k_B$. This may lead to an energy sensitivity sufficient to count individual thermal phonons at 10–100 mK and observe the particle nature of phonons.