Basic Science of Nanomaterials: Quantum Phenomena

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

❑ **Learning Objectives**

❖ Length scales and quantum confinement in nanoscale systems.

❖ Calculate the DOS and its Dimensionality dependence.

❖ Understand the basis of Quantum Transports (Quantum Conductance and Coulomb Charging).

❖ Understand the basis of Single Electron Transistor (SET).

❖ Understand the basis of mesoscopic behavior in nanoscale magnetic particles.

❖ Explain the origin of optical properties and use of Brus formula to calculate the band gap energy of nanoscale semiconductor particles.

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

❖ Describe the emerging analytical and biomedical applications of magnetic, semiconductor, and metallic nanoparticles.

➢ Materials with nanoscale structures often have unique *optical, electronic, or mechanical properties.* In this section we will learn about the basic science of some quantum phenomena of nanomaterials.

➢ 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**.

➤ The **properties of a material depend** on *the type of motion its electrons can execute, which depends on the space available for them*. Thus, *the properties of a material are characterized by a specific "**length scale**," usually on the nanometer dimension.* **If the physical size of the material is reduced below this length scale, its properties change and become** *sensitive to the size and shape.*

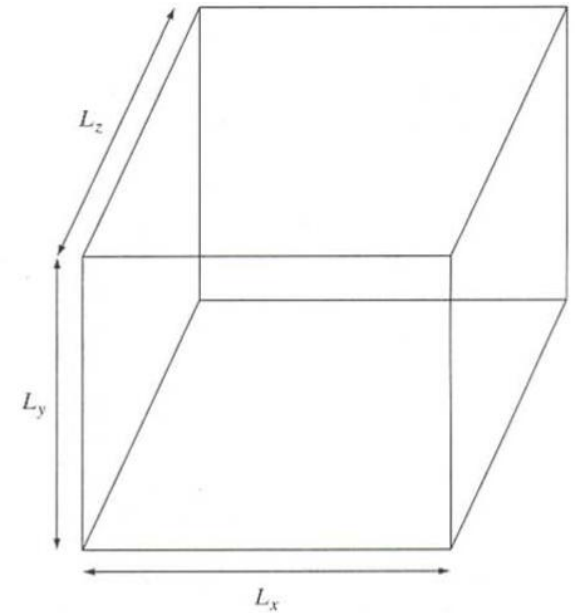➤ We illustrate this point with a few examples later.

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

❑ *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. ***Lφ** 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_BT. 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.

Quantum Limit: Characteristic Lengths in the Nanometer Range from 3-D to 0-D

It was pointed out that a physical phenomenon responsible for a certain property has associated with it a characteristic length scale and when the dimensions of the solid approach this length, the corresponding physical phenomenon is influenced, and the property undergoes a change. *Examples of some of these characteristic lengths are given below.*

de Broglie Wavelength

The dimensionality of a quantum device is obtained by comparing its size in each coordinate with the de Broglie wavelength (λ_F) at the Fermi energy (E_F).

Near the bottom of the conduction band in a semiconductor, the electron energy relation becomes

$$E_F = \frac{\hbar^2 k^2}{2m_e^*}$$

Here, k is the wavevector and m_e^* denotes electron effective mass inside a semiconductor.

Corresponding de Broglie wavelength is

$$\lambda_F = \frac{h}{p} = \frac{h}{\sqrt{2m_e^* E_F}}$$

Considering a 3D structure, λ_F becomes

$$\lambda_F = \frac{2\pi}{(3N_e \pi^2)^{1/3}}$$

where N_e is the *effective density of states*. Computing the values of λ_F for different metals and semiconductors, it comes out:

$\lambda_F \sim 0.5 - 1$ nm for metals and $\lambda_F \sim 10 - 100$ nm for semiconductors.

If any of the dimensions of a device is below the specified limit (λ_F), that dimension becomes quantized (or discrete or digital).

In a bulk semiconductor, no dimension is quantized (all analog, no digital).

In a **2D quantum well, *one dimension is quantized*** but the other two dimensions are analog. In a **quantum wire, *two dimensions are quantized*** and only one dimension is allowed to carry analog energy levels.

In **a quantum dot, all dimensions are quantized** making it a quantum 0-D (zero-dimensional) system.

The de Broglie wavelength for an electron with a momentum p is given by

$$\lambda = \frac{h}{p} = \frac{h}{m^* v}$$

where m^* is the effective mass and v is the velocity of the electron. The *effective mass m^* is different from m_o, the mass of an electron in a vacuum*. It is defined by the relation

$$\frac{1}{\hbar^2} \frac{d^2 E}{dk^2} = \frac{1}{m^*}$$

here $\frac{d^2 E}{dk^2}$ is the curvature of the E *vs.* k (wavevector) plot for the electron.

The use of m^* in place of m_0 **allows one to treat the electrons in the solid as free electrons** (i.e., moving in a zero field), *without worrying about the interactions of the electron with the other electrons or the lattice – **in effect, these interactions are taken care of by using m^*** instead of m_0. The *effective mass is quite small for semiconductors*, e.g., $0.067 m_0$ for GaAs and $0.014 m_0$ for InSb while *for metals, in which the electrons naturally behave as free electrons, it is close to m_0.*

*The de Broglie wavelength is therefore **much larger for the semiconductors.*** **Consequently, the size effects are observed at much larger sizes in semiconductors** than in metals.

➢ *Mean free path of electrons*

➢ *For the properties such as **electrical conductivity, photoluminescence, etc.,** the characteristic lengths associated with the electrons in the solid need to be considered.*

➢ **For the electrical conductivity,** the characteristic length can be the **mean free path** of the electron.

➢ *As the electron moves in a crystal, it is scattered by interactions with crystal imperfections such as lattice vibrations (phonons), impurities, defects, etc. **The scattering event is inelastic, i.e., it causes a change in the momentum and energy of the system. The average distance between two scattering events** is **called the *mean free path, l,*** and **the average time between two successive collisions is called the *relaxation time*.***

➢ For a ***macroscopic solid***, the dimension of the solid is much larger than *l* so that the electron suffers multiple scattering as it travels; this motion of the electron is termed ***diffusive transport***. *This mode is characterized by **a high electrical resistivity**.*

➢ If, however, *the **dimension of the solid is less than the mean free path***, **the electrons can travel through** it *without any scattering except on the surface*s. The electrons in this case move by *ballistic transport* leading to *a high electrical conductivity* as in the carbon nanotubes.

➢ Thus, ***the mean free path is the characteristic length for the conduction to change from diffusive transport to ballistic transport***.

❑ *Exciton and Bohr Exciton Radius*

➢ When ***an electron from the valence band*** of a semiconductor or an insulator is excited to the conduction band (say by a photon having an energy greater than the band gap of the material), ***a hole is left behind in the valence band***.

➢ In most cases, ***the electron will move away and the two exist separately for a short time*** until *an electron recombines* with the hole.

➢ In some cases, *the electron and the hole* stay together *for a longer time (~ milliseconds) as a pair due to the Coulombic attraction between them and have a natural physical separation that depends on the material.* **This (bound) electron-hole pair is called an *exciton*.**

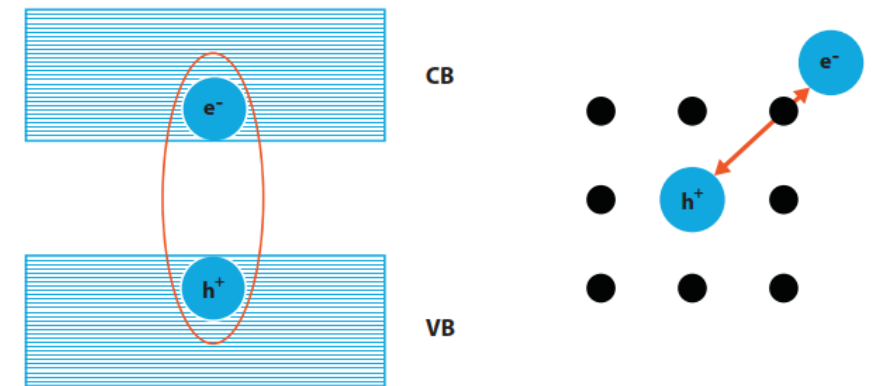➢ *The excitons play an important role in the semiconductor nanostructures.*

Fig. 5.12: Illustration of the formation of an exciton *relative* to the *band structure* on the left and the *crystal structure* on the right.

➢ *Many properties of the **exciton** can be obtained by **modeling it as a Bohr atom**.*

➢ A representation of the ***exciton*** is shown in Fig. 3.17. ***It is shown as a bound electron-hole pair orbiting around its center of mass.*** This is analogous to the Bohr model of an atom.
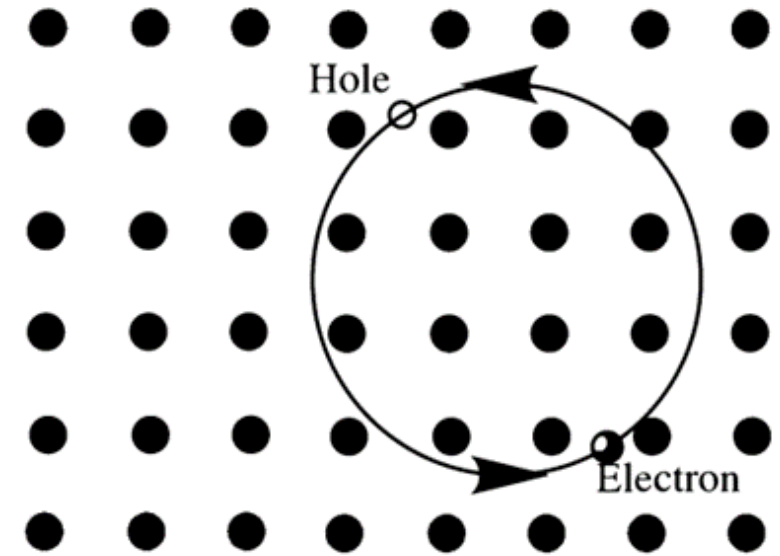

Fig. 3.17. Representation of an exciton as a bound electron-hole pair *orbiting around its center of mass.*

➤ *The magnitude of the energy of an exciton is much smaller than that for the hydrogen atom and the size of the exciton is ~30 nm*, i.e., *of the same order as a typical nanostructure*, and *extends over several atoms in the crystal.*

➤ *In a semiconductor, the charges are screened by a high dielectric constant so that the Coulomb attraction between the electron and the hole is small. The exciton in semiconductors can therefore have a large radius, much larger than the lattice spacing.* The large exciton radius leads to effects such as higher energy of the excitons in the confined space of a nanostructure.

➤ The electron and the hole in an exciton are bound by the coulombic force. Energy, equal to this binding energy, is, therefore, necessary to separate them. *The process of photoexcitation of an electron from the valence band of a semiconductor to its conduction band by a photon can be imagined as consisting of two steps: the creation of an exciton and then breaking up of the exciton into unbound electron and hole.* The exciton energy levels, therefore, lie within the band gap, just below the edge of the conduction band as shown in Fig. 3.19.
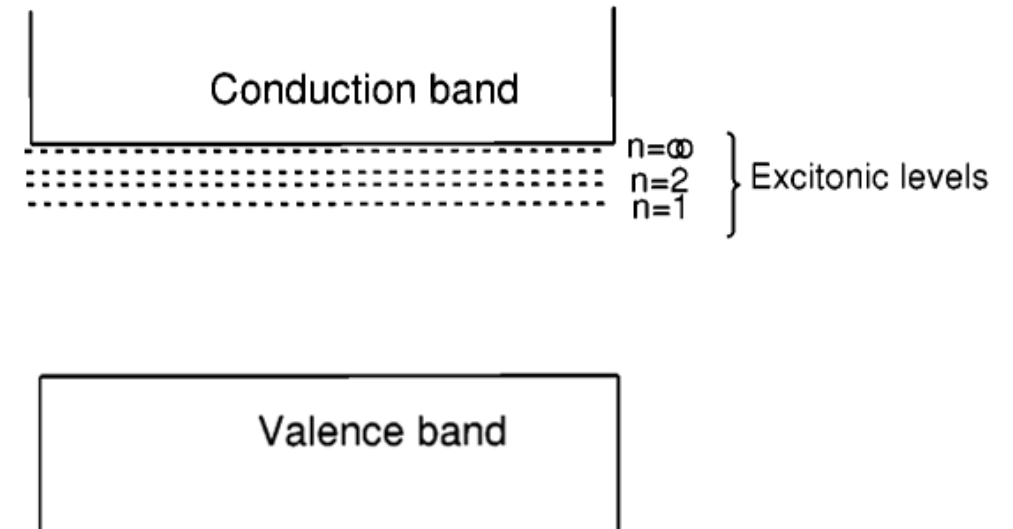

Fig. 3.19. Location of the exciton energy levels in the band gap of a semiconductor.

The exciton energy levels can be probed at very low temperatures where $kT \ll$ exciton binding energy.

Because of the large separation between the hole and the electron, there is difficulty in their wave functions overlapping so that the lifetime of an exciton τ_e, the time before which the electron and the hole recombine, can be large (lifetimes of up to several milliseconds have been observed in Cu_2O).

Exciton radius is often used as the length scale to define a quantum dot. When the radius of the particle R is smaller than the Bohr exciton radius, the exciton cannot achieve the desired separation; an energy called the confinement energy is needed to confine the exciton within the quantum dot. In fact, the confinement energy becomes appreciable for particle radius smaller than about twice the exciton radius ($R < 2r_{exciton}$) *At this size the confinement energy is much larger than the Coulombic attraction energy of the exciton and the particles are treated as quantum dots.* Thus, for CdS, the excitonic Bohr radius is 29 Å so that the particles of CdS smaller than about 50 Å should behave as quantum dots.

Other length scales

The length scales discussed above relate to the electronic and photonic properties. There can be other characteristic length scales for these properties, e.g., *screening length* for the screening of the potential due to the ionized dopant atoms in semiconductors by free carriers. In case of the charged particles in liquid suspension, a characteristic length is the ***double layer thickness*** around charged particles. In materials science, the size of the smallest crystal which is free of defects such as a vacancy or a dislocation is of concern since many properties of crystalline solids depend on the concentration of such defects. ***It can be easily shown that the critical size d_c below which a crystallite cannot contain a vacancy comes out to be in the nanometer range for most crystal***.

The **mechanical properties of crystals** are controlled by dislocations. *It is almost impossible to create a dislocation free crystal but if the size is sufficiently reduced then the dislocations will be pinned by the grain boundaries and the interior of the grain would be essentially dislocation free. The grain size at which the dislocation will be pinned at both ends by the grain boundary of the crystallite comes out to be again in the nanometer range.*

It should be noted that even though reducing the grain size to below critical size can create a perfect, defect free crystal, the fraction of the surface atoms becomes so large, that other effects may intervene, preventing the realization of the properties expected from a perfect crystal. As an example, the hardness increases at first according to the Hall-Petch relation, as the crystal size is decreased but then decreases as the grain size is reduced below a critical value, which is in the nanometer range.

Low Dimensional Systems

When the sizes of materials are reduced in one or more dimensions their physical and chemical properties can change dramatically. In addition to the **quantum size effect** in nanocrystals, **the shape** of nanomaterials also has a remarkable effect on its properties: *electrons experience different confinement depending on the particle shapes*. In materials with one or more nanoscale dimensions, *these properties can be purposefully engineered*. As was mentioned above, *many new phenomena are observed* **when at least one of the dimensions of a solid is reduced to lengths comparable to appropriate scaling length**. **Such nanocrystals are called quantum confined systems**.

The *requirement for quantum confinement is that the size of the nanocrystals should be smaller than the de Broglie wavelength* or *the exciton Bohr radius of the material* (which in simple terms is the Bohr radius of the electron residing in the first allowed excited state). *This means that an excited electron is physically constrained by the small dimension of the nanocrystal.*

The restriction of the quasi-freely mobile electrons in a piece of bulk metal can be reached not only by reduction of the 3D volume but can also be gained by reducing any of the three-dimensions (from 3 to 2 or 1) small enough to confine the electron movement.

Depending on how many dimensions are small enough to confine the electron movement, the *structures are given different names*. These are **quantum well**, **quantum wire,** **and quantum dot** for **one, two** and **three dimensions being small** *respectively* (Table 9.3 and Fig. 2.2).

Table 9.3. Delocalization and confinement dimensionalities of quantum nanostructures

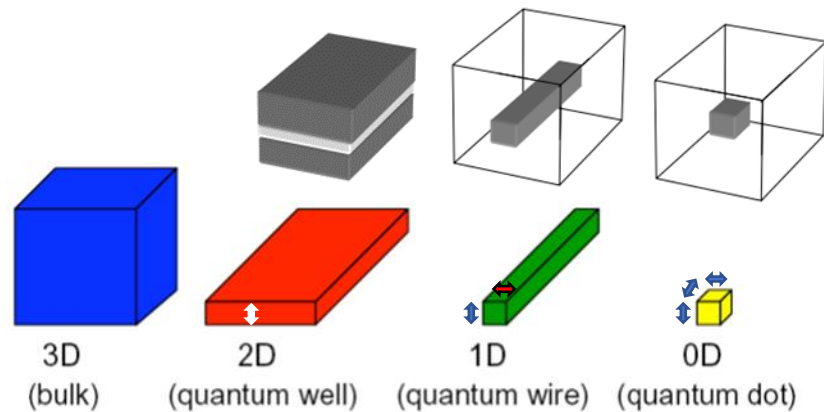| Quantum Structure	Delocalization Dimensions	Confinement Dimensions
Bulk conductor	3 (x, y, z)	0
Quantum well	2 (x, y)	1 (z)
Quantum wire	1 (z)	2 (x, y)
Quantum dot	0	3 (x, y, z)

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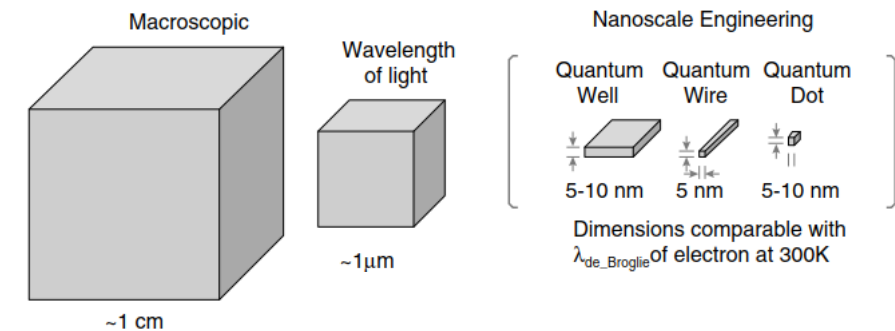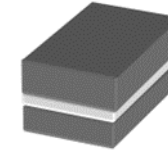
FIGURE 4.62 Comparison of dimension from macroscopic to nanoscale structures.

➢ For **quantum well** or 2D nanomaterials, *the electrons are free to move in two dimensions*, and **confinement is** *imposed **only along one*** dimension. These materials create a two-dimensional layer with a thickness on the order of nanometers.

➢ In the case of a **nanowire** or 1D nanomaterial, *electrons are free to move only in one dimension* and experience **confinement along two** dimensions. These materials are one-dimensional objects with nanoscale cross-sections.
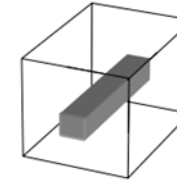
➢ The material is termed as **quantum dot** when *the electrons in the particle experience* **confinement along all the three** *dimensions*.
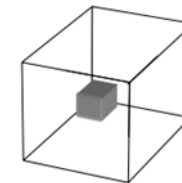
Two-dimensional structures such as quantum wells are particularly important in the development of the next generation of the semiconductor devices (e.g., giant magnetoresistors, lasers and ultra-high-speed transistors). In such structures, a thin semiconductor region is sandwiched between different materials (Fig. 2.2). Other important nanomaterials are described as nanowires, nanobelts and nanorods, which are one-dimensional, and nanoparticles and quantum dots, which are considered zero-dimensional. Fig. 4.62 gives a schematic comparison of the dimensions from macroscopic to nanoscale structures.
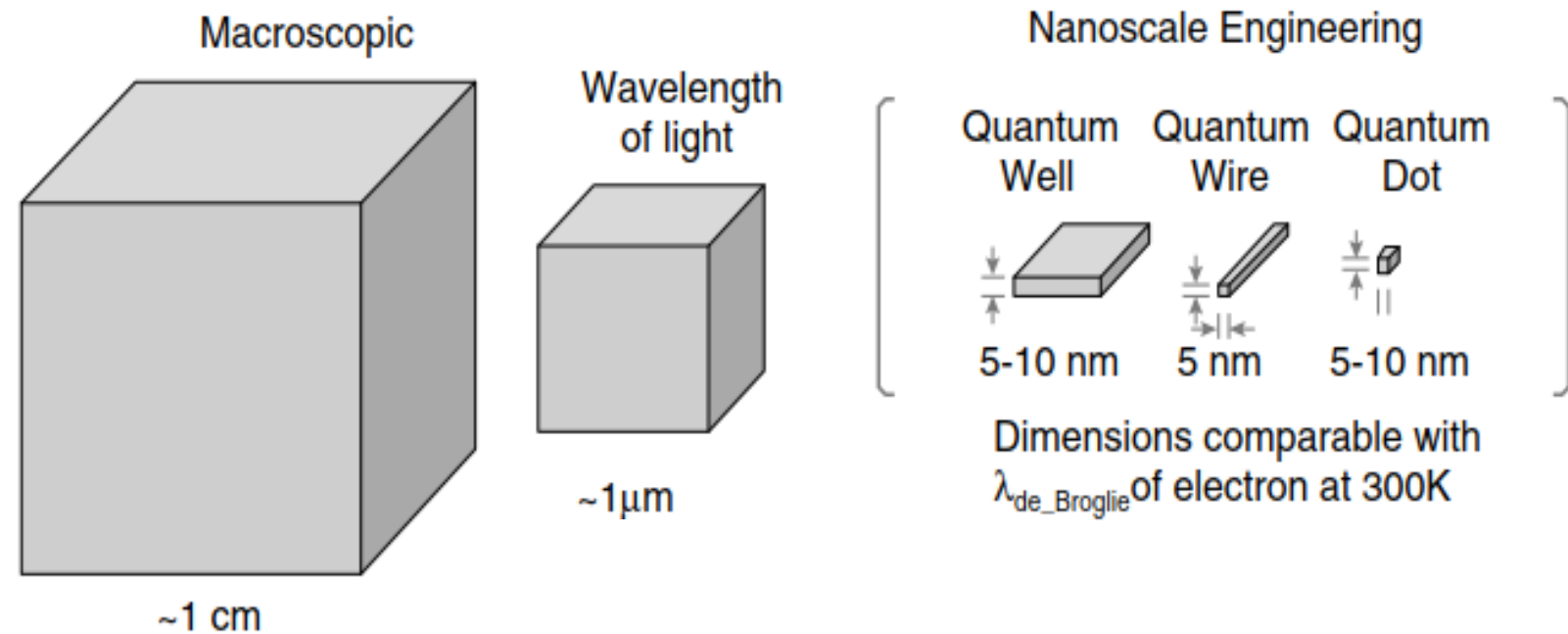

FIGURE 4.62 Comparison of dimension from macroscopic to nanoscale structures.
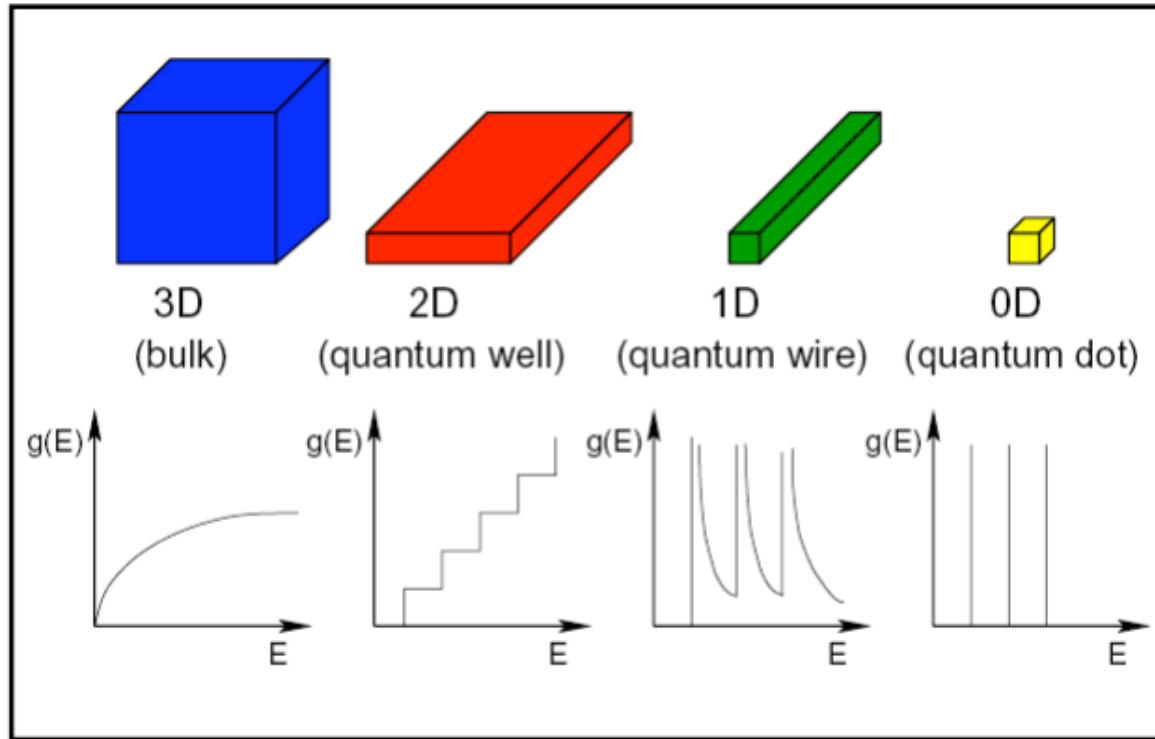
Figure 3: *Density of states for a free electron gas in various dimensions (general trend).*

- 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 space) 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).
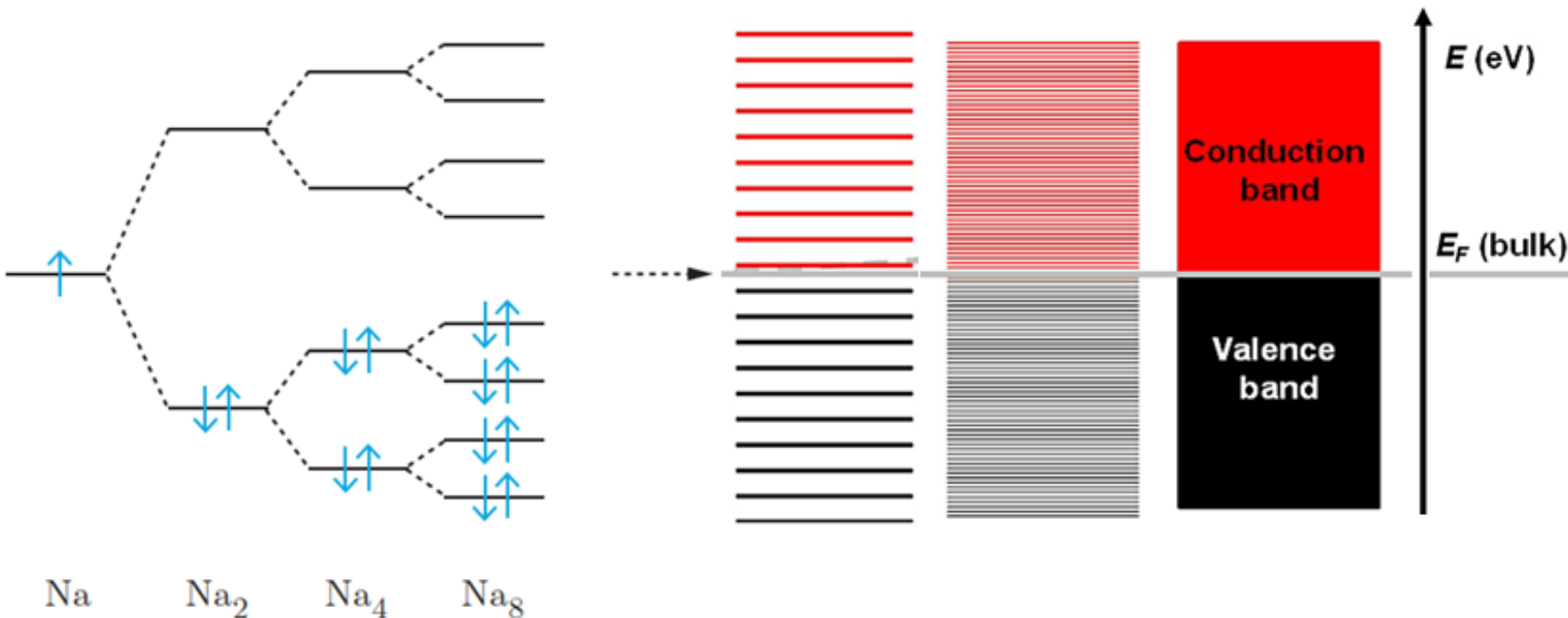

Figure 5.2: Illustration of electron distributions among the energy levels in progressively increasing sizes of clusters of a metal (Na), showing the formation of the valence band (VB) and the conduction band (CB) and the position of the Fermi Level.

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

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

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

$$\delta \geq k_B T$$ ……………………………………………...………… (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

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

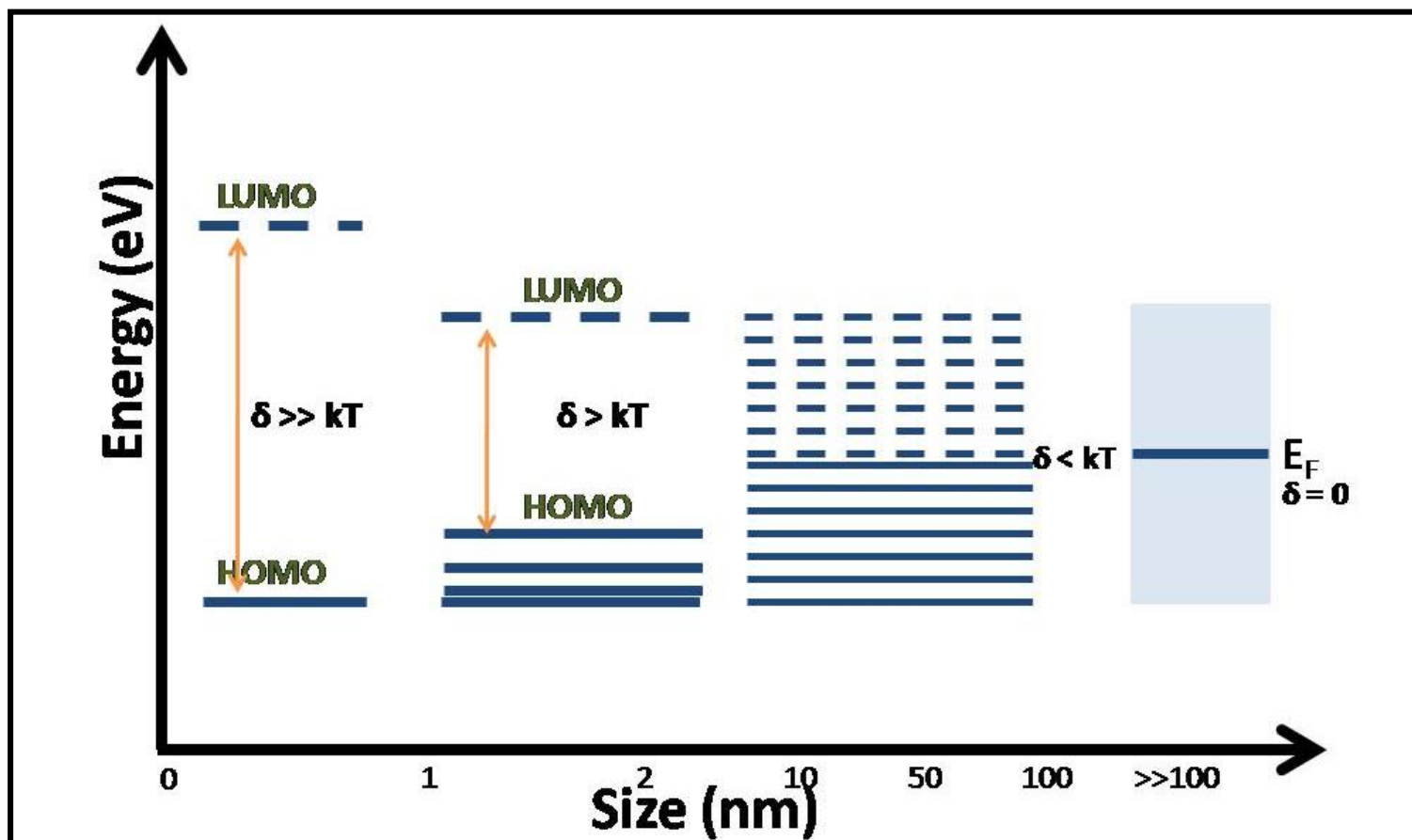The electronic energy gap variation with nanoparticle size is depicted in Figure 1.5.

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 decreases** *or the* **"density of energy states" increases**; *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.
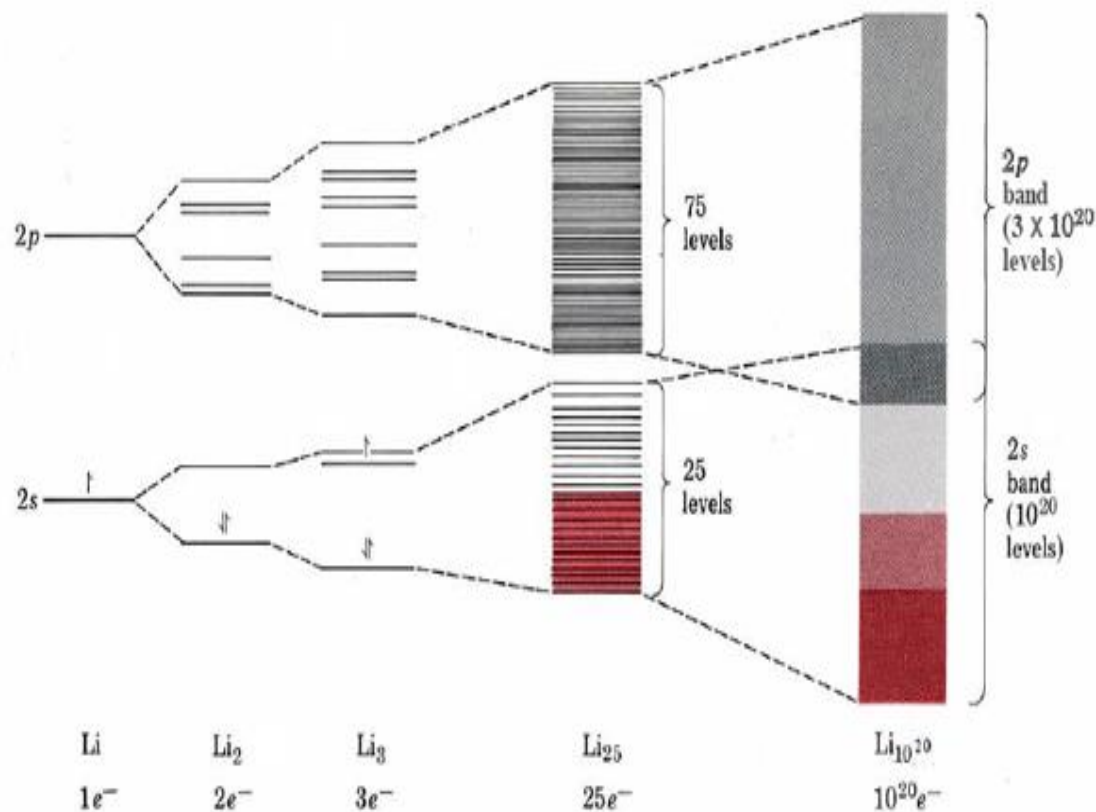

Figure 22.2.1: Molecular-orbital energies corresponding to delocalization of valence electrons over increasing numbers of Li atoms. A 1-mg sample of Li would contain nearly 10^{20} atoms. The corresponding orbital energies are so closely spaced that they constitute essentially continuous bands.

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.

$$\delta \sim \frac{E_F}{N_A} \to 0 \qquad \delta < k_B T \qquad \delta > k_B T \qquad \delta \gg k_B T$$
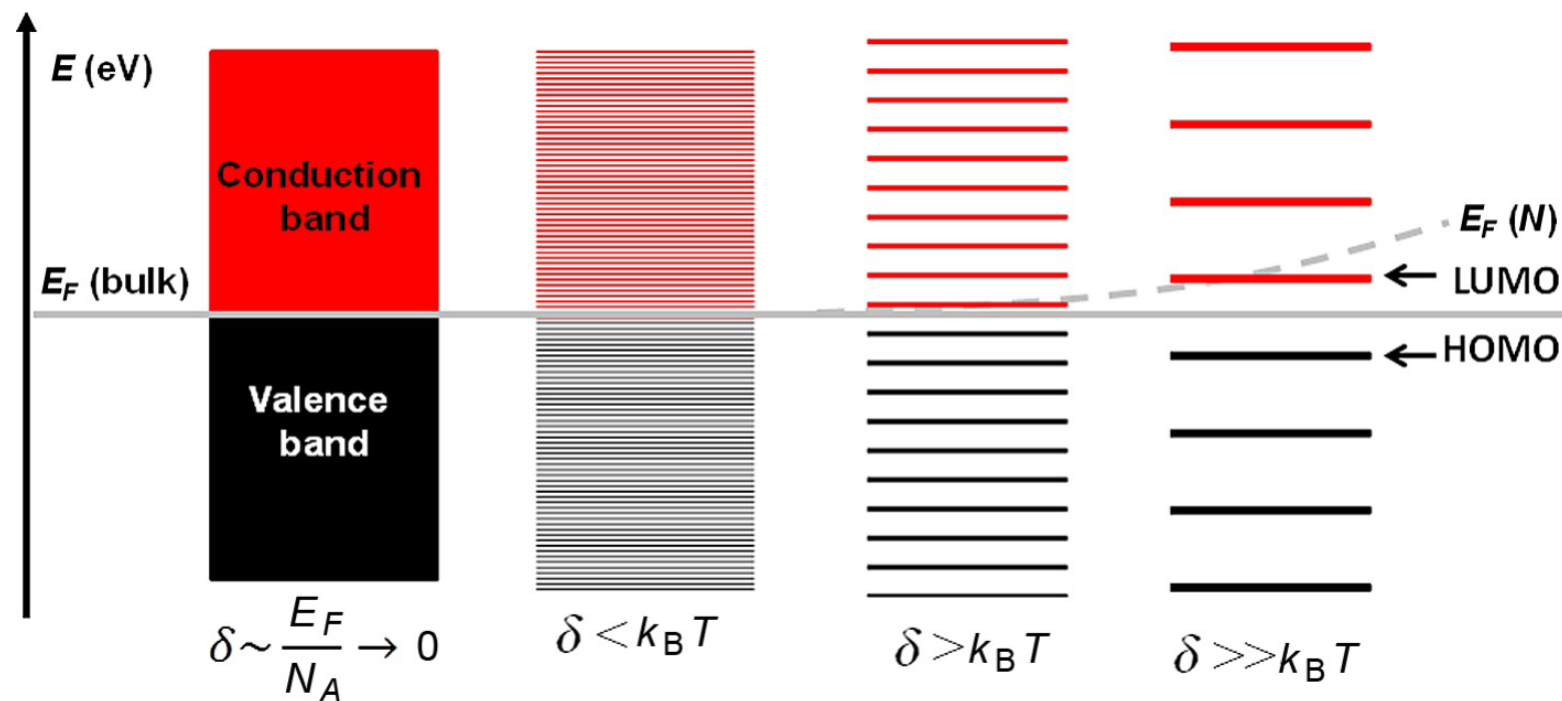
FIGURE 4.9 Confinement in multiple electron systems leads to the size-induced discretization of energy levels from bulk to cluster range, which results in an increasing of energy gaps.

➢ 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*.**

➢ *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**.*

Metal   SizeInduced Metal-Insulator   Transition   Insulator

Diameter : $D \gg 10^4 Å$	$D - 10^4 - 102 Å$	$D - 10^2 - 10 Å$	$D < 10 Å$
Nucleartity : $N \gg 10^{10}$	$N - 10^{10} - 10^4$	$N - 10^4 - 10$	$N < 10$
Kubo Gap : $\delta \ll 10^{-6} K$	$\delta - 10^{-6} - 1K$	$\delta - 1 - 10^3 K$	$\delta > 10^3 K$

Bulk Metal   Metal cluster/nanoparticle   Atoms and Molecules
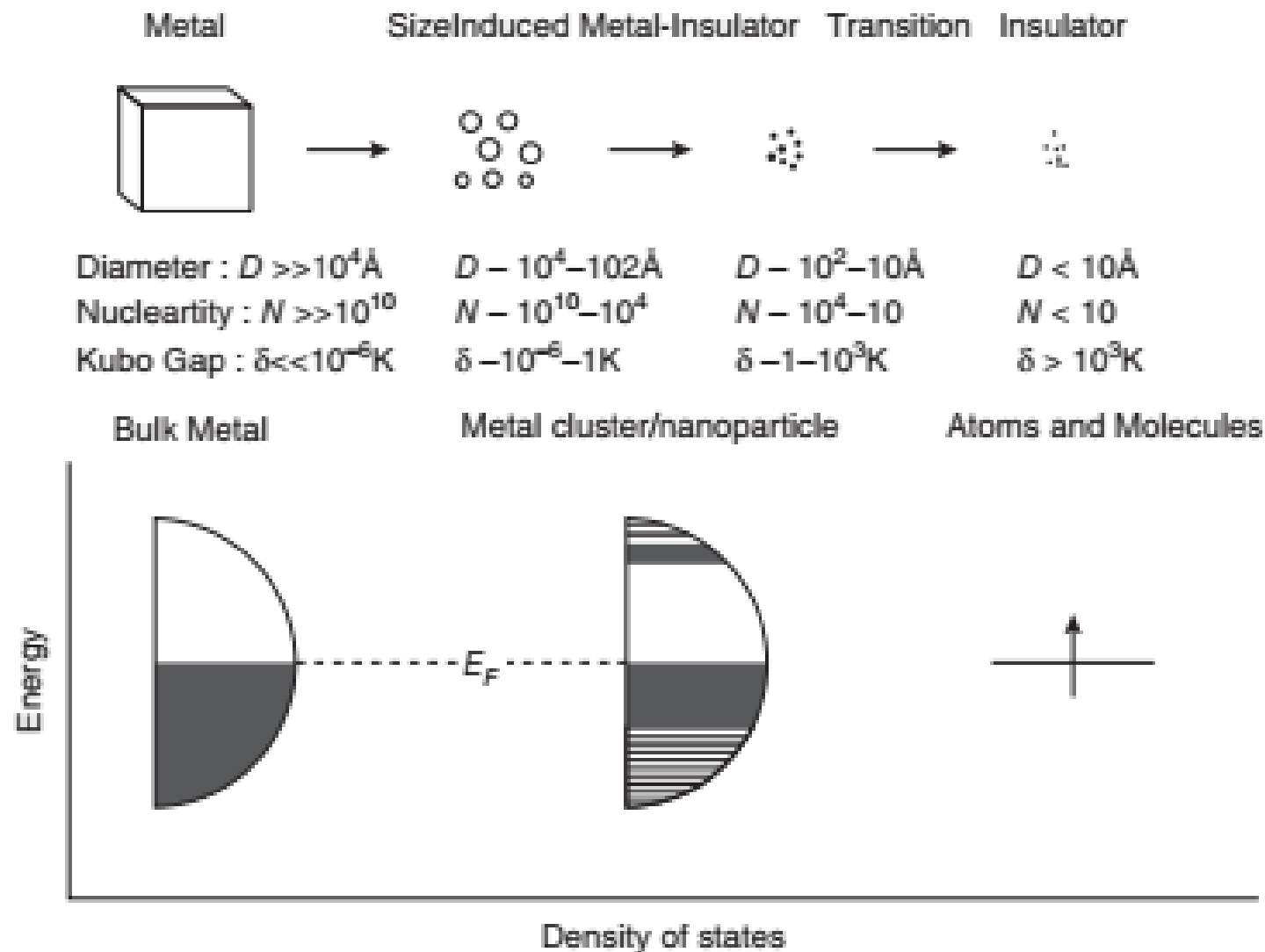
Figure 8.12 Schematic of the density of states exhibited by bulk metal relative to increasingly smaller nanoclusters. The approximate diameter (D), nuclearity (N), and Kubo gap (δ) for each size regime are indicated.

- ➢ 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*.

❖ **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**.
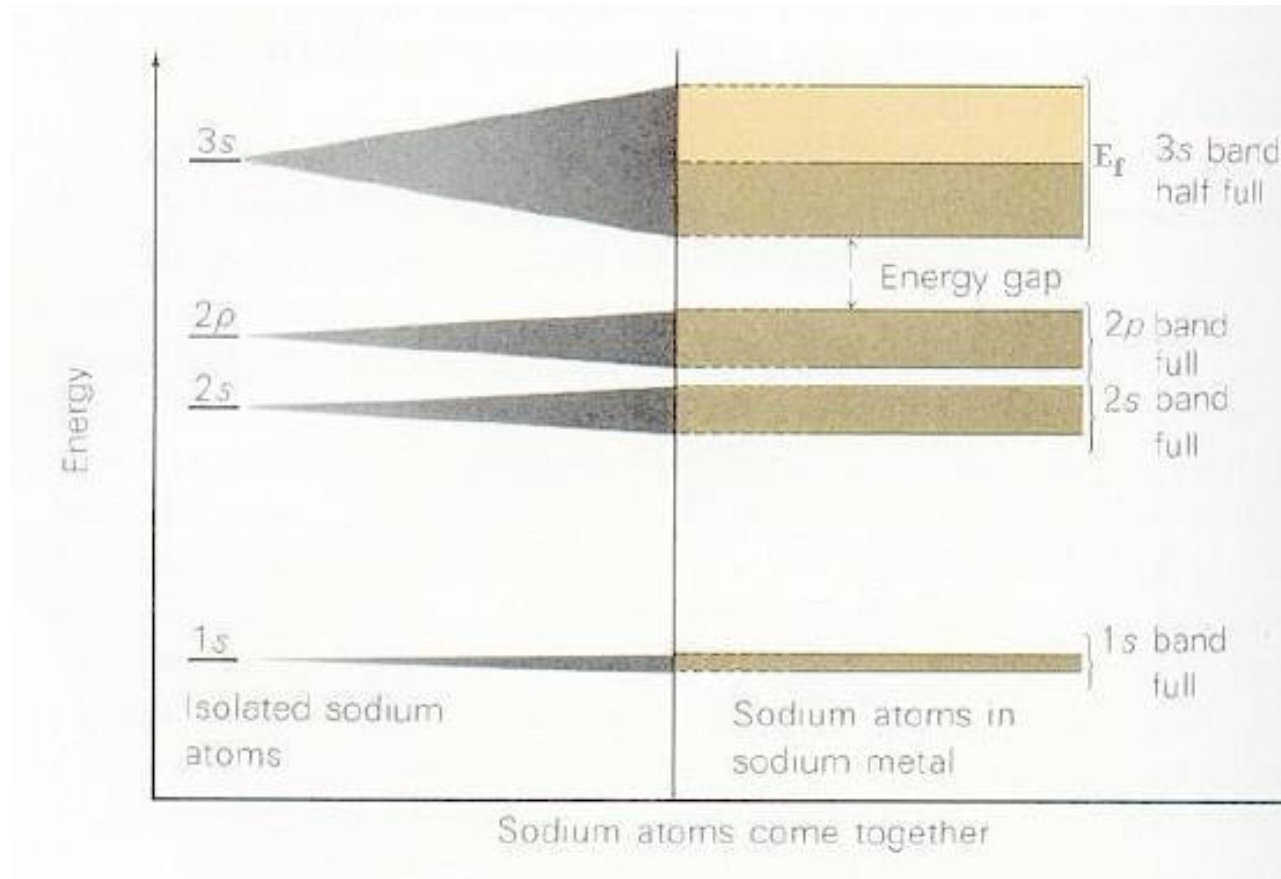

Figure 2.6. Example of sodium atoms' 1s, 2s, 2p, and 3s orbitals splitting into filled and partially filled bands in sodium metal.

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

Electronic properties of bulk metals have been historically studied under theoretical frames considering the crystalline structure of 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 proportional to the number of atoms (valence electrons) becoming almost a continuous magnitude for bulk materials.*

The dimensionality of nanostructures or the confinement of electrons in the nanometer regions results in **a drastic change in the quantum mechanical states of the electrons**, namely the number of states (NOS, *N(E)*) and *electron density of states* function, (DOS, *D(E) or g(E)*), in a nanomaterial (as shown in Fig. 3).

*The NOS (N(E)), and the DOS (D(E)) which can be defined as a function of energy E, **affect the physical and chemical properties of the nanomaterials**. These changes in the density of states for excited electrons alters the way excitation energy interacts with the valence electrons, thus changing the fundamental properties with size as well as shape in quantum confined nanomaterials. These changes affect their **electromagnetic** (electronic, magnetic, dielectric, etc.), **mechanical** (lattice dynamics, mechanical strength, etc.), **thermal** (Seebeck coefficient, thermal resistance, etc.), **optical** (Stokes shift, resonance, etc.) and **chemical** properties (chemiluminescence, surface functionalization, etc.).

*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). For 0D nanomaterials, the excited electrons are completely confined in all the three dimensions and they behave analogous to atomic/molecular clusters with discreet 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 density of states is *quasi-discreet* 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 individual in bulk to quantum-confined matter is expressed in a scheme of the type shown in the Figure 3.
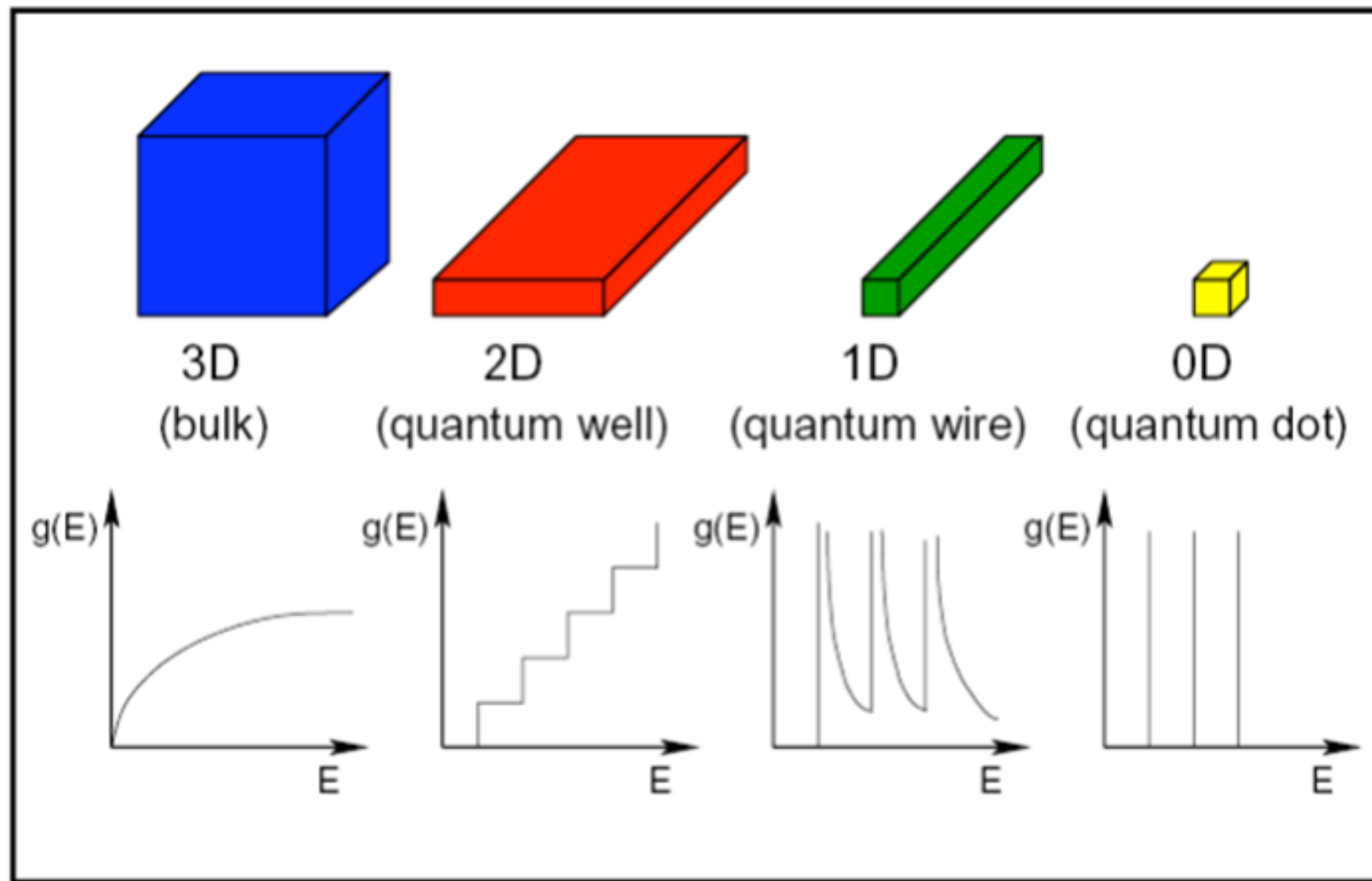
Figure 3: *Density of states for a free electron gas in various dimensions (general trend).*

➢ *For materials with larger dimensions, (although the bulk of the material is treated classically) the phenomena occurring at the boundaries and surfaces are best treated quantum mechanically.* Therefore, in the case of larger nanocrystals (not quantum confined 3D bulk material, the parabolic shape of DOS), size and shape of the nanocrystals also affects its properties due to differences in surface to volume ratio.

➢ For a given mass, 0D nanomaterials have the maximum exposed surface, followed by 1D, and finally 2D nanomaterials have the least.

➢ The NOS and DOS can be calculated using quantum mechanical analytical and computational evaluations. The 2D, 1D, and 0D approximations can be utilized to analyze structures such as quantum wells, nanowires and nanoparticles, where quantum effects are observed in dimensions of less than a few nanometers.

➢ In this section, the numerical calculations for the NOS and DOS will be presented.

➢ ***Often, we are not interested in the total number of particles in all states, but rather the number of particles dN with energies in a narrow energy interval.*** This value can be expressed by $dN = n(E)dE = g(E)dE \cdot F$, where $n(E)$ is the electron number density, or the number of electrons per unit volume; $g(E)$ is the density of states, or the number of allowed quantum states per unit energy; dE is the size of the energy interval; and F is the Fermi factor.

➢ The Fermi factor is the probability that the state will be filled. For example, if $g(E)dE$ is 100 available states, but F is only 5%, then the number of particles in this narrow energy interval is only five. Finding $g(E)$ requires solving Schrödinger's equation (in three dimensions) for the allowed energy levels.

❖ How do we calculate the DOS? What is its significance?

➤ The density of states, denoted by *D(E)*, refers to the ***number of allowed states*** *available for occupation, in units of per unit energy and unit space.* In other words, *it is* the ***number of allowed states*** with ***energies between E and E+dE***, *in unit space (**length, area** or **volume** depending on the dimensionality).* ***D(E) indicates how densely packed quantum states in a particular system. D(E) is defined more precisely*** by the mathematical expressions:

❖ In 3-Dimensional: The density of state for 3D is defined as the number of electronic or quantum states per unit energy range per unit volume and is usually defined as:

$$D(E)_{3D} = \frac{1}{V}\frac{dN}{dE}$$

❖ In 2-Dimensional: The density of state for 2D is defined as the number of electronic or quantum states per unit energy range per unit area and is usually defined as:

$$D(E)_{2D} = \frac{1}{A}\frac{dN}{dE}$$

❖ In 1-Dimensional: The density of state for 1-D is defined as the number of electronic or quantum states per unit energy range per unit length and is usually denoted by:

$$D(E)_{1D} = \frac{1}{L}\frac{dN}{dE}$$

➢ In the following, we will consider the density of states of a **free electron gas** that is spatially confined:

❖ Density of state of a **three-dimensional** electron gas. This occurs, for example, in metals. The density of states can be used to determine the charge carrier density in the metal.

❖ Density of state of a **two-dimensional** electron gas. This occurs in 2d materials, such as graphene or in the quantum Hall effect.

❖ Density of state of a **one-dimensional** electron gas. 1d density of states is useful for materials where electrons can propagate in only one dimension. 1d materials include, for example, nanotubes and nanowires.

➤ Modeling our electronic material as a box allows us to ignore atoms and assume that the material is perfectly homogeneous. We will consider boxes in different dimensions: either three dimensions (typical bulk materials), 2-d (quantum wells), 1-d (quantum wires), or 0-dimensions (this is a quantum dot). The label "quantum" here refers to the confinement of electrons. When we say that an electron is "confined" in a low dimensional material we mean that critical dimensions of the material are on the order of the wavelength of an electron. We've seen that when particles are confined, their energy levels become discrete.

➤ In quantum dots, electrons are confined in all three dimensions, in quantum wires, electrons are confined in only two dimensions and so on. So when we say that a given structure is 2-d, we mean that the electron is *unconfined* in 2 dimensions. In the unconfined directions, we will assume that the electron described by a plane wave.

Figure 2.6.2: (a) In quantum wells, electrons are confined only in one dimension. Quantum wells are usually implemented by burying the confining material within a barrier material. (b) Quantum wires confine electrons in two dimensions. The electron is not confined along the wire. (c) In a quantum dot, an electron is confined in three dimensions.

(a) 2-d: Quantum Well
L_y
L_x
barrier
L_z
quantum well
barrier

(b) 1-d: Quantum Wire
L_z
L_y
L_x

(c) 0-d: Quantum Dot
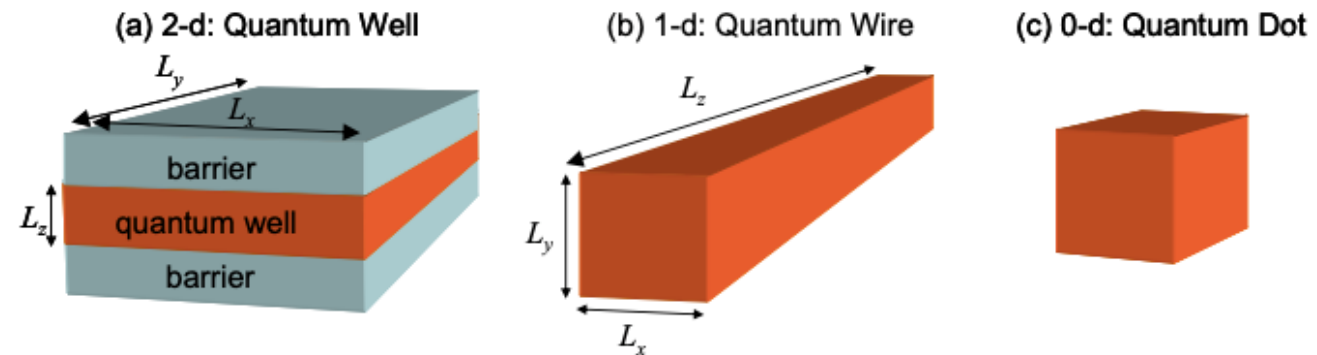
❑ Density of States (DOS) Calculation

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

➤ 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 $L \gg \lambda_e$, and "small" if $L \leq \lambda_e$.**

➤ 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, $L_z \gg \lambda_F$.
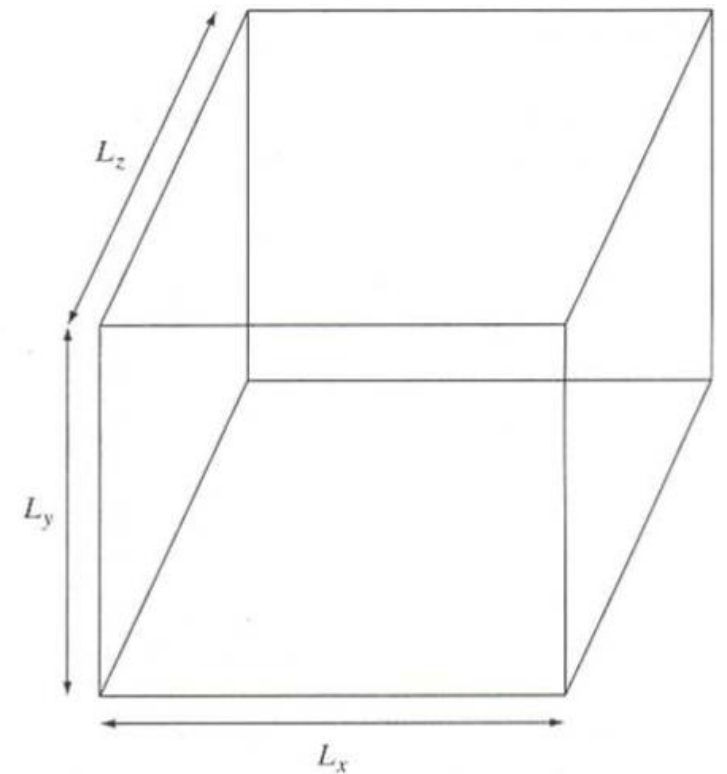

Figure 4.15 An effectively three-dimensional region of space; $L_{x,y,z} \gg \lambda_e$.

➤ 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:

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

➤ *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.

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

➢ Consider first the **3-dimensional case** and the energy levels of the **electrons** (of mass *m*) are given by: $E = \dfrac{\hbar^2}{2m}[(\dfrac{n_x\pi}{L_x})^2 + (\dfrac{n_y\pi}{L_y})^2 + (\dfrac{n_z\pi}{L_z})^2]$

➢ 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.

➢ For simplicity, let's use a cubical box that has equal length sides *L*. In this case, the total energy *E* is: $E = \dfrac{\hbar^2\pi^2}{2mL^2}[n_x^2 + n_y^2 + n_z^2]$.

➢ The latter quantity $[n_x^2 + n_y^2 + n_z^2]$ can be thought of as the square of the length of a vector $\boldsymbol{n}$ having three components n_x, n_y, n_z. Then… $E = (\hbar^2\pi^2/2mL^2)\, n^2$ and $n = (2mL^2E/\hbar^2\pi^2)^{1/2}$.

➢ We can consider three Cartesian axes labeled n_x, n_y, and n_z and view a sphere of radius *n* in this space.

➢ The sphere is divided into many shells of a particular combination of quantum numbers (n_x, n_y and n_z) and, therefore, represents a particular energy value.
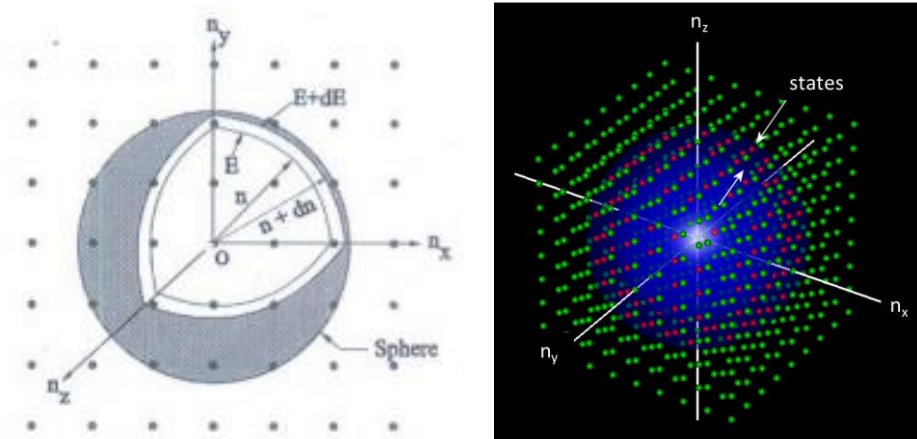
➤ In other words, each *cube having unit length* along the n_x, n_y, and n_z axes corresponds to a *single quantum wave function and its energy.*

➤ Let us consider two energy values E and $(E + dE)$. The number of energy states between E and $E + dE$ can be found by finding the number of energy states between the shells of radius n and $(n + dn)$, from the origin.

➤ The number of energy states within the sphere of radius n is $\frac{4}{3}\pi n^3$.

➤ Remembering that we only have positive quantum numbers (n_x, n_y, and n_z will have only positive values (*quantum states*)), we have to take only one octant of the sphere, i.e., 1/8th of the sphere volume.

➤ The number of ***available energy states*** within the sphere of radius n:

➤ $$N_{tot} = 2 \times \frac{1}{8} \times \left(\frac{4}{3}\pi n^3\right) = \left(\frac{1}{3}\pi n^3\right) = \frac{1}{3}\pi\left[\left(\frac{2mL^2 E}{\hbar^2 \pi^2}\right)^{\frac{1}{2}}\right]^3 = \frac{1}{3}\pi\left[\frac{2mL^2}{\hbar^2 \pi^2}\right]^{\frac{3}{2}}.E^{\frac{3}{2}}$$

➤ We have *multiplied by 2, each energy level can occupy 2 electrons of opposite spin. For phonons this factor is 3.*

➤ *Although derived for a cubic box, these results are not dependent on the shape of the system.*

➢ The number of available energy states between the shells of radius n and $(n + dn)$ or between the energy levels with energies between E and $(E + dE)$ is

    ➢ $\frac{dN_{tot}}{dE} dE$

Bulk

➢ $\frac{dN_{tot}}{dE} = \frac{1}{3}\pi\left[\frac{2mL^2}{\hbar^2\pi^2}\right]^{3/2} \cdot \frac{3}{2}E^{\frac{1}{2}} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot L^3 \cdot \sqrt{E}.$

➢ $\frac{1}{L^3} \cdot \frac{dN_{tot}}{dE} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \sqrt{E}$

➢ The **density $D(E)$ of states** near energy E *is therefore given as*:

➢ $D(E)_{3D} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \sqrt{E}$

$D(E)$ ∝ $E^{1/2}$

➢ Notice that *the **density of states increases** with the square root of **the energy**.* More states are available at high energy (due to growing degeneracy of the states) than at low energy.

➢ This expression does not provide information of the density of the electrons in physical space, but rather the density of energy levels in "energy space." For example, in our study of the atomic structure, we learned that the energy levels of a hydrogen atom are much more widely spaced for small energy values (near than ground state) than for larger values.
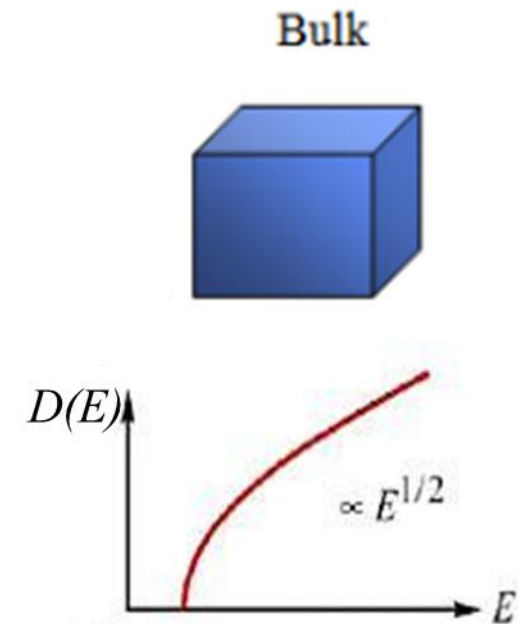
➤ Notice that this state density increases as E increases. This means that, in the 3-dimensional case, the number of quantum states per unit energy grows; in other words, *the spacing between neighboring state energies decreases*, very unlike the 1-dimensioal case where the spacing between neighboring 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.

➤ The specific electrical properties of semiconductors and superconductors will depend on density of states.

➤ The most relevant application of density of states is that it provides information about nanomaterials.

➤ In the **2-dimensional case (in QUANTUM WELL)**, 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 $E=(\hbar^2\pi^2/2mL^2)n^2$, but with $n^2=n_x^2+n_y^2$.

➤ The total number $N_{tot}(E)$ of quantum states with positive n_x and n_y with energy between zero and $E=(\hbar^2\pi^2/2mL^2)n^2$ is the $1/4^{th}$ of the circular area having radius, n:

➤ $N_{tot} = 2 \times \dfrac{1}{4} \times (\pi n^2) = \dfrac{1}{2}\pi n^2 = \left(\dfrac{1}{2}\pi\left[\dfrac{2mL^2 E}{\hbar^2\pi^2}\right]\right) = \dfrac{1}{2}\pi\left[\dfrac{2mL^2}{\hbar^2\pi^2}\right]E = \dfrac{mL^2}{\pi\hbar^2}E$

➤ We have *multiplied by 2, since each state can be occupied by two electrons of opposite spin.*

➤ $\dfrac{dN_{tot}}{dE} = \dfrac{mL^2}{\pi\hbar^2}$

➤ $\dfrac{1}{L^2}\cdot\dfrac{dN_{tot}}{dE} = \dfrac{m}{\pi\hbar^2}$

➤ The **density $D(E)$ of states** near energy E is:

➤ $D(E)_{2D} = \dfrac{m}{\pi\hbar^2}$

➤ 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).
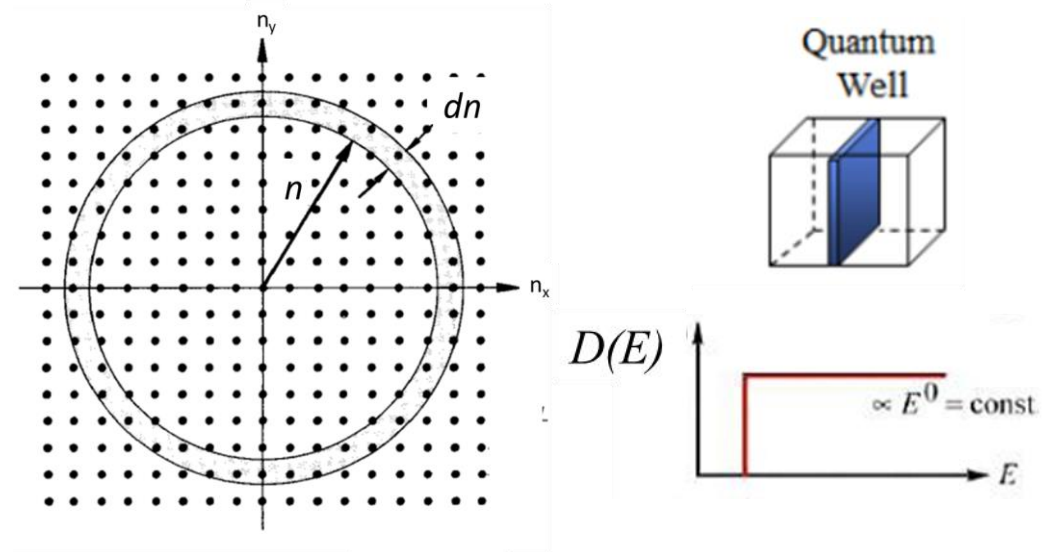
➢ This kind of analysis for the **1-dimensional (nanowire) case** (with $n^2=n_z^2$) gives

➢ $N_{tot} = 2 \times \frac{1}{2} \times (n) = n = [\frac{2mEL^2}{\hbar^2\pi^2}]^{\frac{1}{2}} = [\frac{2m}{\hbar^2\pi^2}]^{\frac{1}{2}} \cdot L \cdot E^{\frac{1}{2}}$

➢ We have *multiplied by 2, since each state can be occupied by two electrons of opposite spin. Also, we have divided by 2 corresponding to the two directions (positive and negative) of the wire.*
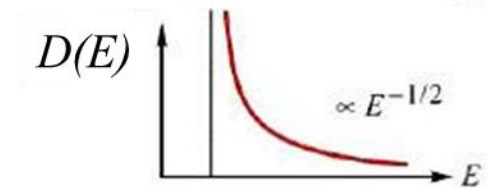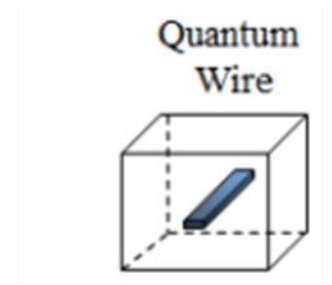
➢ $\frac{dN_{tot}}{dE} = [\frac{2m}{\hbar^2\pi^2}]^{\frac{1}{2}} \cdot L \cdot \frac{1}{2} \cdot E^{(-\frac{1}{2})}$

Quantum Wire

➢ $\frac{1}{L} \cdot \frac{dN_{tot}}{dE} = \frac{\sqrt{m}}{\hbar\pi\sqrt{2}} \cdot E^{(-\frac{1}{2})}$

➢ The **density $D(E)$ of states** near energy E *is therefore given as:*

$D(E)$

$\propto E^{-1/2}$

E

➢ $D(E)_{1D} = \frac{\sqrt{m}}{\pi\hbar\sqrt{2}} \cdot E^{(-\frac{1}{2})}$

➢ 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.

➢ 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.
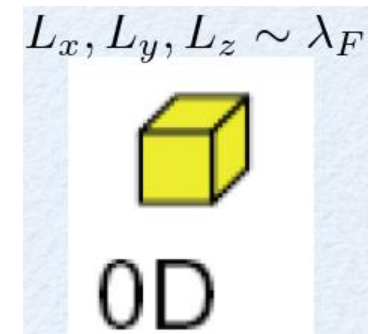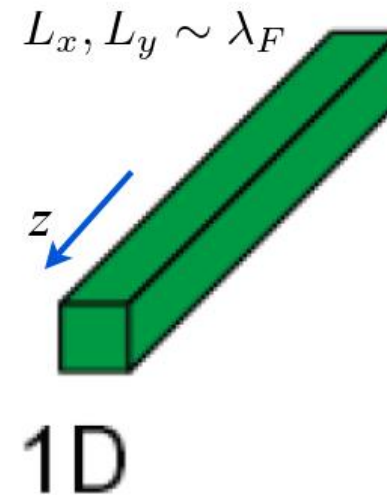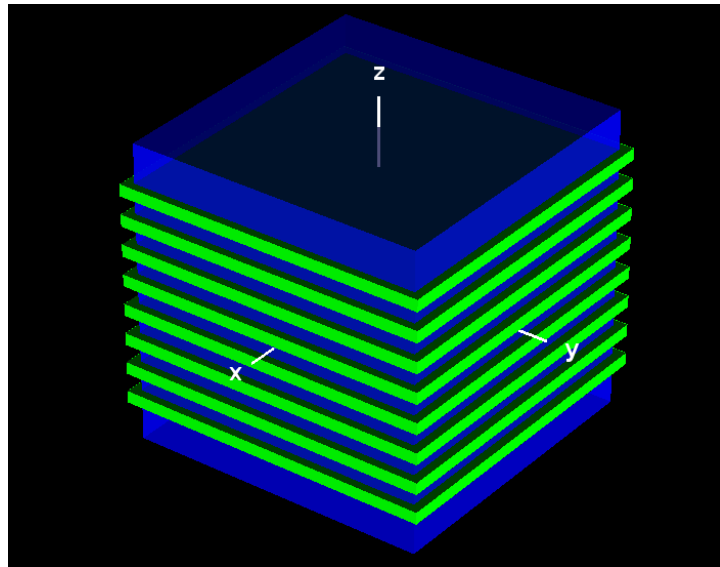
As depicted in the above Fig., the charge carriers (e.g., electrons) as in a thin metal or semiconductor film are confined with a film thickness scales with the de Broglie wavelength λ_F as: $L_z \leq \lambda_F << L_x, L_y$.

❏ 0D Density of States: Quantum Dots

The DOS concept is not valid in a quantum dot as there is no densely packed quantum levels. In a quantum dot all the three dimensions are of the order of the de Broglie wavelength of the charge carriers. In a quantum dot all three Cartesian directions are squeezed so that L_x, L_y and $L_z \leq \lambda_F$.

Electron movement will be confined in all three directions (i.e., electrons will "feel" the boundaries in the x-, y-, and z-directions), exhibiting energy quantization in three dimensions and will not be free in any direction. This makes for an effectively zero-dimensional system called a quantum dot.

➢ The 0-D DOS is a special case because the particle is confined in all directions.

➢ Like a particle in a well with discrete energy levels, we might assume that the density of states in a 0-D might be a series of delta functions at the allowed energy levels. This is indeed true for an isolated 0-D particle.

➢ The *lifetime of a charge* in *an orbital* of *an isolated particle* is *infinite*. From the uncertainty principle, infinite lifetimes are associated with perfectly discrete energy states in the isolated molecule, i.e. if $\Delta t \rightarrow \infty$, $\Delta E \rightarrow 0$.

➢ But when, for example, a molecule is brought in contact with a metal electrode, the electron
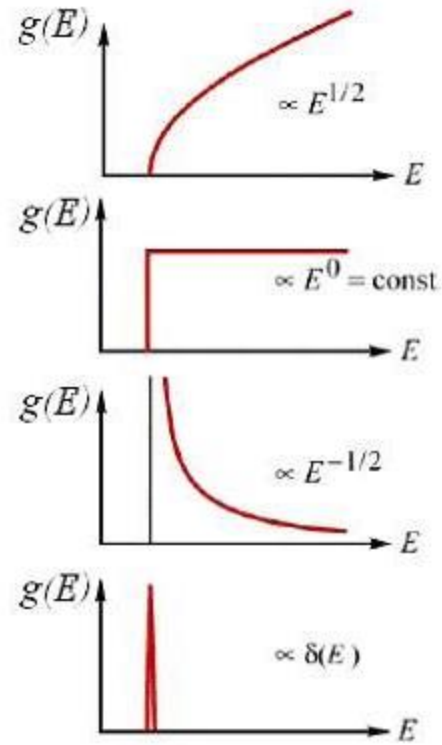
may eventually escape into the metal. Now, the electron's lifetime on the molecule is finite, and hence the molecule's energy levels should also exhibit a finite width. Thus, molecular energy levels are broadened in a coupled metal-molecule system – the greater the coupling, the greater the broadening of the molecular energy levels.

➢ For semiconductors, this is in the range of 10 to 100 nm. Semiconductor quantum dots can be prepared by wet chemical methods, by lithography as well as by deposition of a semiconductor film on a substrate with a slightly different lattice parameter.

➢ Since the typical electron of interest has a Fermi wavelength on the order of a nanometer in metals and many tens of nanometers in semiconductors, quantum dots are nanoscale pieces of material, typically ranging in size from, several nm to hundreds of nm. As such, quantum dots can contain from several hundred to several hundred thousand atoms. For example, as a rough estimate, assuming that the size of an atom is 0.1 nm ($= 1$ Å), then about 10 atoms can fit along a 1 nm line.

➢ A cube having sides of 1 am will contain approximately $10^3 = 1,000$ atoms. A cube having sides of 10 run will contain approximately 10^6 atoms. Thus, quantum dots are typically much larger than atoms but are generally too small to act like a bulk solid. An electron in a quantum dot will act more like an electron in a molecule than an electron in a bulk solid, and for this reason, quantum dots are sometimes called *artificial molecules or artificial atoms*. In general, one would tend to call nanoscopic material regions quantum dots if quantum confinement effects are important, and nanoparticles otherwise. Thus, a 10-nm-radius sphere of GaAs would be a quantum dot, whereas the same size sphere made from copper would be a nanoparticle.

$$g(E) = \frac{1}{2\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{\sqrt{E}} \qquad 1-D$$

$$g(E) = \frac{1}{2\pi}\left(\frac{2m}{\hbar^2}\right) \qquad 2-D$$

$$g(E) = \left(\frac{1}{2\pi}\right)^2\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E} \qquad 3-D$$

➢ The most striking effect of dimension reduction is that the energy dependence of the density of states (DOS) exhibits different functional form. The dependence may be generalized in the form $D(E) \sim E^{((D/2)-1)}$, where "D" represents the dimension of the system.

➢ These relations establish the densities of states for electrons that have some freedom of movement while being circumscribed due to confinement in some of the degrees of freedom. When these states are occupied by electrons, the permitted freedom of movement leads to current when an external force is applied on the system. It is because of this density of states that electrons are available with freedom of movement when the energy separation—a kinetic energy separation—of the states is small. The channels of conduction arise in the free directions of movement.

➢ The density of states determines the channels available to give rise to current.

Bulk | Quantum Well | Quantum Wire | Quantum Dot
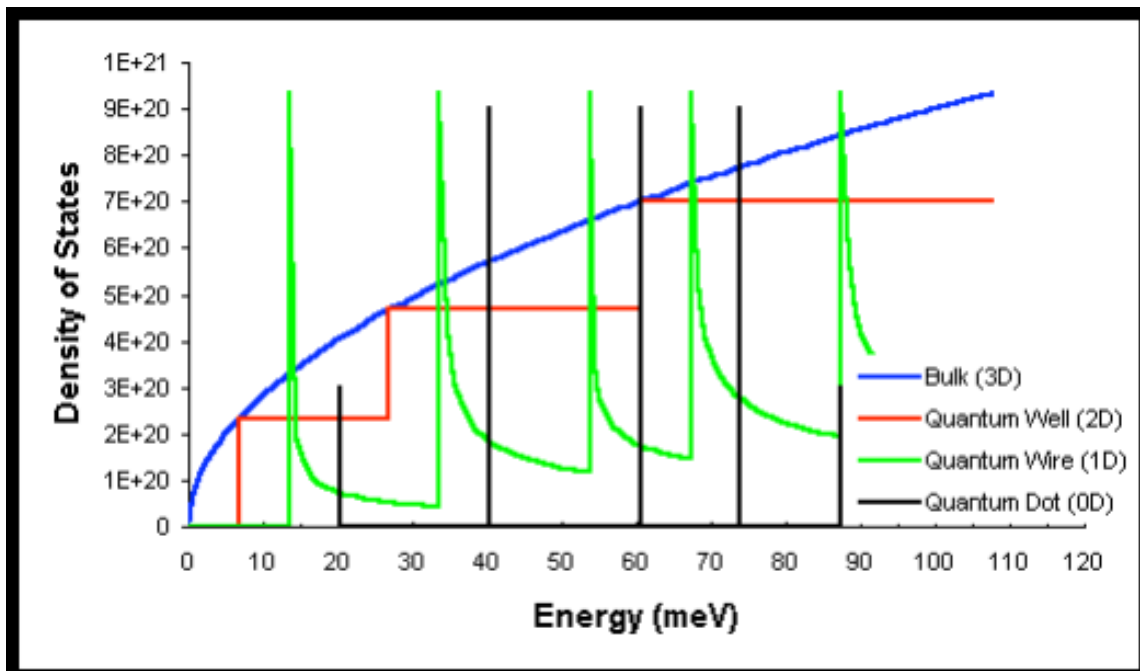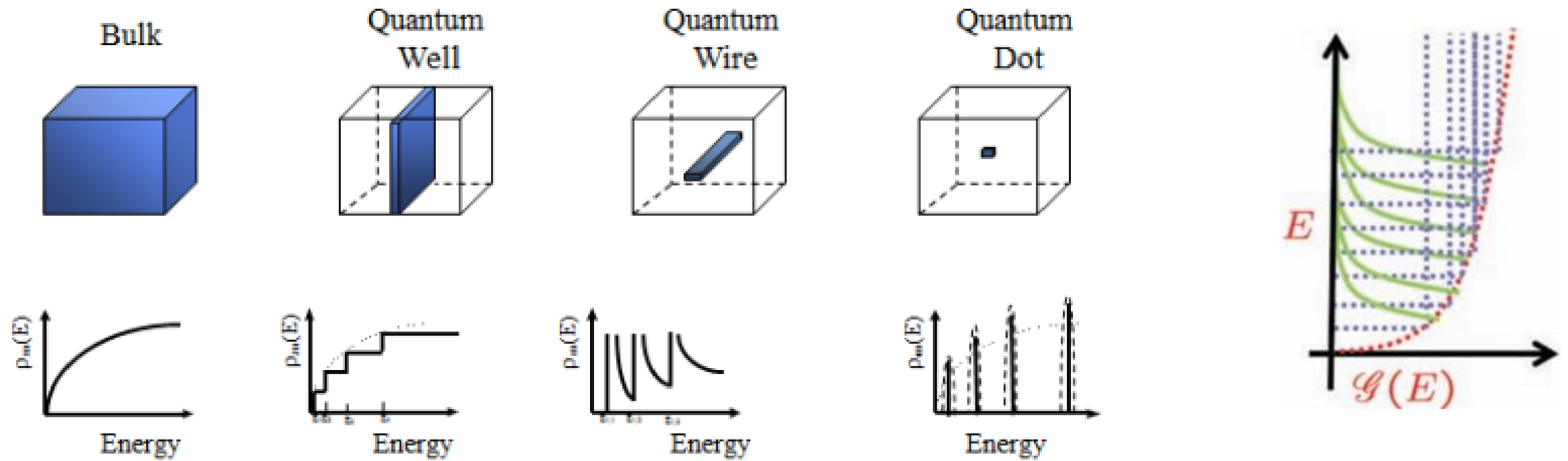
Figure… Density of states D(E) plotted as a function of the energy E for conduction electrons delocalized in one (Q-wire), two (Q-well), and three (bulk) dimensions and confined in all three dimensions.
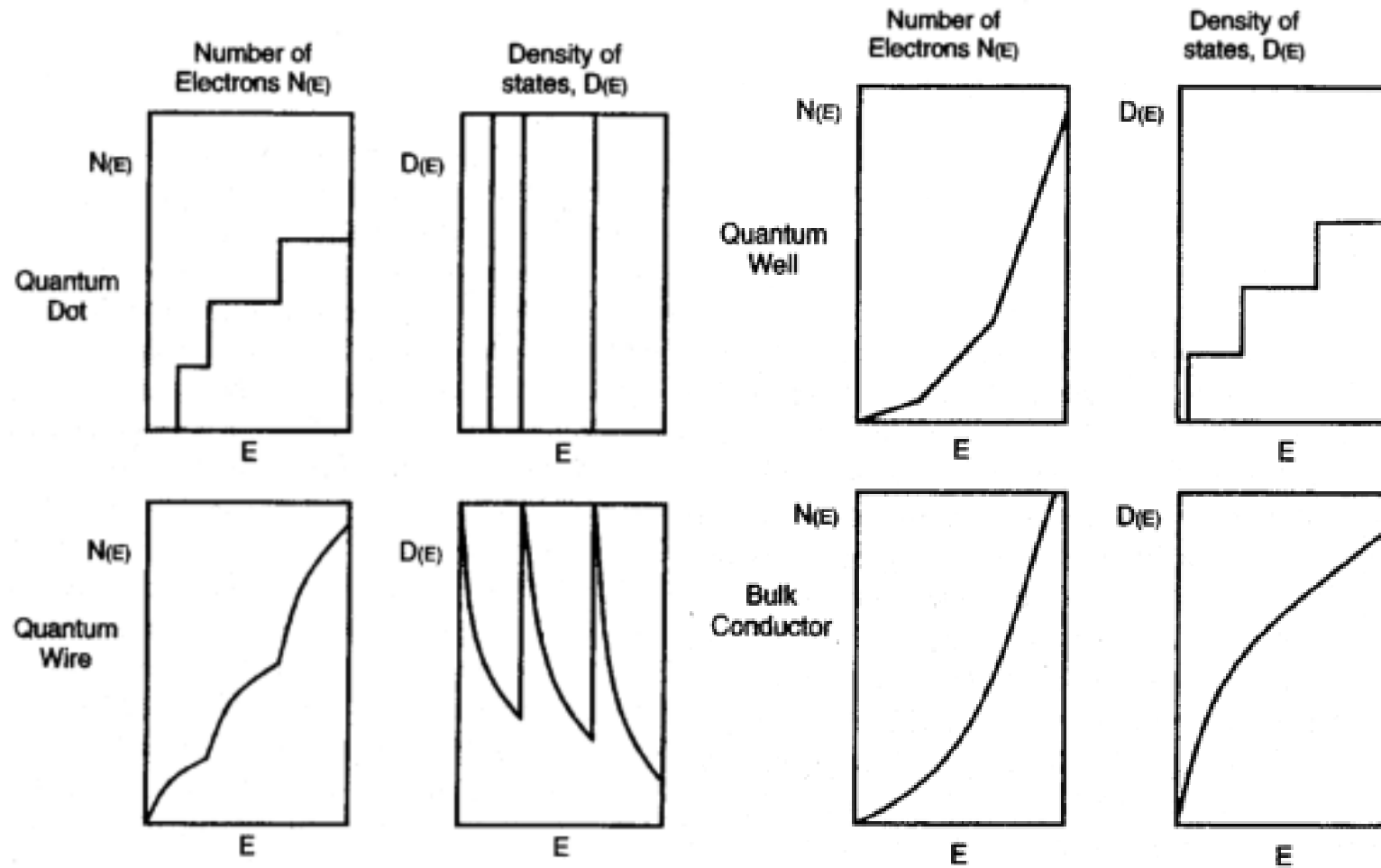
Figure 9.15. Number of electrons N(E) (left side) and density of states D(E) (right side) plotted against the energy for four quantum structures (quantum dot, quantum wire, quantum well, and bulk material) in the square well-Fermi gas approximations.

Properties Dependent on Density of States

It is now clear that lower dimensional devices behave differently than the bulk 3D device and one needs to calculate the Density of States (DOS) function separately for quasi 2D or 1D devices. The DOS function and corresponding energy eigenvalues are presented in a concise manner for low dimensional devices. *Quantum well (QW), on the other hand, has shown applications especially in the field of optoelectronics as QW laser diodes are popular due to their capability of producing really short wavelengths.*

We have discussed the **density of states D(E) of conduction electrons** and have shown that it is strongly affected by the dimensionality of a material. Phonons or quantized lattice vibrations also have a density of states $D_{PH}(E)$ that depends on the dimensionality, and like its electronic counterpart, it influences some properties of solids. In this section we mention some of the properties of solids that depend on the density of states. The specific heat of a solid, *C*, is the amount of heat that must be added to it to raise its temperature by one degree Celsius (centigrade). The main contribution to this heat is the amount that excites lattice vibrations, and this depends on the phonon density of states $D_{PH}(E)$. At low temperatures there is also a contribution to the specific heat C_{el} of a conductor arising from the conduction electrons, and this depends on the electronic density of states at the Fermi level: $C_{el} = \pi^2 D(E_F)k_B^2T/3$, where k_B is the Boltzmann constant. The susceptibility $\chi = M/H$ of a magnetic material is a measure of the magnetization *M* or magnetic moment per unit volume that is induced in the material by the application of an applied magnetic field *H*. The component of the susceptibility arising from the conduction electrons, called the *Pauli susceptibility*, is given by the expression $\chi_{el} = \mu_B D(E_F)$, where μ_B is the unit magnetic moment called the Bohr magneton, and is hence χ_{el} characterized by its proportionality to the electronic density of states *D(E)* at the Fermi level, and its lack of dependence on the temperature. When a good conductor such as aluminium is bombarded by fast electrons with just enough energy to remove an electron from a particular Al inner-core energy level, the vacant level left behind constitutes a hole in the inner-core band. An electron from the conduction band of the aluminium can fall into the vacant inner-core level to occupy it with the simultaneous emission of an X-ray in the process. *The intensity of the emitted X-radiation is proportional to the density of states of the conduction electrons because the number of electrons with each particular energy that jumps down to fill the hole is proportional to D(E).* Therefore, a plot of the emitted X-ray intensity versus the X-ray energy *E* has a shape very similar to a plot of *D(E)* versus *E*. These emitted X-rays for aluminium are in the energy range from 56 to 77eV.

Some other properties and experiments that depend on the density of states and can provide information on it are photoemission spectroscopy, Seebeck effect (thermopower) measurements, the concentrations of electrons and holes in semiconductors, optical absorption determinations of the dielectric constant, and so on. Experimental measurements of these various properties permit us to determine the form of the "density of states *D(E)*, both at the Fermi level *E*, and over a broad range of temperature.

❑ Electrical Properties

➢ There are *three categories of materials based on their electrical properties*, namely **conductors, semiconductors, and insulat**ors. 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.**
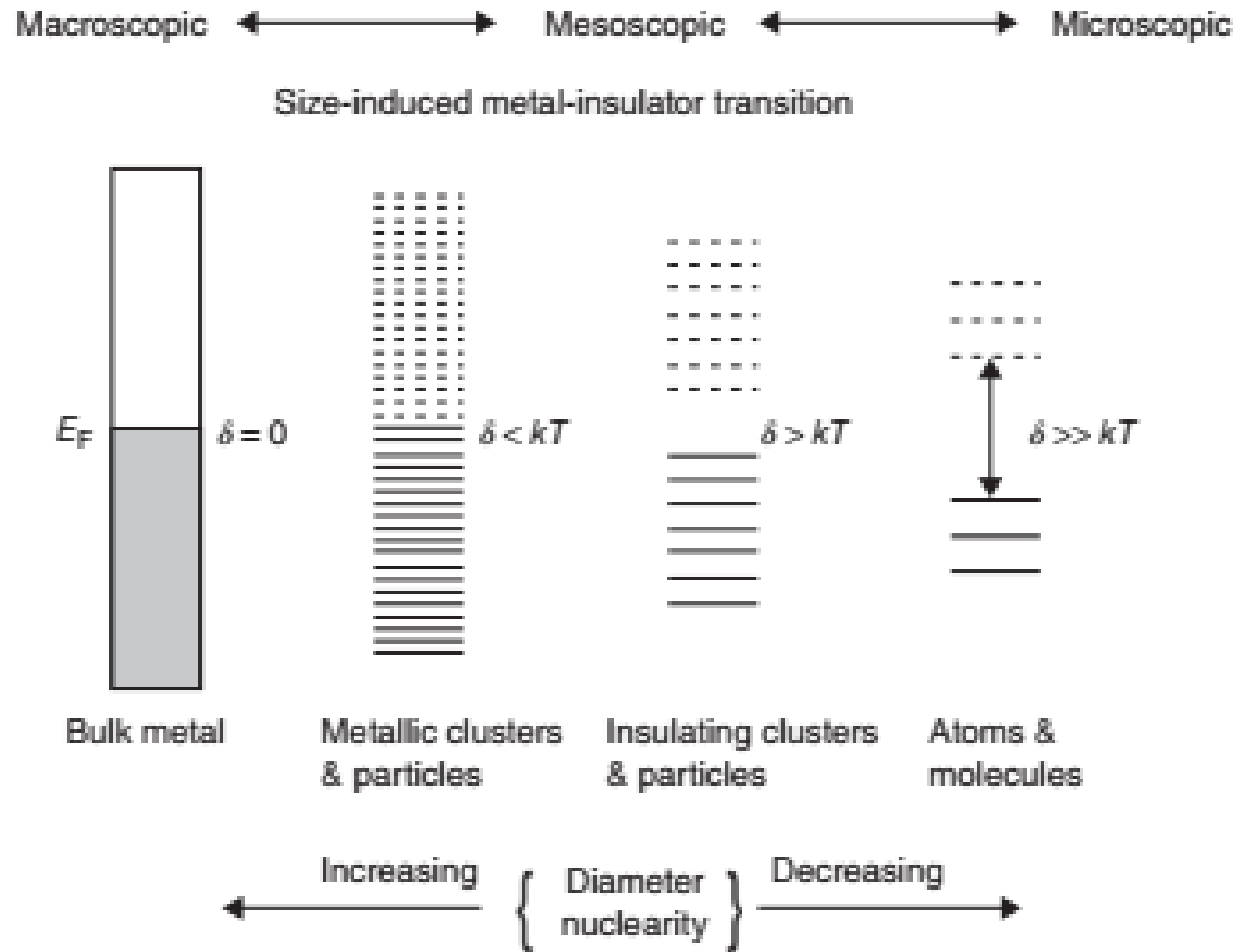
Figure 8.3 Evolution of the band gap and the density of states as the number of atoms in a system increase.

➢ *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.

➢ *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 $\textbf{\textit{V= R·I}}$ (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 CONDUCTANCE and QUANTUM RESISTANCE

❖ *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, $R = L/\sigma A$ $=L/[(5.9 \times 10^7 \text{ S/m})(2\pi aL)] = 5.395 \times 10^{-5}$ 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, $R = 5.395$ x 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 **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 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 nm*.

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 **quantum mechanics**, *the **conductance of a metallic wire is** not a continuous function of area A, but changes in steps, or* **$G = n \times (2e^2/h)$** **$= n \times (7.75 \times 10^{-5})$** *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*.

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

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

➢ In this case, each *transverse* waveguide mode or conducting channel contributes $G_0 = 2e^2/h = 12.9 \text{ k}\Omega^{-1}$ 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, $J > 10^7 \text{ A/cm}^2$ have been attained.
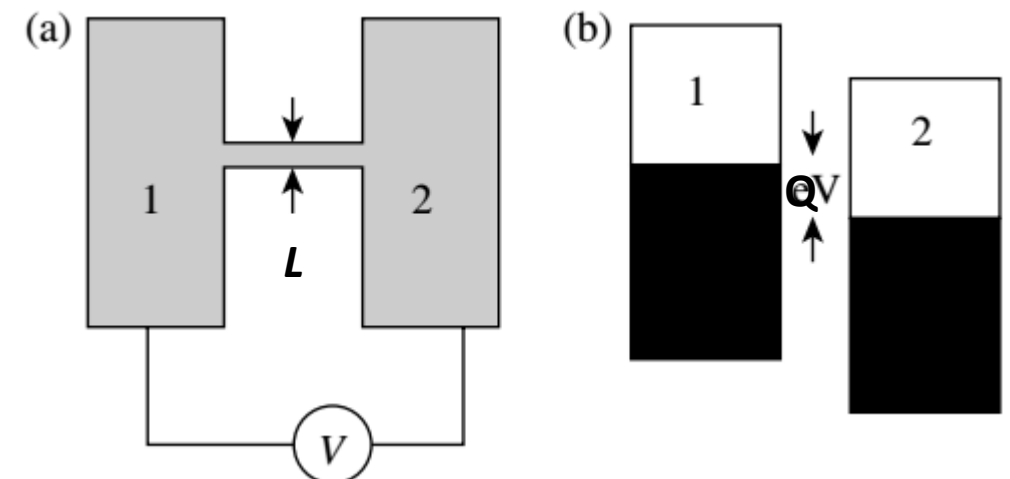

Fig. 7.5 (a) Arrangement of two bulk conductors connected by a small channel with bias *V* applied across the gap. (b) Corresponding energy diagram where the filled states are shown in black.

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.

Conductance G_0 is defined by a change of current when voltage (ΔV) is applied (also reciprocal of resistance): $G_0 = 1/R = \Delta I/\Delta V$.

Current is defined as the rate flow of charge; thus, it is $\Delta I = \Delta Q/\Delta t$. Net charge ΔQ (=Ne), 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, $\Delta I = \Delta Q/\Delta t = Ne/\Delta t = Ne/(L/v) = Nev/L$.

Then $G_0 = \Delta I/\Delta V = Nev/L\Delta V$.

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

Therefore, the conductance, $\boldsymbol{G_0 = Ne^2v/L\Delta E}$.

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

Thus, the conductance, $G_0 = Ne^2v/L\Delta E = (\frac{2L\cdot\Delta E}{hv}e^2v)/L\Delta E = \frac{2e^2}{h} = 7.748 \times 10^{-5}$ S, which is the *quantum of electrical conductance* or *quantum limited 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_0 **is a truly fundamental unit.**

- If there are n electronic channels, then equation becomes

- $G = nG_0 = \dfrac{2e^2}{h} n = \boldsymbol{n} \times (7.75 \times 10^{-5})$ *Siemens* $= 77.5 \, \mu S$.

- The above equation is called **Landauer formula.**

- i.e., Conductance $G = n \, G_0$ ....

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

- We can write, Resistance, $R = \dfrac{h}{2e^2 n} = \dfrac{R_0}{n}$. Consequently, the two-terminal **resistance (R_0)** is calculated to be 12.906 kΩ (the **Landauer resistance** ($h/2e^2$)) for such a 1D structure.

- 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**.

- *As the number of channels increases, conductance increases and resistance decreases.*

- The classical theory also predicts this behavior, although the quantum theory shows that this happen in discrete steps, as the number of electron channels increases. *As **n** gets very large*, the electron channels essentially form a continuum, and *the quantum theory tends towards the classical limit*.

➢ 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.

➢ 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.

➢ *It yields the surprising conclusion that even ballistic conductors have a resistance*, *although this resistance is independent of the length* of the conductor.

➢ But *a resistance implies that power is dissipated when a current flows*. Given that electron transport in the wire is ballistic, where do the resistive power losses occur?

➢ We can find that carriers entering the wire from the source propagate without change in potential until they reach the drain where they must come to equilibrium at chemical potential. Thus, *the power is dissipated in the drain*.

➢ The quantum limit in conductance arises as a consequence of the interface between the contact with its (ideally) infinite modes and infinite number of electrons all at equilibrium, and a

➢ conductor with a small number of modes supporting non-equilibrium electrons. Thus, the quantum limit can be thought of as a contact resistance. Of course, as the number of modes in the conductor increases, the contact resistance decreases. In the classical limit, it can be completely ignored.
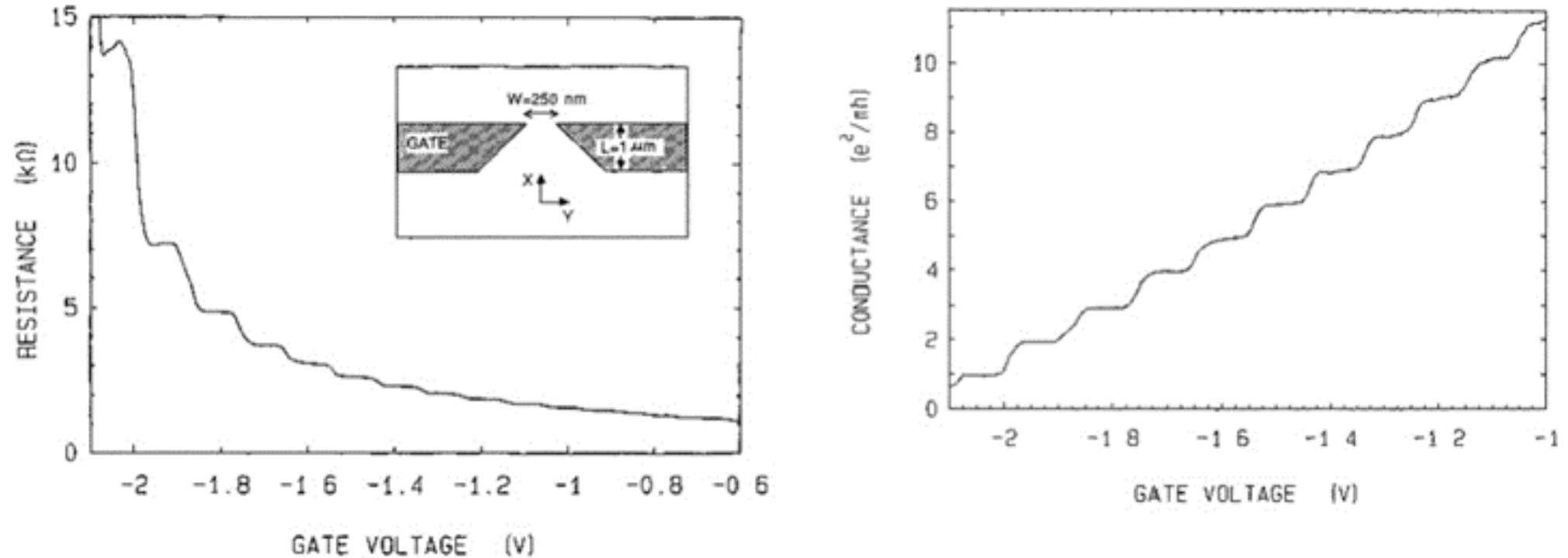

Figure 3: **Left**: Resistance of the point contacts as a function of gate voltage **at 0.6 K**. Inset: Point-contact layout.

Right: Point-contact conductance obtained from resistance after subtraction of the lead resistance. *The conductance shows plateaus at multiples of $2e^2/h$.*
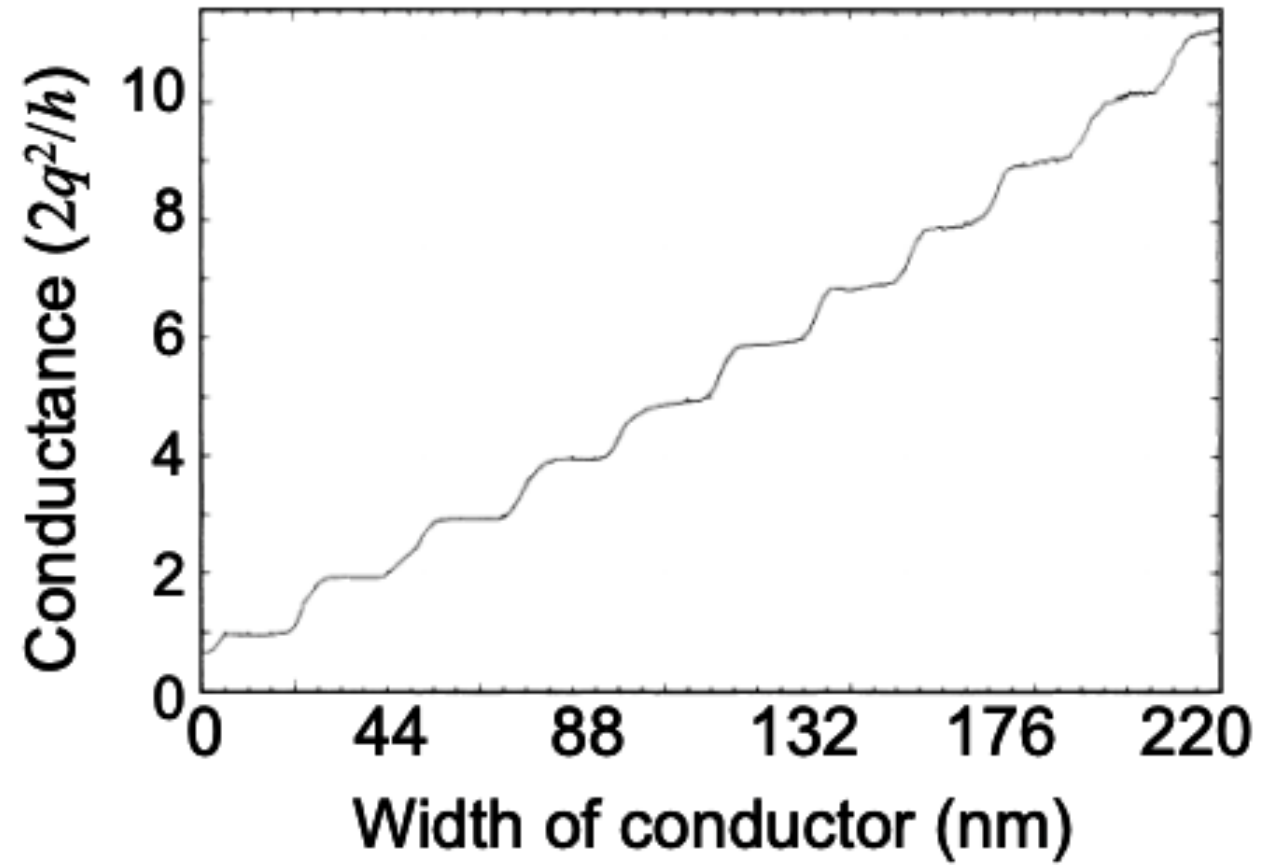
Figure 4.6.2: Experimental data from van Wees, et al PRL 60, 848 (1988) clearly showing conductance in a narrow conductor quantized in steps of 2q2/h.
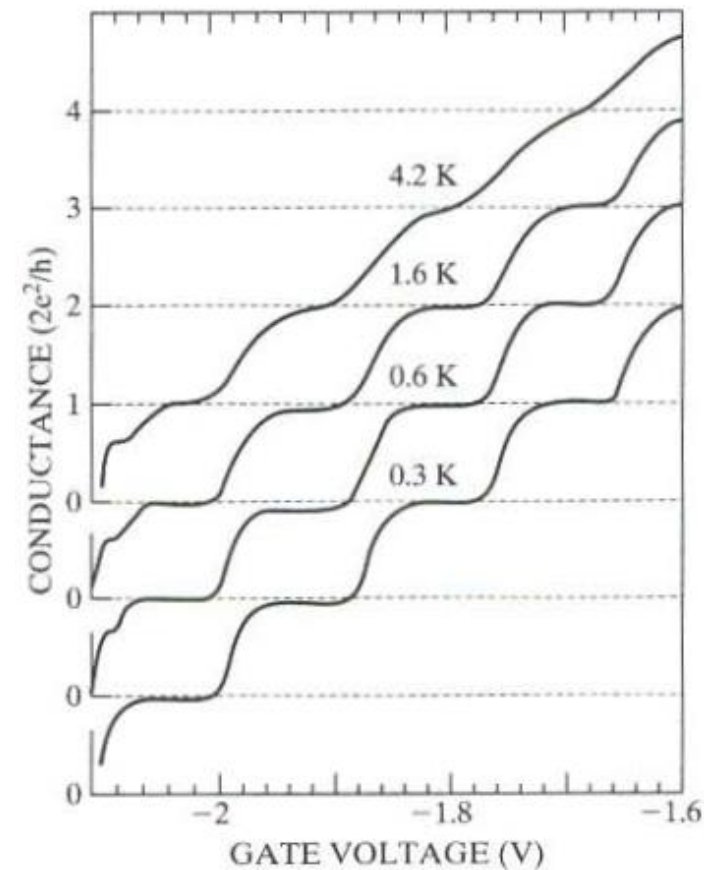
Fig. 6.6 Conductance quantization of a quantum point contact in units of $2e^2/h$. As the gate voltage defining the constriction is made less negative, the width of the point contact increases continuously, but the number of propagating modes at the Fermi level increases stepwise. The resulting conductance 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.)

➢ The **quantization of conductance** is readily **shown in low-temperature experiments** (**for near-zero Kelvin temperatures**). *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 next excited state n_y, n_z = 1, 2 we have, $E_{1,1} = 0.0075$ eV and $E_{1,2} = 0.0188$ eV, such that $\Delta E = 0.0113$ 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 **$\Delta E = 1.13$ 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.

- ***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 on molecular transistors*

➢ **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* double bond (**C = C**). 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:

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

➢ Say, *the design parameters call for this transistor to operate at* *3 GHz clock speed*.

➢ 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 **3·10⁹ electrons must flow per second** at maximum.

Remember the following relations:

- 1A = 1C/1s

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

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

Current flow is measured in amperes and one ampere equates to $6.242 \cdot 10^{18}$ electrons passing a cross-sectional area per second.

- *V=IR*

- *V*=1J/1C

- *R*=1027.3Ω

➢ 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**.

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

➢ 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) $\xi = 8$ 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 ($R_N = 9k\Omega$) 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).
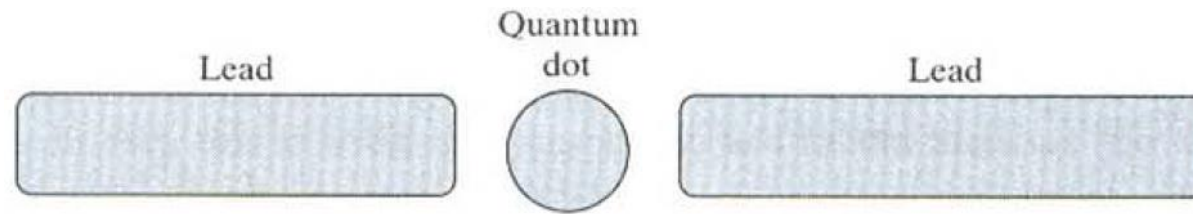

Figure 6.1 Nano-object coupled to external leads.

➤ *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.
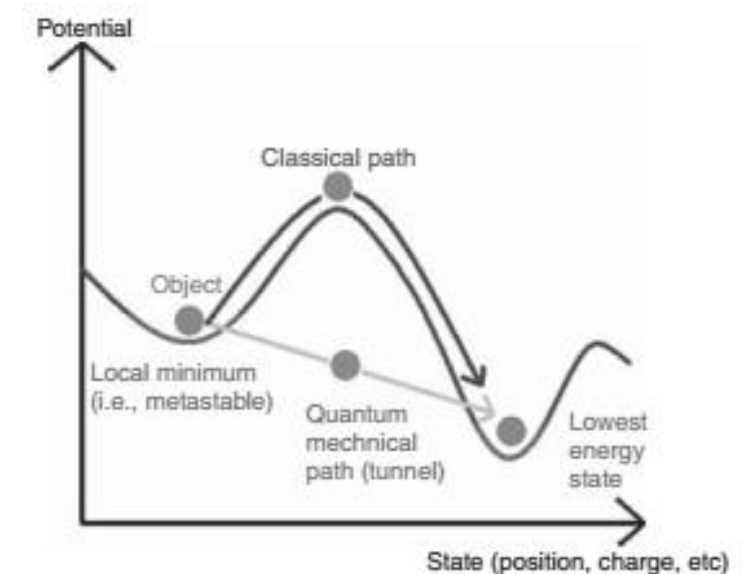

Figure 8.1 Schematic representation of tunneling.

❑ **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 (± Q) on the two plates that is proportional to the voltage: $Q = CV,$ where Q is the charge on the conductors (+Q on one conductor and -Q on the other), C **is the capacitance**, and V **is the d.c. voltage** between the conductors.

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

➤ where $\varepsilon_0 = 8.854 \times 10^{-12}$ 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.

Conductive plates
A
d
Dielectric
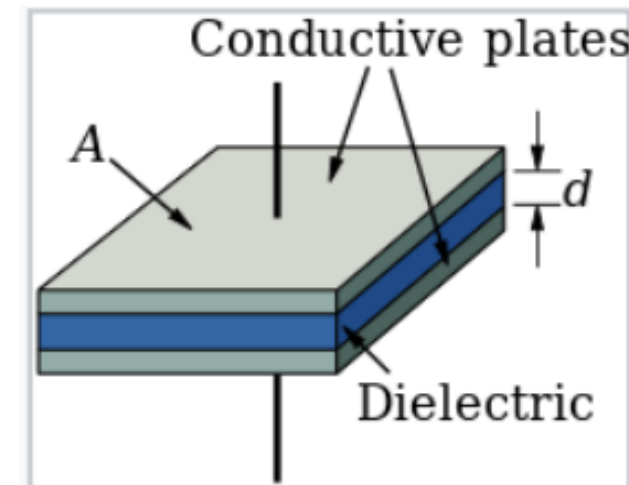
➢ We can also calculate the work done in charging the capacitor up (i.e., the energy stored by charging the capacitor) by integrating the voltage times the charge:

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

➢ 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 (nm^2)	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	$(5 \times 10^6)^2$	2×10^6	1.1×10^{-13}	7.3×10^{-7}
μ capacitor	$(5 \times 10^3)^2$	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 (Charge Quantization): 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*.

➢ A discrete electronic configuration of metal or semiconductor nanocrystals of a few nanometers permits one to pick up the electric charge one electron at a time, at specific voltage values. This ***Coulomb charging or 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 N electrons to the particle is given by the charging energy:

➢ $E_C = \dfrac{N^2 e^2}{2\,C} = E_C N^2$ where e is the electronic charge ($Q = Ne$) and C is the capacitance of the nanoparticle. For a single electron charging: $E_C = \dfrac{e^2}{2\,C}$.

➢ 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: $\boldsymbol{C = (4\pi\varepsilon_0\varepsilon_r)\cdot r}$, where r is the radius of the spherical nanoparticle and ε_0 is the permittivity of vacuum. The notable aspect of this and the above Equations is that *the electrostatic capacitance scales with the size of the conductor*. Consequently, the charging energy of a small conductor can be very large.

➢ For example, the energy Equation predicts that the capacitance of a sphere with a radius of $r = 1$ nm is approximately $C = 10^{-19}$F. The charging energy is then $E_C = 1.6$ eV per charge.

➢ 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

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

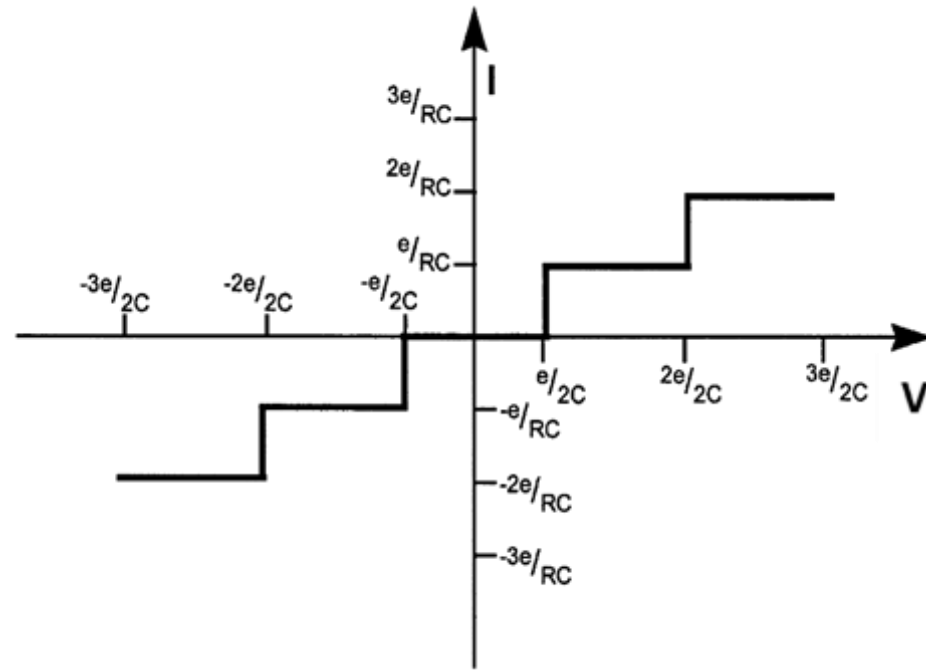➤ If this value is reached, an electron can be transferred.

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*.

➢ **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.**

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

➢ 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.

➢ 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.*

- Suppose we add an extra electron to the island, transferring it from a metal with the same Fermi energy. Since we are charging the island, we have to pay the energy E_C. This energy cost rises if we add more electrons: we must provide $E_C N^2 - E_C(N-1)^2 = E_C(2N-1)$ extra energy to add the N-th electron.
- The same goes for extraction, since we also charge the island, although with positive charge.
- The fact that the addition energy depends on the number of particles added is in contradiction with the paradigm of non-interacting electrons: the charging energy produces an electron–electron interaction. The bigger the island, the bigger the capacitance. Because of this, the charging energy $\propto 1/C$ vanishes in the traditional thermodynamic limit when the energies are counted per particle. However, it presents a finite energy scale for any finite island.
- We see that the charging energy E_C is in fact a classical concept since it is expressed in terms of classical capacitance of the island with no regard for quantum mechanics forming the electron states in there. The charging energy is also an electrostatic part of the addition energy: the energy required to add one extra electron to the neutral island. To see how good the classical description is, let us compare this part with quantum effects. Due to quantum mechanics, the electron levels in the island are discrete; there is a typical energy distance between the electron levels, the mean level spacing δ_S. This also contributes to the addition energy, since the added electron would go to the first unoccupied level separated by δ_S from an occupied one (Fig. 3.1).
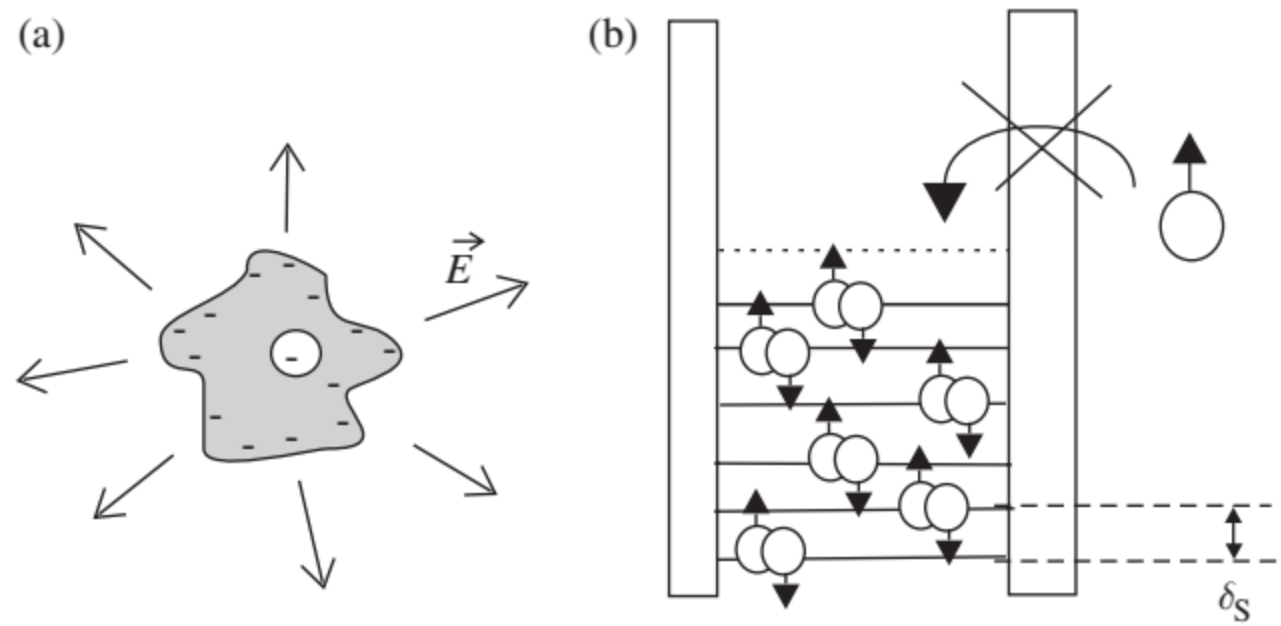
Fig. 3.1. (a) Excess charge in an isolated metallic island produces an electric field outside, thus accumulating charging energy.

(b) The energy cost to put an electron into the island is not just a typical level spacing δ_S: it includes charging energy $E_C \gg \delta_S$.

➢ To get a feeling of the energy scales involved, let us take a cubic island of size L. It consists of $N_{at} \approx (L/a)^3$ atoms, a being the interatomic distance. Typically, there is one valence electron per atom, and these electrons fill up the energy band E_F. The mean level spacing is therefore given by $\delta_S \approx E_F/N_{at}$. From Coulomb's law, we estimate that the charging energy is of the order of e^2/L: the charge e is spread over a typical distance L. The ratio of the two energy scales is estimated as follows:

$$\frac{\delta_S}{E_C} \simeq \frac{E_F L}{e^2 N_{at}} = \frac{E_F a}{e^2} \frac{L}{a N_{at}} \simeq \frac{1}{N_{at}^{2/3}}.$$

➢ Here we make use of the fact that $e^2/a \approx E_F$. The conclusion is that δ_S/E_C is small provided the island consists of many atoms. To illustrate this with numbers, let us take $L = 100$ nm corresponding to $N_{at} = 10^9$, and $e^2/a \approx E_F \approx 10$ eV. We obtain $E_C \approx 1$ mV, $\delta_S \approx 10^{-8}$ eV. So, for practical purposes, $\delta_S \approx 0$, and one may safely disregard all effects related to the discreteness of the electron spectrum. This discreteness only becomes important for nanostructures consisting of several natural atoms, like a molecule, or those comprising an artificial atom, such as a quantum dot in a semiconductor heterostructure. For such nanostructures, $\delta_S/E_C \approx 0.1$–0.5.

➢ We have learned that it costs us some extra energy to add an electron to an isolated island, and to good accuracy ***it is an electrostatic***, ***Coulomb energy***. To transfer electrons to the island, this energy must be supplied either by an external voltage source or by a thermal fluctuation. Otherwise, the electron transport is blocked, and Coulomb blockade takes place.

SINGLE ELECTRON PHENOMENA: Conditions for *Coulomb Blockade (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.

➢ The coulomb blockade should be such that can ***prevent unwanted tunneling***.

➢ If any electron on one side of the barrier could just tunnel across it, there would not be any isolation. The dot would not be a quantum dot because it would still essentially be part of the bulk, so we need to control the addition and subtraction of electrons.

➢ Such single-electron behaviors, e.g. Coulomb oscillations and the Coulomb blockade, are only relevant when ***the thermal energy is lower than the Coulomb energy***. Where this does not apply, thermal flux will interrupt the electron movement and remove the impact of quantization. The required condition can be expressed: $Ec = e^2/2C > k_B T$, where k_B and T indicate Boltzmann's constant and absolute temperature, respectively. Thus, at liquid nitrogen or ambient temperature, it is necessary for the capacitance, C, to be lower than 12 nF or 3 nF, respectively, in order to achieve charging effects.

➢ A second criterion required to appreciate the ***charging effects is that there should be minimal quantum fluctuations in the island population of electrons; the latter needs to be discretely regionalized***. Failure of island electron localisation would prevent the charge effects as the islets would not comprise individual particles, but instead, a single large homogeneous domain. Thus, all tunnel junctions must be sufficiently obscured to restrict the electrons to the islets. A tunnel junction's transparency can be expressed in terms of the resistance of the tunnel, R_T, which has to meet the criteria for discrete charging effect discernment, where h indicates Planck's constant. This should be appreciated as a measure represented by an order of magnitude, rather than a specific threshold. $R_T > h/e^2 = 25813\ \Omega$. Therefore, these effects are experimentally verifiable only for very small high-resistance tunnel junctions, meaning

small particles with small capacitances and/or very low temperatures.

➢ Advanced fabrication techniques, such as the production of granular films with particle sizes down to 1 nm, and deeper physical understanding allow today the study of many charging effects at room temperature.

➢ Based on the Coulomb blockade many interesting devices are possible, such as precise current standard, very sensitive electrometers, logic gates and memories with ultra-low power consumption, down-scalability to atomic dimensions, and high speed of operation. Altogether, single-electronics will bring new and novel devices and is a very promising candidate to partly replace MOS technology in the near future.

i) 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 ***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 << 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 << 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 << 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, 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.

ii) *Minimum Tunnel Resistance for Single Electron Charging*

➢ A tunnel junction is characterized by its conductance (or resistance), so the question is about the resistance of the junction. Let us put an extra electron in the island. We have paid the energy E_C. What is a typical time that it remains there?

➢ As an estimation, we use the Heisenberg energy uncertainty relation.

➢ If the energy gap associated with a single electron is ΔE and the characteristic time for charge fluctuations is Δt, then from the Heisenberg Energy Uncertainty of an electron we can write

➢ $\quad \Delta E \Delta t > h/4\pi$

➢ The related Heisenberg uncertainty of energy ΔE leads to *unexpected tunneling if it exceeds the Coulomb energy*. The Coulomb energy gap associated with a single electron charging for capacitance C is given by $\qquad \Delta E = e^2/2C$

➢ The characteristic time for charge fluctuations can be obtained as follows. With an additional charge, a voltage $V = e/C$ is produced, leading to a tunneling current $I = e/\Delta t$.

➢ Again $I = V/R_T = e/(R_T C)$ (where R_T = tunnel resistance).

➢ Thus, the resulting additional charge on the particle has a mean lifetime $\Delta t = R_T C$.

- Substituting $\Delta E = e^2/2C$ and $\Delta t \approx R_T C$ into the above Heisenberg Energy Uncertainty eqn. one obtains $(e^2/2C)(R_T C) > h/4\pi$ or $(e^2 R_T) > h/2\pi$.

- Thus, it can be estimated that ***the condition for the tunnel resistance:***

$$R_T > h/2\pi e^2$$

- Substituting the values for $h = 6.625 \times 10^{-34}$ Js and $e = 1.6 \times 10^{-19}$ C, we get

- $h/e^2 \approx 25878$ is the resistance.

- In other words, the **tunnel resistance** ≈ 25 kΩ 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.*

- Therefore, the ***junction must be sufficiently resistive***, and **the conductance should not exceed the conductance quantum G_0.**

- 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.

- This high resistance value is like a thick insulating material surrounding the quantum dot.

❏ *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.

❖ *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.

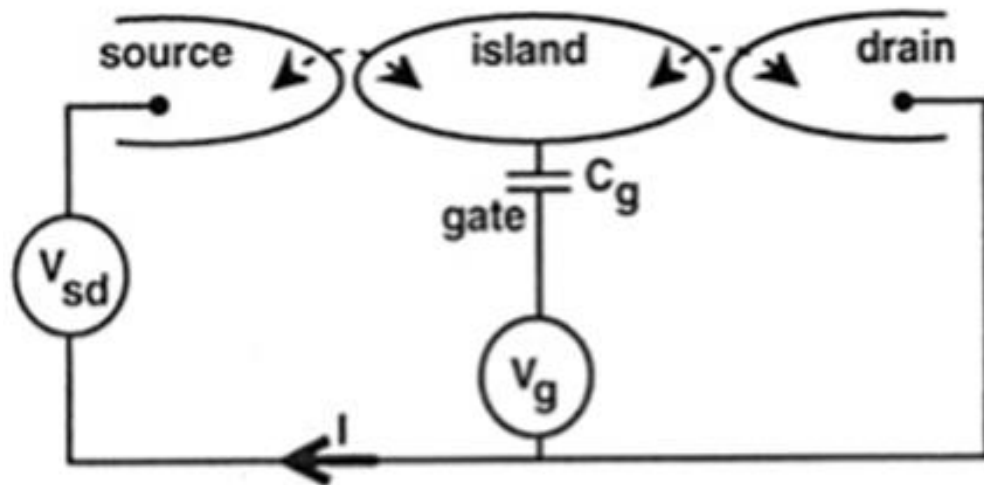➢ The adjoining Figure illustrates the schematic SET device.

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.
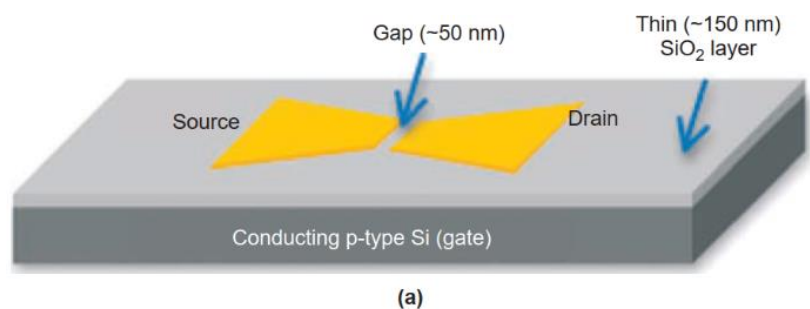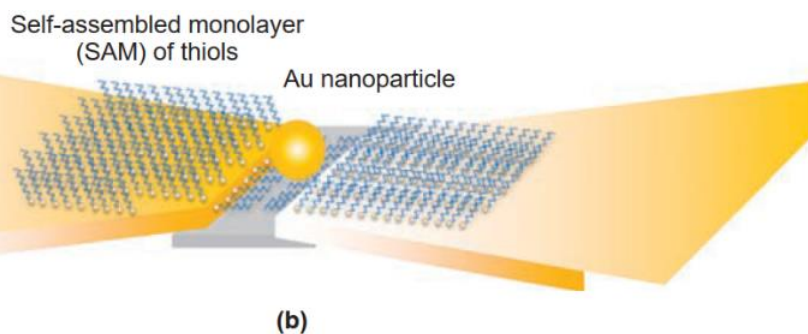

Fig. 5.12 Synthesis of single-nanoparticle SET. Synthesis of SET with the channel consisting of a single Au nanoparticle following the method of Hong et al.

(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 added 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.
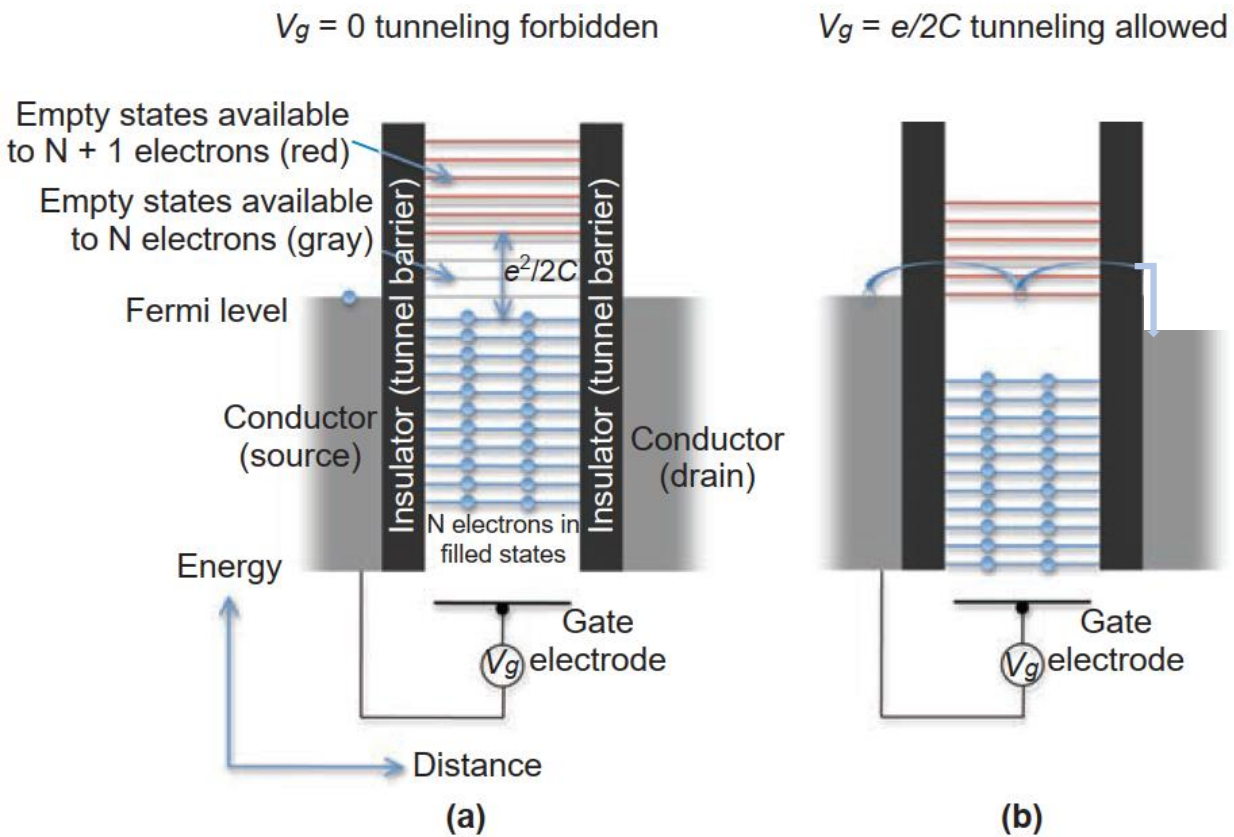
Fig. 5.11 Coulomb Blockade in a nanoparticle FET. (a) Energy level diagram of nanoparticle with discrete states due to the quantum size effect connected to source and drain electrodes via thin insulating tunnel barriers and a gate electrode in close proximity. The highest filled state of the particle 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.
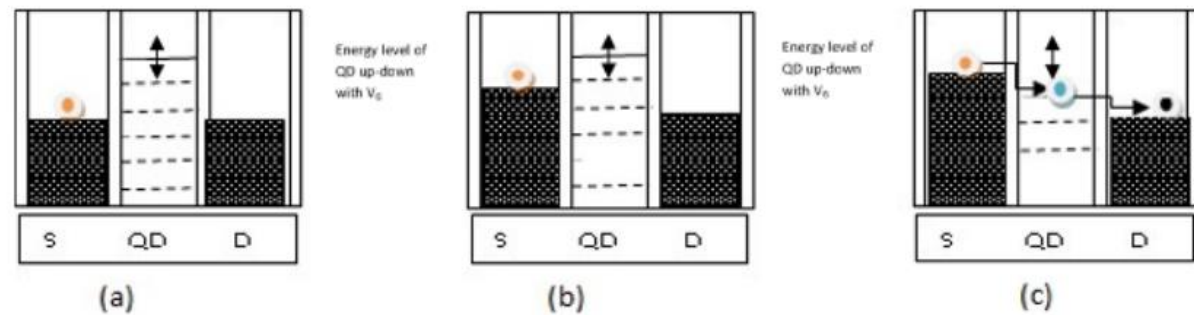
Figure 5.12: (a) No bias (b) with bias, V_{DS} (c) with gate voltage, V_g.
(a) Under no bias condition, no transportation of electron from source to drain and the Fermi levels of both the source and drain will be in the same level.
(b) Now if a bias voltage applied between drain to source (V_{DS}), then the Fermi level of sources, S will go up and of drain, D will go down.
(c) By sweeping the gate voltage (for a fixed V_{DS}), by $\Delta V_g = e/C_g$, tunneling of one electron from source to QD to drain is possible. When electron enters the QD, its Fermi level goes up and by sweeping the gate voltage, the energy levels of QD are brought down below the Fermi level of source region but above the Fermi level in the drain region. Under this condition, electron from source will hop to the QD and from QD to drain.

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).
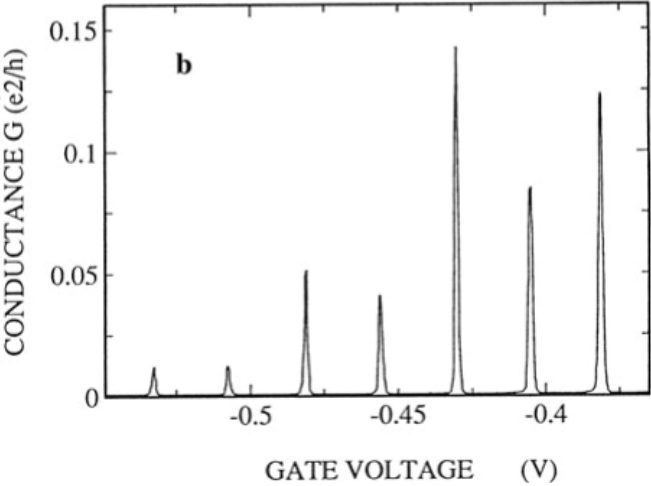

Fig. 1.14 (b) Coulomb oscillations for illustrating the effect of single electronic charges on the macroscopic conductance I/V$_{sd}$. The period in the gate voltage is about e/Cg.

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.
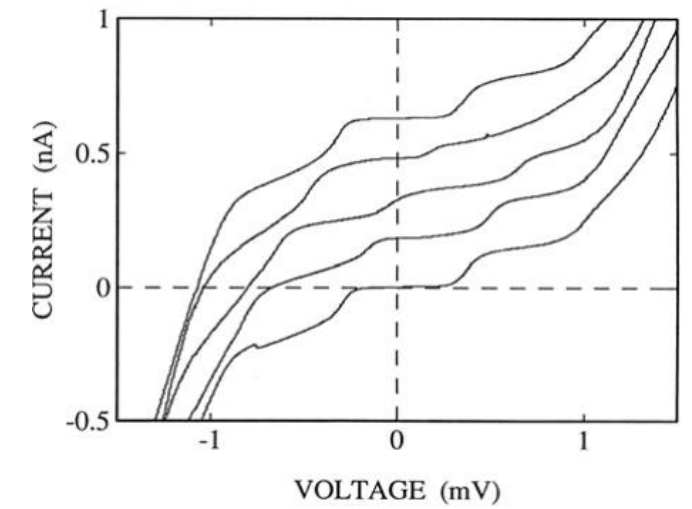

Fig. 1.15 Coulomb staircases in the I−V_{sd} characteristics of a GaAs/AlGaAs heterostructure.

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).

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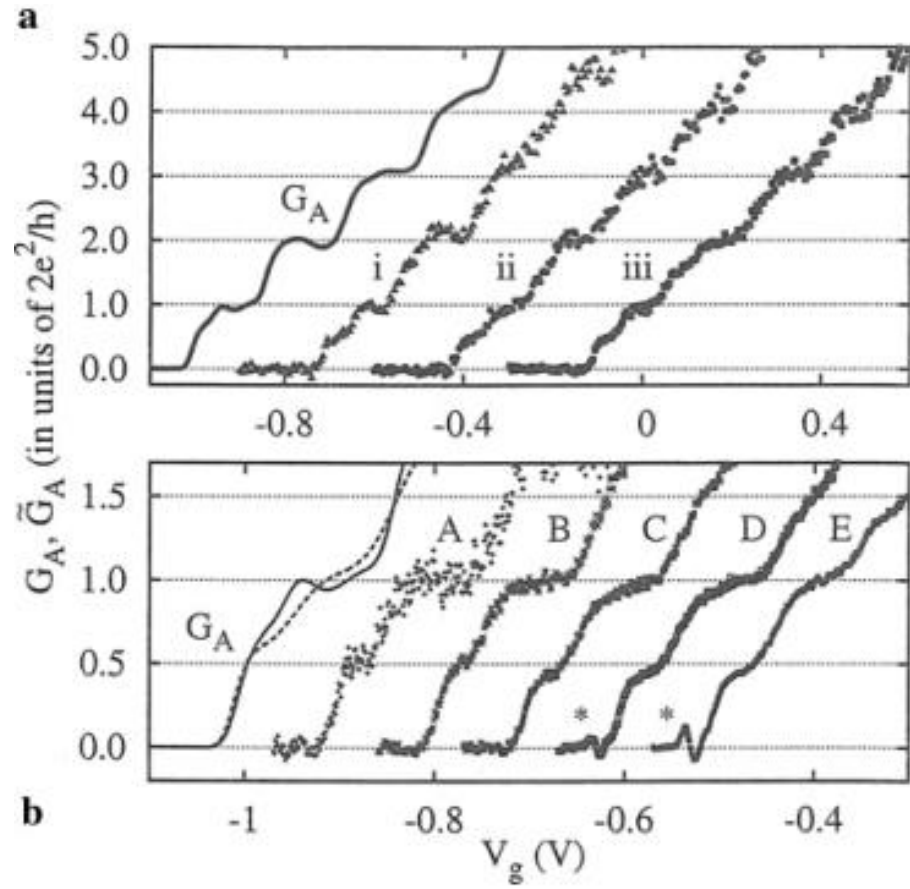
Fig. 1.10 (a) Quantized step-like behavior of the thermal conductance $\tilde{G}_A$(i, ii, iii) and of the electrical conductance G_A of a semiconductor quantum wire at 0.27 K obeying the Wiedemann–Franz relation. (b) Close-up of (a) with a half plateau $\kappa = L_o T(G_o/2)$ for $G < G_o$. (Reprinted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