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UNIT II

Size and dimensionality effects:

Size effects,

Conduction electrons & dimensionality,

Fermi gas & density of states,

Potential wells,

Partial confinement,

Properties dependent on density of states,

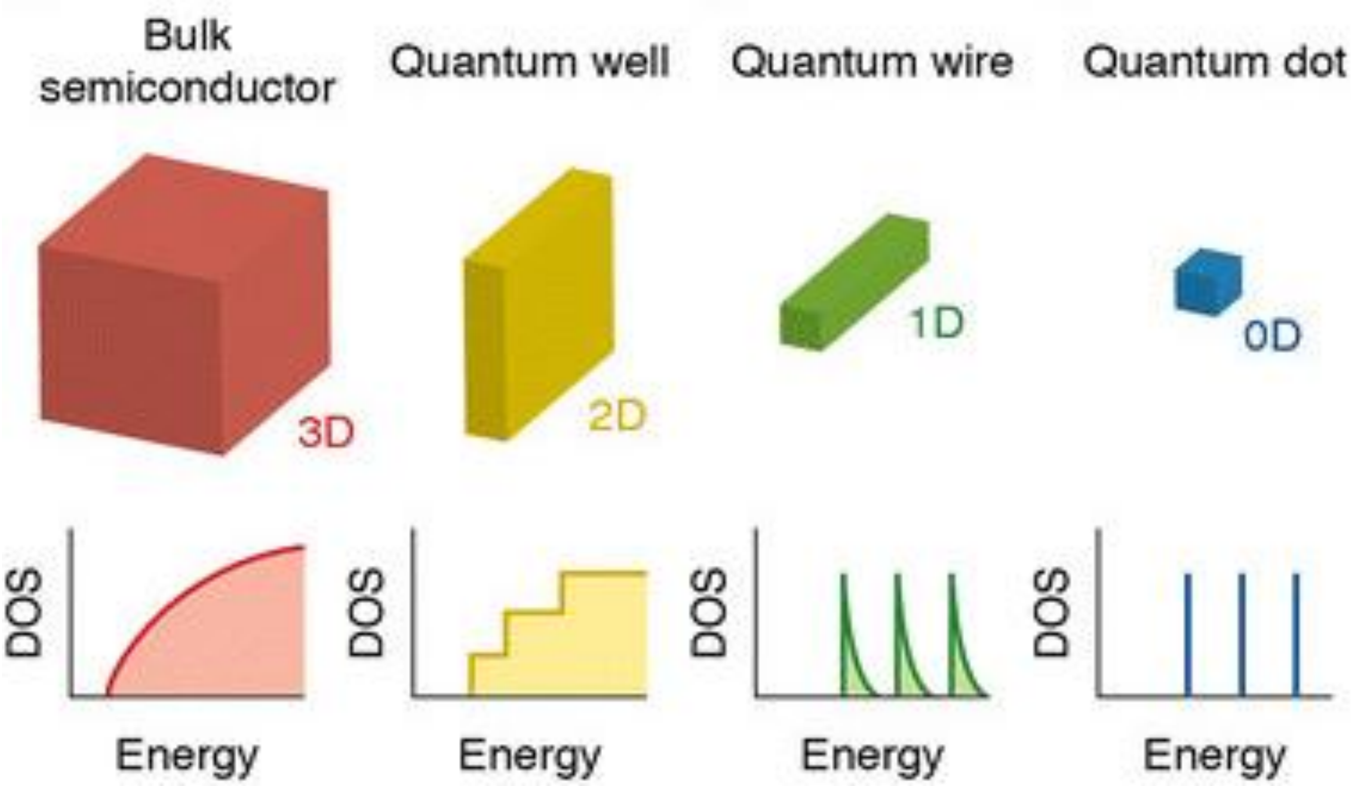
excitons,

single electron tunneling.

Electron statistics in a solid

Density of states

DOS in a 3D uniform solid
DOS for a 2D solid
DOS for a 1D solid
DOS for a 0D solid



Energy Band

band theory of the solid : **N atoms** with **N atomic orbitals**: formed **N molecular orbitals**…… Each **MO can take 2 electrons** (opposite spin) ….total of **2N energy states**. These are **discrete states** but for large values of N the spacing b/w … so small ….. considered to be continuous, forming an **energy band**

Density of states (DOS) -

the number of available energy states per unit energy per unit volume

Or

No's of different states at a particular energy level that e-s are allowed to occupies

units are $J^{-1}m^{-3}$ or $eV^{-1}cm^{-3}$ It is typically denoted as ***g(E)***

Provides information on how energy states are distributed in a given solid or how close together the energy levels are to each other

Experimental DOS a material can be measured by PES photo electron spectroscopy or Scanning Tunneling Microscopy (STM) or Electron Energy Loss spectroscopy (EELS). These techniques probe the density of empty or filled states around the Fermi energy, called Local DOS (LDOS). Density functional calculations can also be used to calculate the density of states.

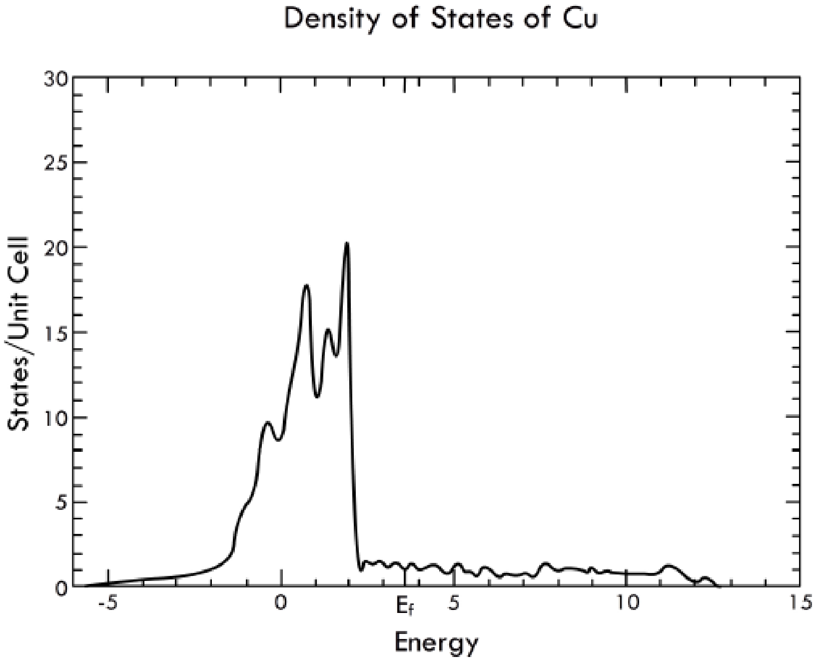


Figure 1: Calculated DOS of Cu around the Fermi level. The filled states lie below E_F while the empty states lie above E_F. The broad peak below E_F corresponds to the filled $3d$ states. Adapted from *http://www.personal.psu.edu/ams751/VASP-Cu/*

The density of states has a functional dependence on energy.

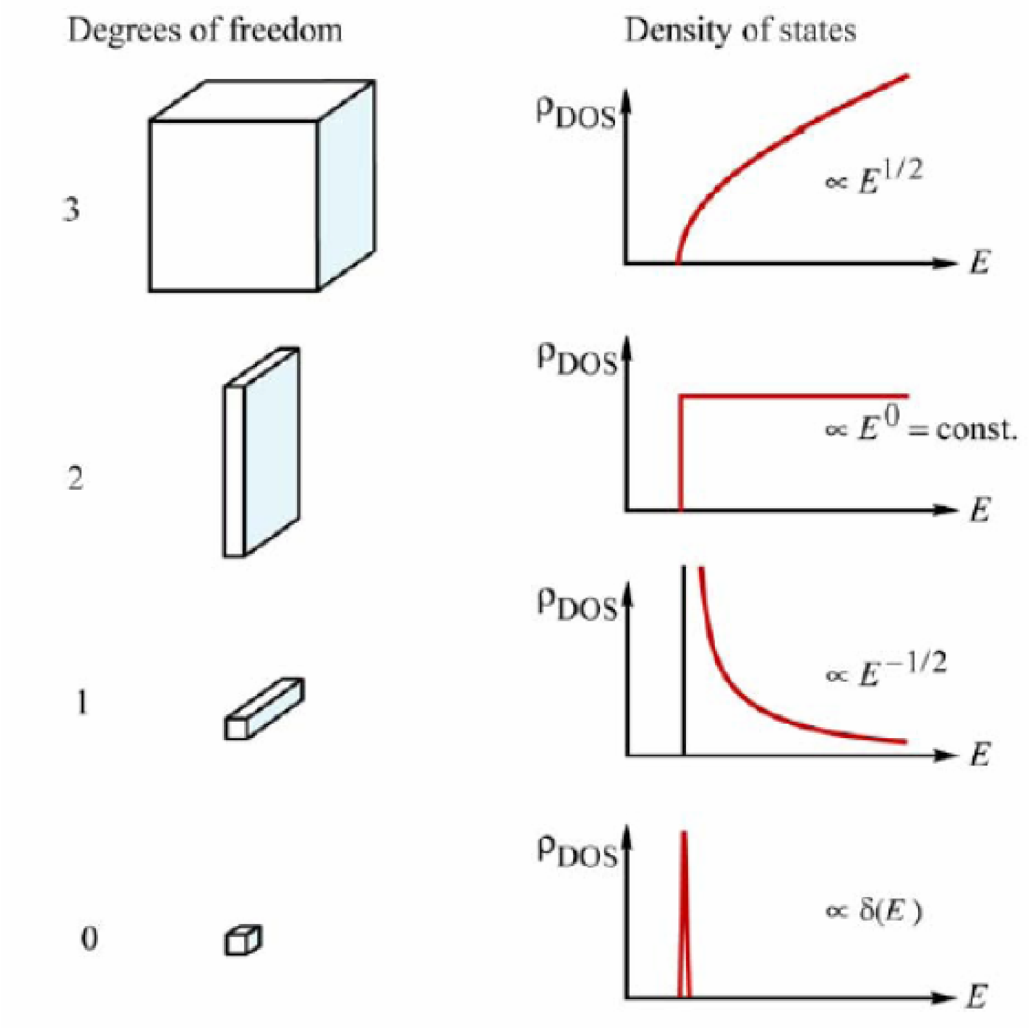
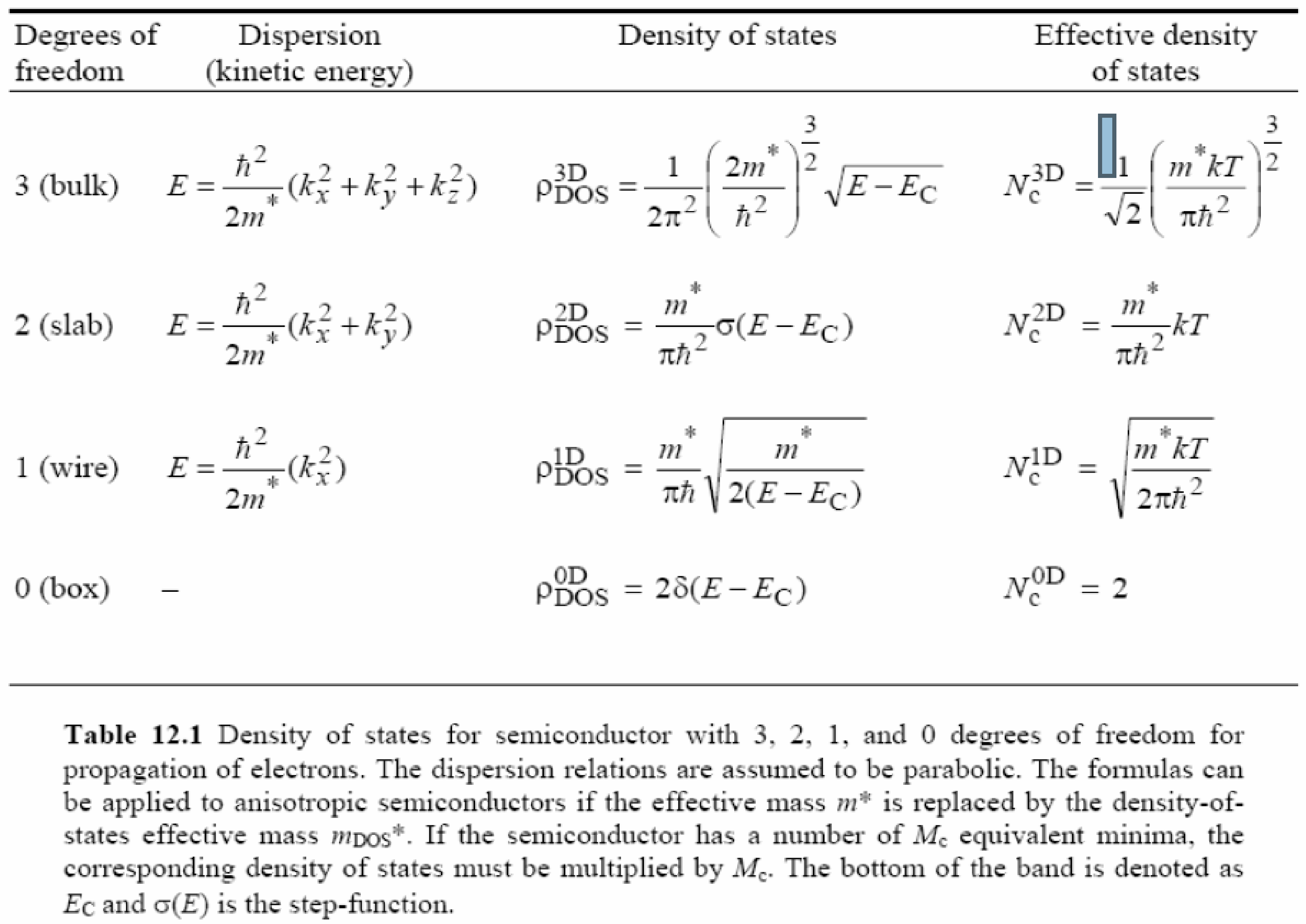


Fig. 12.7. Electronic density of states of semiconductors with 3, 2, 1, and 0 degrees of freedom for electron propagation. Systems with 2, 1, and 0 degrees of freedom are referred to as quantum wells, quantum wires, and quantum boxes, respectively.



Degrees of freedom	Dispersion (kinetic energy)	Density of states	Effective density of states
3 (bulk)	$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2 + k_z^2)$	$\rho_{\mathrm{DOS}}^{\mathrm{3D}} = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{E - E_C}$	$N_c^{\mathrm{3D}} = \frac{1}{\sqrt{2}}\left(\frac{m^* kT}{\pi\hbar^2}\right)^{\frac{3}{2}}$
2 (slab)	$E = \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2)$	$\rho_{\mathrm{DOS}}^{\mathrm{2D}} = \frac{m^*}{\pi\hbar^2}\sigma(E - E_C)$	$N_c^{\mathrm{2D}} = \frac{m^*}{\pi\hbar^2}kT$
1 (wire)	$E = \frac{\hbar^2}{2m^*}(k_x^2)$	$\rho_{\mathrm{DOS}}^{\mathrm{1D}} = \frac{m^*}{\pi\hbar}\sqrt{\frac{m^*}{2(E - E_C)}}$	$N_c^{\mathrm{1D}} = \sqrt{\frac{m^* kT}{2\pi\hbar^2}}$
0 (box)	–	$\rho_{\mathrm{DOS}}^{\mathrm{0D}} = 2\delta(E - E_C)$	$N_c^{\mathrm{0D}} = 2$

Table 12.1 Density of states for semiconductor with 3, 2, 1, and 0 degrees of freedom for propagation of electrons. The dispersion relations are assumed to be parabolic. The formulas can be applied to anisotropic semiconductors if the effective mass m^* is replaced by the density-of-states effective mass m_{DOS}^*. If the semiconductor has a number of M_c equivalent minima, the corresponding density of states must be multiplied by M_c. The bottom of the band is denoted as E_C and $\sigma(E)$ is the step-function.

Conduction Electrons & Dimensionality

we will discuss- delocalization aspects of conduction electrons in a bulk metal – electrons referred to as ***free electrons,***
but perhaps ***unconfined electrons would be a better word for them***

Familiar with electronic systems - exist in 3-D & are large or macro in size

In this case **conduction e-** delocalized & move freely throughout entire conducting medium- **Cu-wire**.

wire dimensions are very large compared to distances between atoms

Situation changes when **one or more dimensions** of **Cu- becomes** so small that it approaches several times the spacings b/w atoms in lattice. When this occurs, **delocalization is impeded** & electrons experience confinement.

e.g, consider a flat plate of **Cu**-10x10 cm^2 & 3.6 nm thick.

This thickness corresponds to length of only 10 unit cells, which means that 20% of the atoms are in unit cells at Cu-surface

conduction e- would be delocalized in plane of plate, but confined in narrow dimension (thickness), a configuration referred to as a ***quantum well.***

A quantum wire *is a structure such as a Cu- wire:* ***e- long in*** one dimension, but has a nanometer size as its diameter.

electrons are delocalized & move freely along wire, but are confined in transverse directions

Finally, a ***quantum dot,***

which might have shape of a tiny cube, a short cylinder, or a sphere with low nanometer dimensions,

exhibits confinement in all three spatial dimensions, so there is **no delocalization**

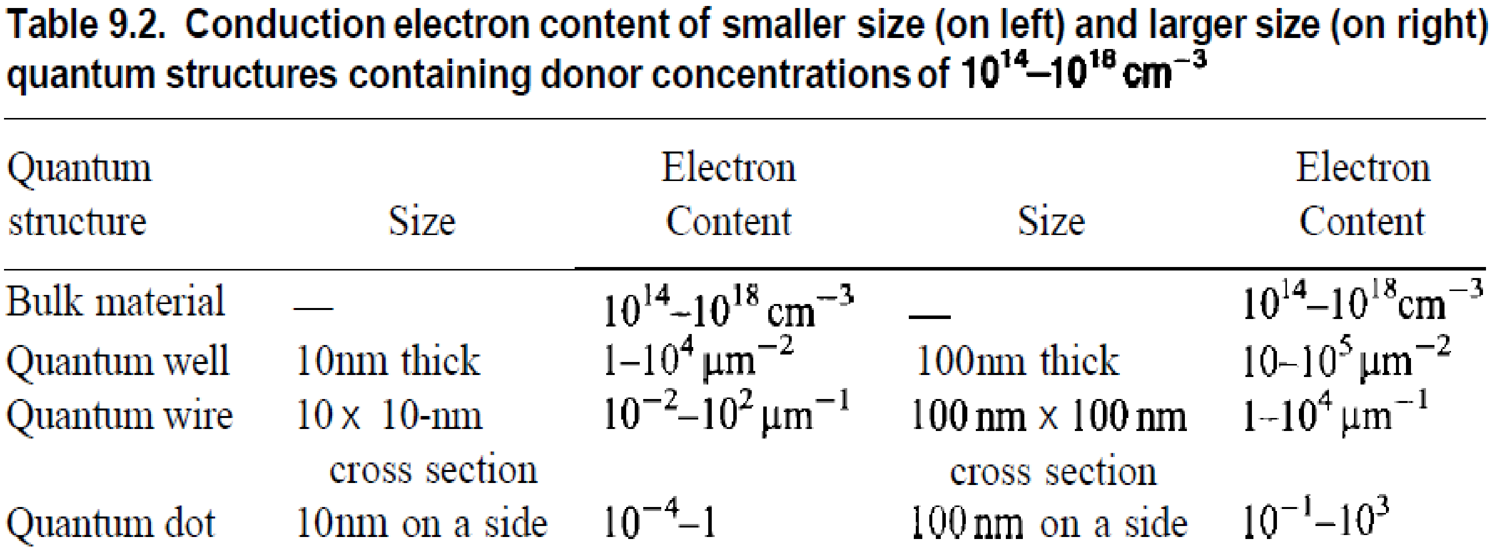
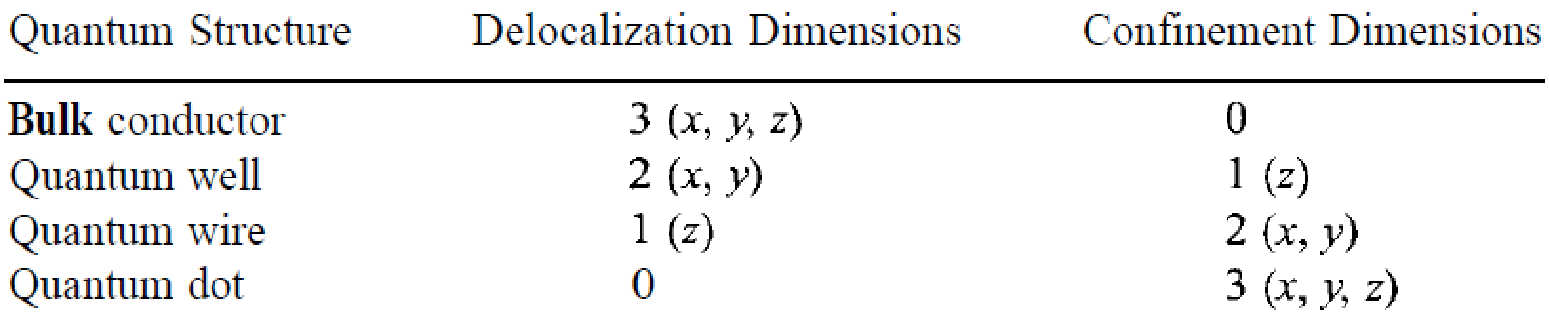
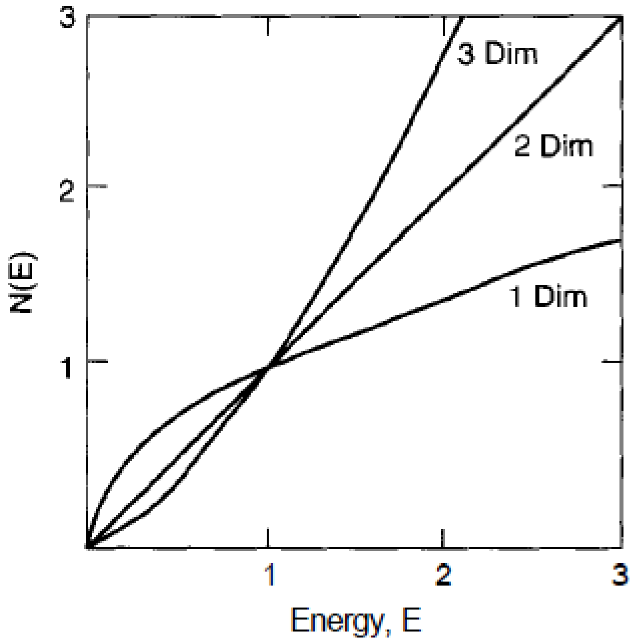


Table 9.2. Conduction electron content of smaller size (on left) and larger size (on right) quantum structures containing donor concentrations of 10^{14}–10^{18} cm^{-3}

Quantum structure	Size	Electron Content	Size	Electron Content
Bulk material	—	10^{14}–10^{18} cm^{-3}	—	10^{14}–10^{18}cm^{-3}
Quantum well	10nm thick	1–10^{4} µm^{-2}	100nm thick	10–10^{5} µm^{-2}
Quantum wire	10 x 10-nm cross section	10^{-2}–10^{2} µm^{-1}	100 nm x 100 nm cross section	1–10^{4} µm^{-1}
Quantum dot	10nm on a side	10^{-4}–1	100 nm on a side	10^{-1}–10^{3}

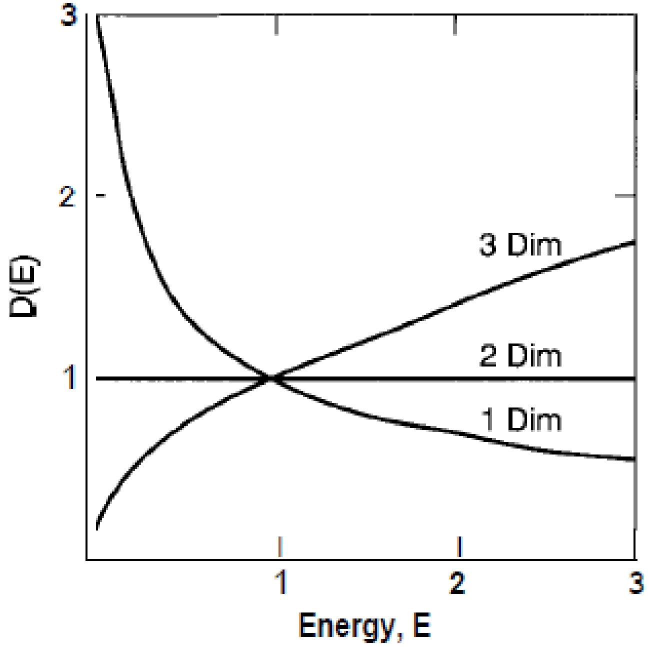


Quantum Structure	Delocalization Dimensions	Confinement Dimensions
Bulk conductor	3 (x, y, z)	0
Quantum well	2 (x, y)	1 (z)
Quantum wire	1 (z)	2 (x, y)
Quantum dot	0	3 (x, y, z)



No’s e-s *N(E) plotted as a function of* ***E for conduction* e-s** delocalized in one (quantum wire), two (quantum well), and three dimensions (bulk material).

DOS; *D(E) = dN(E)/dE* *plotted as a function of E for* **conduction** e-s delocalized in one (Q-wire), *two (Q-well), and three (bulk) dimensions*



Fermi Gas and Density of States

In classical-mechanical description :

Many Properties of good conductors of electricity are explained – **basis** - assumption that valence **e-s** of metal dissociate themselves from their atoms & become delocalized conduction e-s that move freely through background of positive ions such as Na^+ or Ag^+ .

On average they travel a mean free path distance ***&*** act like a gas called a ***Fermi gas in their ability to move with very little*** hindrance throughout the metal.

They have an energy of motion called ***kinetic energy,*** $E = 1/2mv^2 = p^2/2m$
This model - good explanation of Ohm's law, $V = IR$.

In quantum-mechanical description:

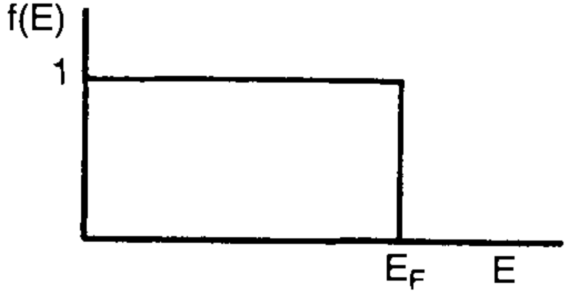
component of electron's momentum $p, = \hbar k_x$
$k_x\, k_y\, k_z$ *values of various e- form a lattice in k space, -* ***reciprocal space.***

At temperature of absolute zero, e-s of Fermi gas occupy all lattice points in reciprocal space out to a distance $\boldsymbol{k_F}$ *from origin k = 0, corresponding to a value of energy –*

called Fermi energy $$E_F = \frac{\hbar^2 k_F^2}{2m}$$

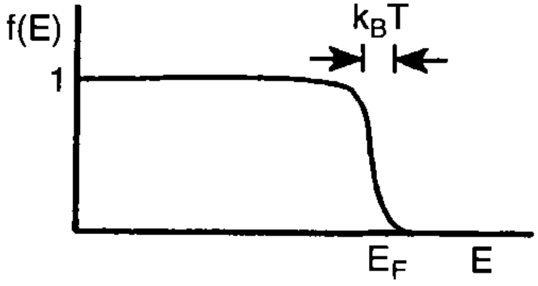
We assume that sample - a cube - side L, & volume V= L^3
Distance b/w two adjacent electrons in ***k space is 2π/L,***

& **at Absolute zero** – all conduction e-s equally spread out Inside sphere of radius k_F & volume $4/3\pi k^3$ in k-space



(a)

This equal density is plotted (fig a) for absolute zero and
we see that deviations from equal density occur near Fermi energy *level at higher temperatures*



(b)

no's of conduction e-s with a particular energy depends **on value of energy**
& also **on dimensionality of space**

This is becuz in 1D- size of Fermi region has length 2k$_F$,
In 2D -area of Fermi circle πk^2, &
3D-volume of Fermi sphere 4πk^3/3.

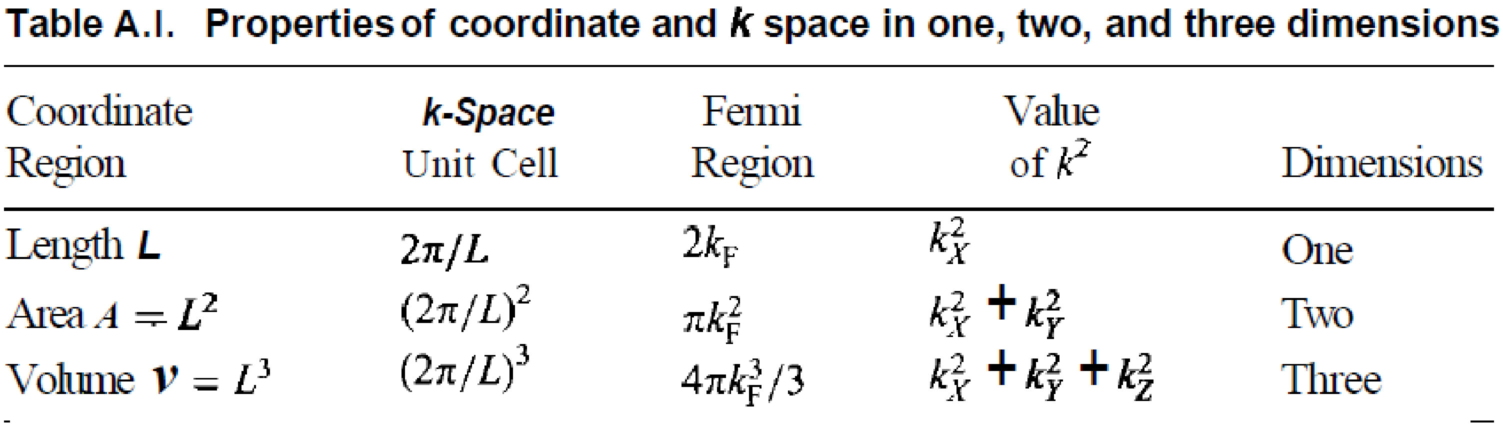


Table A.I. Properties of coordinate and *k* space in one, two, and three dimensions

Coordinate Region	*k*-Space Unit Cell	Fermi Region	Value of k^2	Dimensions
Length L	$2\pi/L$	$2k_F$	k_X^2	One
Area $A = L^2$	$(2\pi/L)^2$	πk_F^2	$k_X^2 + k_Y^2$	Two
Volume $V = L^3$	$(2\pi/L)^3$	$4\pi k_F^3/3$	$k_X^2 + k_Y^2 + k_Z^2$	Three

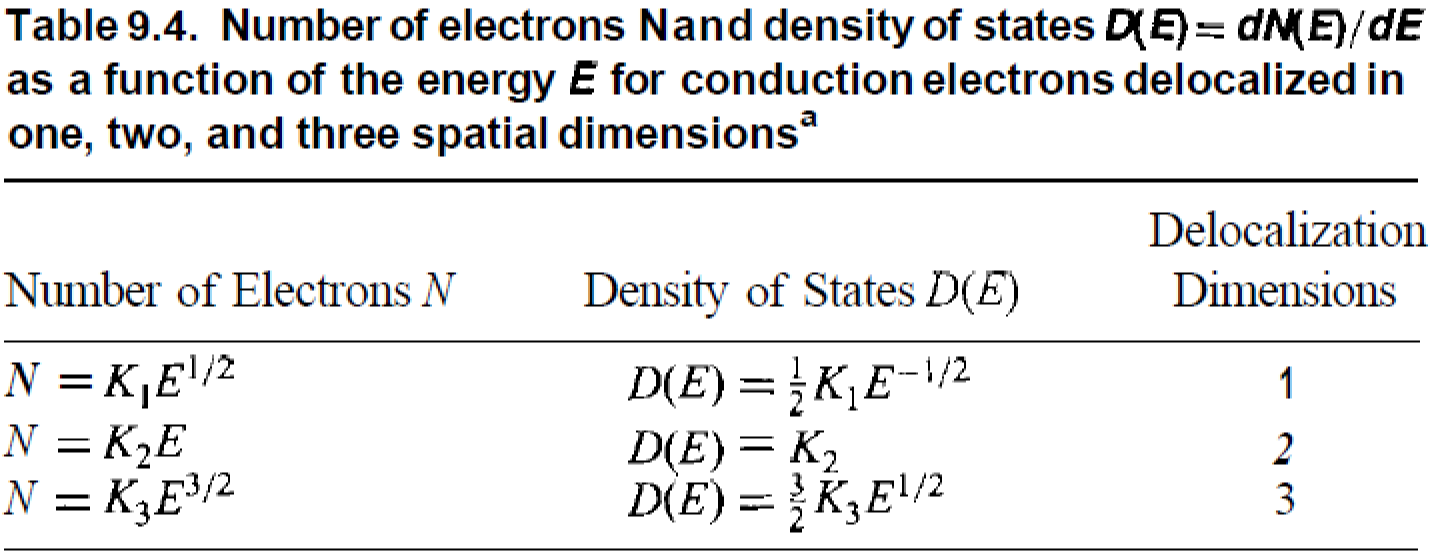


Table 9.4. Number of electrons N and density of states $D(E) = dN(E)/dE$ as a function of the energy *E* for conduction electrons delocalized in one, two, and three spatial dimensions[a]

Number of Electrons N	Density of States $D(E)$	Delocalization Dimensions
$N = K_1E^{1/2}$	$D(E) = \frac{1}{2}K_1E^{-1/2}$	1
$N = K_2E$	$D(E) = K_2$	2
$N = K_3E^{3/2}$	$D(E) = \frac{3}{2}K_3E^{1/2}$	3

Potential Wells

discussed- delocalization aspects of conduction electrons in a bulk metal – electrons referred to as ***free electrons,***
but perhaps ***unconfined e- would be a better word for them***

This is because when size of a conductor diminishes to **nano-region, experience effects of confinement**, i.e motion limited by physical size of region or domain in which they move.

electrostatic forces becomes more pronounced & e-s –restricted by a potential barrier that must be overcome before they can move more freely.

More explicitly, e-s become **sequestered** in a *potential well*- enclosed region of -ve energies.

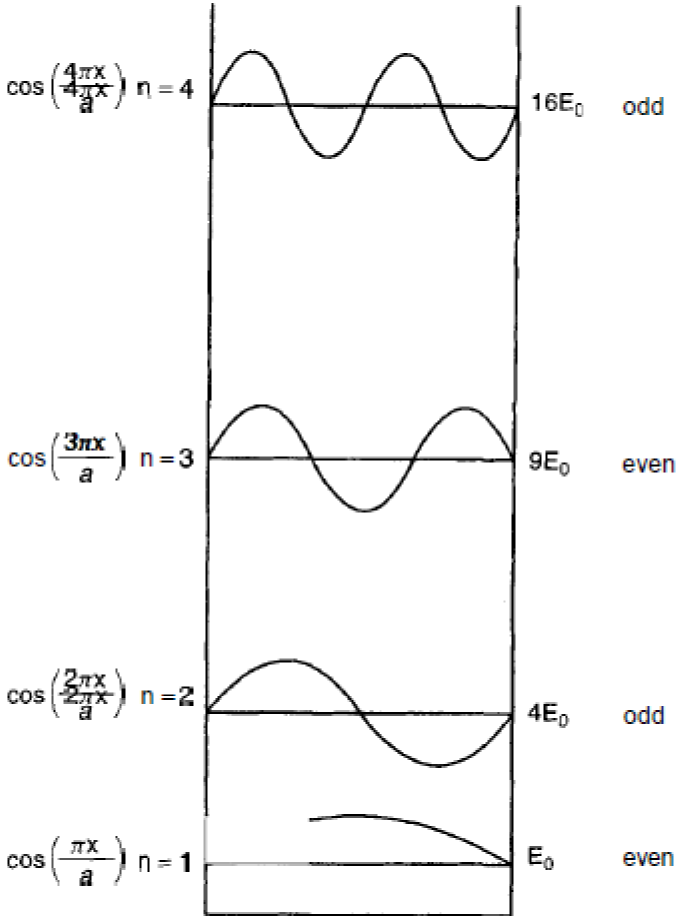
A simple model that exhibits principal characteristics of such a potential well - exist in 1,2,3 & higher dimensions for simplicity, **describe a 1-D case**:

Standard quantum-mechanical- infinitely deep square potential well in 1D **range** $-\frac{1}{2}a \le x \le \frac{1}{2}a$

and energies $$E_n = \left[\frac{\pi^2\hbar^2}{2ma^2}\right]n^2 = E_0 n^2$$

where $E_0 = \pi^2\hbar^2/2ma^2$ is the ground-state energy

quantum number *n assumes = 1,2,3, ...*



Sketch of wavefunctions for four lowest energy levels *(n = 1-4) of 1D* infinite square well.

For each level form of **wave-function** is given ***On*** left,

and its parity (even or odd) **is on the right**

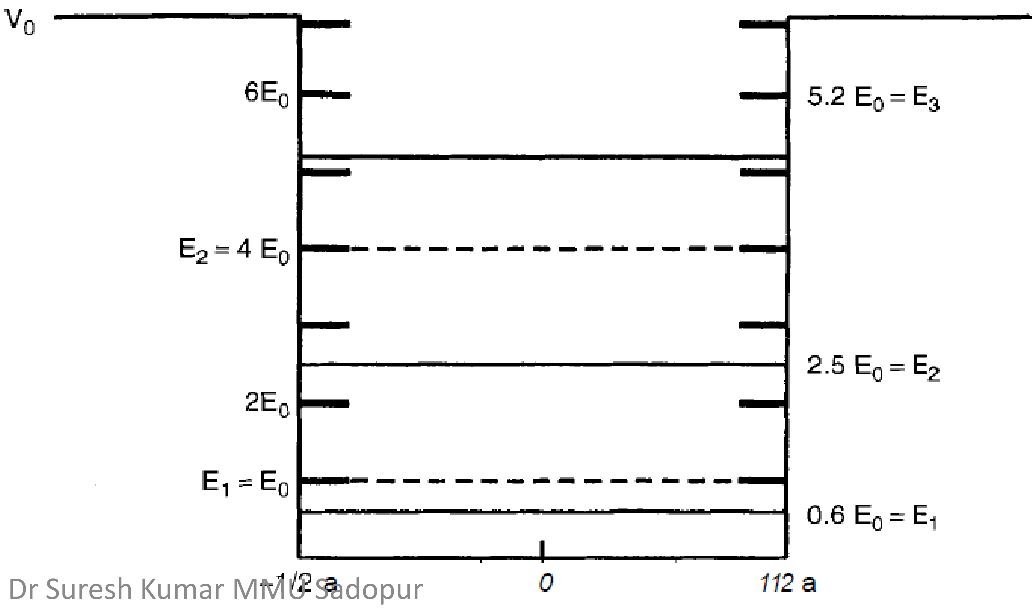
e-s that are present fill-up energy levels starting from bottom, until **all available** e-s are in place

An infinite square well *has infinite number of energy levels,* with ***ever-widening spacings*** *as QN (**n**) increases.*

If well is finite*, then its quantized energies E_n all lie below corresponding infinite well energies & there are only a limited number of them*

Fig. illustrates the case for a finite well of potential depth $V_o = 7E_0$ *which has only 3-allowed energies. No* matter how shallow the well, there is always at least one bound state E_n.

Sketch of a 1D-square well showing how the energy levels E_n *of a* **finite well** (RHS, solid horizontal lines) lie below their **infinite well** counterparts (LHS, dashed lines)



e-s confined to PW move back & forth along direction ***x,***

Probability of finding an e- at a particular value of x = $|\psi_n(x)|^2$ *for the* ***particular level n*** *where* electron is located.

There are even & odd wave-functions *that alternate for the* levels in 1D-square well, & for infinite square well we have un-normalized

$$\psi_n = \cos(n\pi x/a) \qquad \mathrm{n} = 1, 3, 5, \ldots \qquad \text{even parity}$$
$$\psi_n = \sin(n\pi x/a) \qquad \mathrm{n} = 2, 4, 6, \ldots \qquad \text{odd parity}$$

The property called ***parity is defined as even when*** $\psi_n(-x) = \psi_n(x)$,
& odd when $\psi_n(-x) = -\psi_n(x)$.

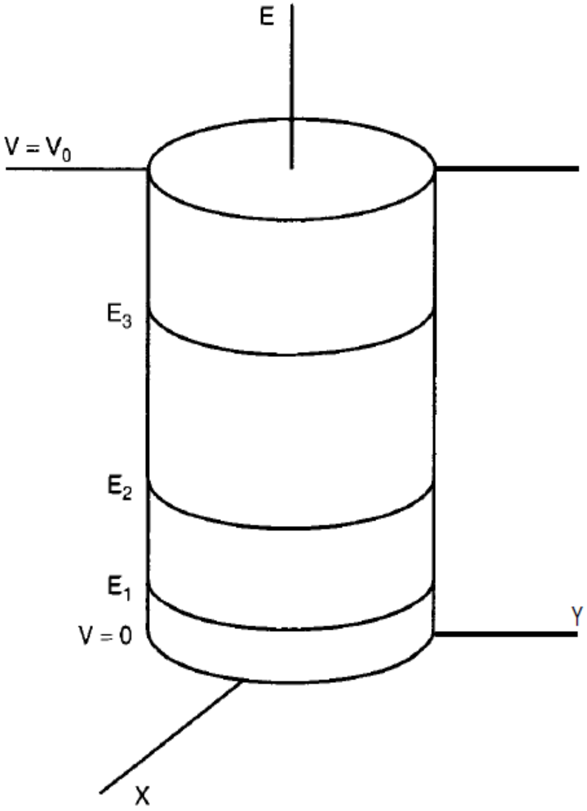
variety of Potential Well:

Square Well, Circular well, Parabolic Well

PW one with a curved cross section of radius ***a in 2-D***

potential is ***V = 0*** *in range* $0 \leq \mathbf{p} \leq a$ *&*
value $V=\mathbf{V_o}$ *at top & outside, where*
$p = (x^2+y^2)^{1/2}$ *&* $\tan \vartheta = y/x$ *in polar coordinates*

Particular finite well sketched in Fig. has only 3-allowed energy levels with values ***E_1, E_2, & E_3.***



There is also a ***3D*** *analog of circular well in which* $V = 0$ for radial coordinate ***in range*** $0 \leq \mathbf{r} \leq a$***,*** *&* *has value* $V = \mathbf{V_o}$ ***outside****, where* $\mathbf{r} = (x^2+y^2+z^2)^{1/2}$

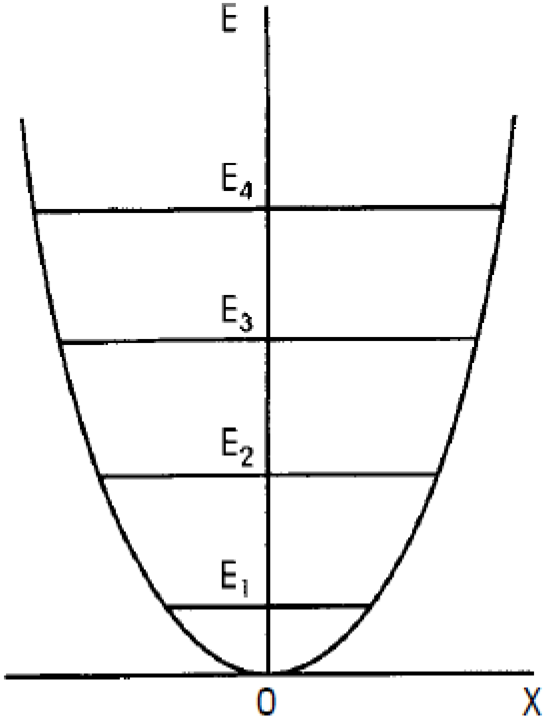
Another type of commonly used PW well is ***parabolic well, which is characterized by V(x) = 1/2kx^2, V(p) = 1/2kp^2, V(r) = 1/2kr^2 in 1,2,3-D***

Another characteristic of a **particular energy state *E***, *is*
No's of e-s that can occupy it,
&
this depends on no's of different combinations of
QN's that correspond to this state.

$$E_n = \left[\frac{\pi^2\hbar^2}{2ma^2}\right]n^2 = E_0 n^2$$

e.g 1D square well has only 1-allowed value of QN (***n)*** for each energy state.

Fig. provides a sketch of potential in 1D-case



Sketch of 1D-parabolic PW showing positions of 4-lowest energy levels

An electron also has a spin QN (***m_s***) two values, ***m_s* = +1/2** *&* ***-1/2*** *for spin states* ***up & down****,*
and **for square well** both spin states ***m_s* = ±1/2** *have* ***same*** **energy**.

a/2 P**auli exclusion principle**, no 2-electrons can have same set of QN's so each square well energy state *E_n can be occupied by 2-electrons, one with spin up & one with spin down.*

No's of combinations of QN's corresponding to each spin state is called its ***degeneracy***

& ***degeneracy of all 2-D square well*** **energy levels** is ***2.***

Energy of a 2D infinite rectangular square well $$E, = \left(\frac{\pi^2\hbar^2}{2ma^2}\right)(n_x^2 + n_y^2) = E_0 n^2$$

depends on two quantum numbers, $n, = 0, 1, 2, 3, \ldots$ and $n_y = 0, 1, 2, 3, \ldots$, where $n^2 = n_x^2 + n_y^2$. This means that the lowest energy state $E_1 = E_0$ has two possibilities, namely, $n_x = 0, n_y = 1$, and $n_x = 1, n_y = 0$, so the total degeneracy (including spin direction) is 4. The energy state $E, = 25E_0$ has more possibilities since it can have, for example, $n, = 0, n_y = 5$, or $n, = 3$ and $n_y = 4$, and so on, so its degeneracy is 8.

Partial Confinement

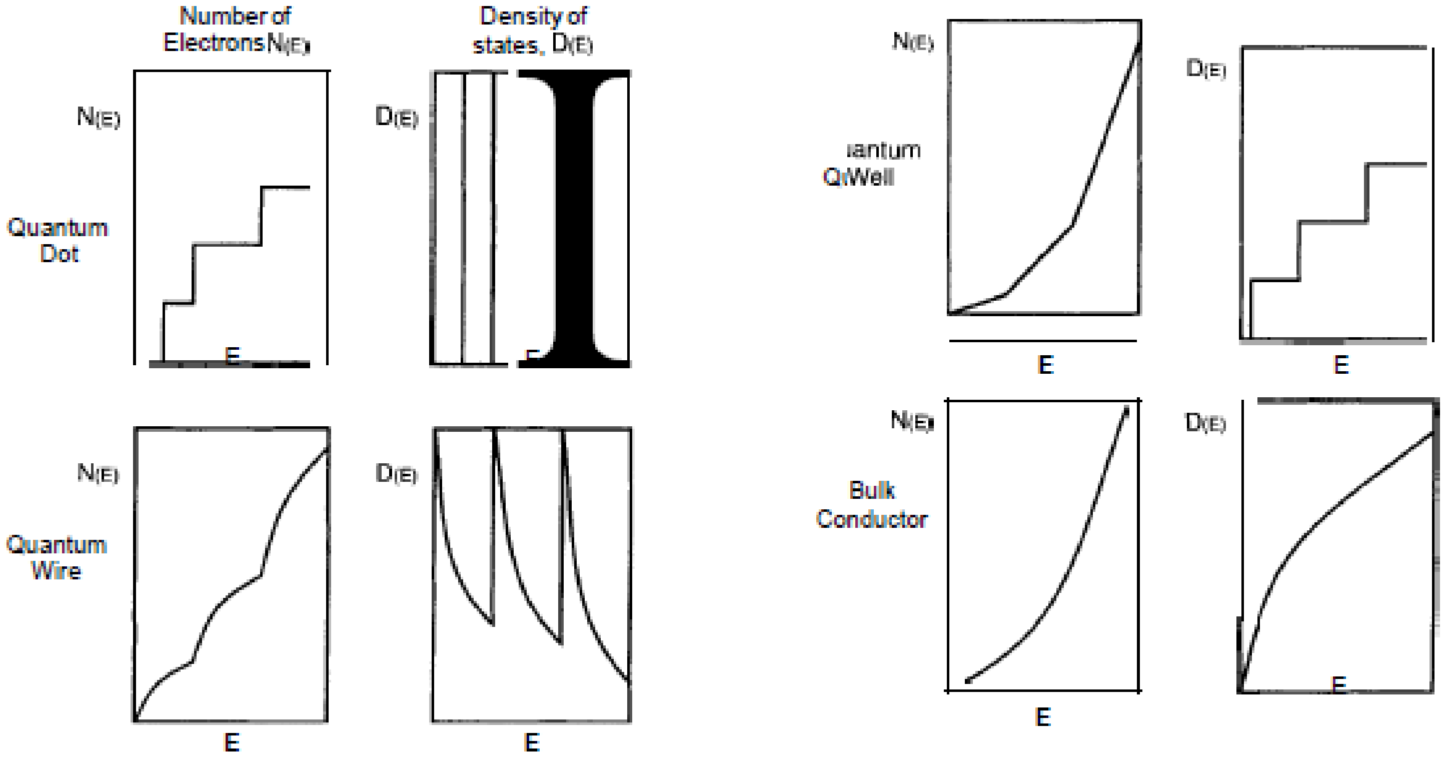
In previous section - **confinement of e-s in various dimensions** & found that it always leads to a qualitatively **similar spectrum of discrete energies.** This is true for a broad class of potential wells, irrespective of their dimensionality and shape

Also, **Fermi gas model for delocalized e-s** in these same dimensions & found that the model leads to energies & DOS that differ quite significantly from each other.
This means - many electronic & other ***properties*** of metals & semiconductors ***change dramatically when dimensionality changes***.

Some nanostructures of technological interest exhibit both potential well confinement & Fermi gas delocalization, confinement in one or two dimensions, & delocalization in two or one dimensions,

so it will be instructive to show how these two strikingly different behaviors coexist

Type	Number of Electrons $N(E)$	Density of States $D(E)$	Dimensions Delocalized	 Confined
Dot	$N(E) = K_0 \sum d_i \Theta(E - E_{iW})$	$D(E) = K_0 \sum d_i \delta(E - E_{iW})^2$	0	3
Wire	$N(E) = K_1 \sum d_i (E - E_{iW})^{1/2}$	$D(E) = \frac{1}{2} K_1 \sum d_i (E - E_{iW})^{-1/2}$	1	2
Well	$N(E) = K_2 \sum d_i (E - E_{iW})$	$D(E) = K_2 \sum d_i$	2	1
Bulk	$N(E) = K_3 (E)^{3/2}$	$D(E) = \frac{3}{2} K_3 (E)^{1/2}$	3	0



N(E) & DOS D(EJ plotted for 4-quantum structures in square well-Fermi gas approximations

In 3D- Fermi sphere,
Energy varies 0 at origin to **E**, at Fermi surface & similarly for 1D & 2D analogs.

When there is confinement in 1D & 2D directions,
conduction e-s distribute themselves in corresponding PW levels (below FL) & for each case e-s will delocalize in remaining dimensions by populating Fermi gas levels in delocalization direction of reciprocal lattice.

QDs total confinement,
QWs & QWis partial confinement &
bulk material no confinement.

From Figs:
N(E) increases with E, *so 4-nanostructures vary* qualitatively from each other.
However, it is ***D(E) that*** **determines** various electronic & other properties - these differ dramatically for each of 3-nanostructure types.

This means : **nature of dimensionality & confinement** - nanostructure - pronounced effect on its properties.
These considerations helps to predict properties of nanostructures, their types from their properties

Properties dependent on density of states,

excitons,

single electron tunneling.

Exciton

- ☐ Exciton is a bound state of an electron and hole. The binding is due to electrostatic (Coulomb) attraction → the exciton has lower energy than the unbound electron + hole.
  - ➢ This brings the energy levels closer to the conduction band (and the Bohr radius increases)
- ☐ It is an electrically neutral quasiparticle that exists in insulators and semiconductors.
- ☐ The exciton can be considered as an elementary excitation in materials which can transport energy without transporting electric charge (excited state can travel through lattice without transfer of charge). [The free exciton (Mott-Wannier) can move in the crystal. Exciton trapped by an impurity is a bound exciton (has a higher binding energy than free exciton)].

☐The effective reduced mass of exciton (μ):

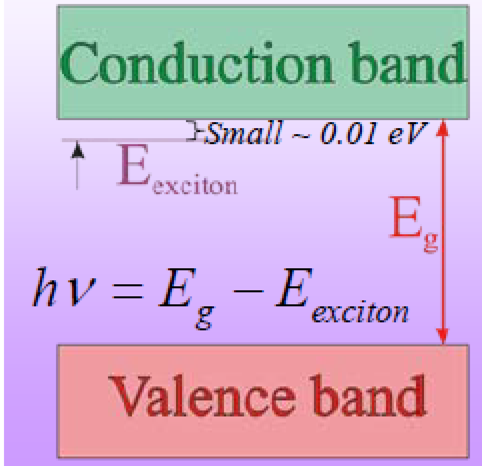
For GaAs: $\mu^{*}_{exciton} = 0.059 m_e$ *(this is much smaller than the free electron mass m_e)*

$$\boxed{\mu^{*}_{exciton} = \frac{m_e^{*} m_h^{*}}{m_e^{*} + m_h^{*}}}$$

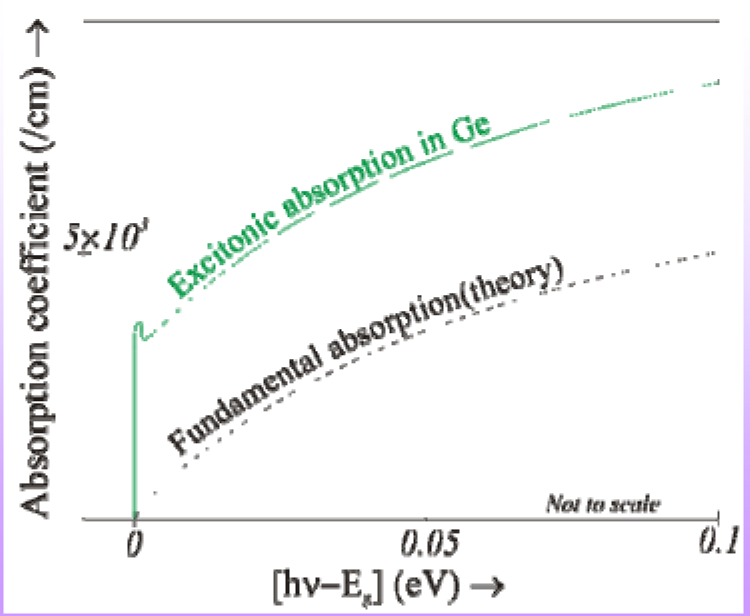
- m_e^{*} → effective mass of electron
- m_h^{*} → effective mass of hole

- Photon absorption by a semiconductor can lead to the formation of an exciton.
- The exciton binding energy for most semiconductors is in the range of few to few 10s of meV (milli-electron volts) [$E_{exciton}$(GaAs)= 4.6 meV, $E_{exciton}$(CdS)= 28 meV] .

  For comparison:
  - the binding energy of H_2 atom is 13.6 eV and
  - kT at room temperature is 40 meV.
- Given the small value of E_{ex} → an exciton can be dissociated by thermal energy at RT.
- The exciton spectrum has a sharp line, just below the fundamental edge → usually observed at low temperature where thermal energy is lower than the binding energy.



$$h\nu = E_g - E_{exciton}$$



❑The exciton diameter can be calculated as:

$$r_{Bohr}^{Exciton} = \frac{\varepsilon r_B m_e[1+(m_e^* / m_h^*)]}{\varepsilon_0 m_e^*}$$

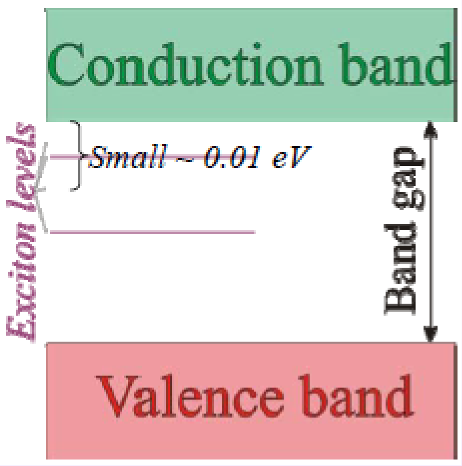
$$r_{Bohr}^{Exciton} = \frac{\varepsilon_0\, \varepsilon\, h^2}{\pi\, \mu\, e^2}$$

- r_B → Bohr radius in the absence of exciton
- ε → dielectric constant of the medium
- ε_0 → dielectric constant of free space
- m_e → mass of free electron
- m_e^* → effective mass of electron
- m_h^* → effective mass of hole

Exciton radius has nanoscale dimensions

	Exciton energy (meV)	Exciton radius (nm)	Band-Gap energy (eV)
GaAs	4.6	~11.8	1.43
CdSe		~5	1.74
CdS	28	~3 (2.4)	2.58

Hydrogen atom ground state: 13.6 eV



- If the dimension of the crystal ~ of the exciton diameter (or less)
  → confinement effects become prominent.

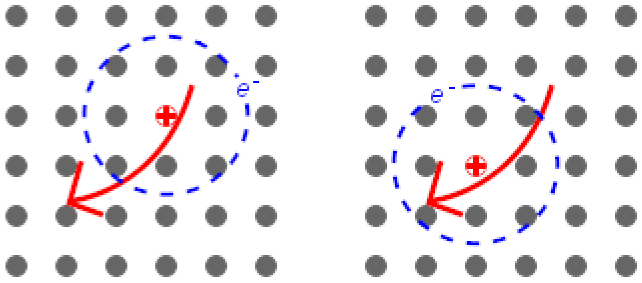
An **exciton** is a bound state of an electron & an electron hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and in some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.[1][2]

An exciton can form when a photon is absorbed by a semiconductor.[3] This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively charged electron hole. The electron in the conduction band is then effectively attracted to this localized hole by the repulsive Coulomb forces from large numbers of electrons surrounding the hole and excited electron.

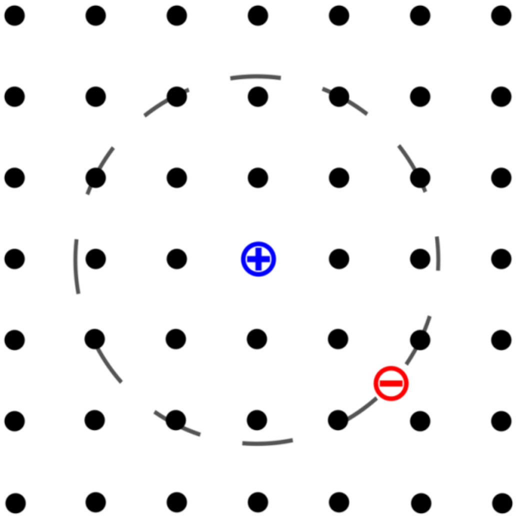
This attraction provides a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound electron and hole. Thewavefunction of the bound state is said to be *hydrogenic*, an exotic atom state akin to that of a hydrogen atom. However, thebinding energy is much smaller and the particle's size much larger than a hydrogen atom. This is because of both the screening of the Coulomb force by other electrons in the semiconductor (i.e., its dielectric constant), and the small effective masses of the excited electron and hole. The recombination of the electron and hole, i.e. the decay of the exciton, is limited by resonance stabilization due to the overlap of the electron and hole wave functions, resulting in an extended lifetime for the exciton.

The electron and hole may have either parallel or anti-parallel spins. The spins are coupled by the exchange interaction, giving rise to exciton fine structure. In periodic lattices, the properties of an exciton show momentum (k-vector) dependence.

The concept of excitons was first proposed by Yakov Frenkel in 1931,[4] when he described the excitation of atoms in a lattice of insulators. He proposed that this excited state would be able to travel in a particle-like fashion through the lattice without the net transfer of charge.



Wannier-Mott exciton, bound electron-hole pair that is not localized at a crystal position. This figure schematically shows diffusion of the exciton across the lattice.



Frenkel exciton, bound electron-hole pair where the hole is localized at a position in the crystal represented by black dots

Classification[edit]

Excitons may be treated in two limiting cases, depending on the properties of the material in question.

Frenkel excitons[edit]

In materials with a small dielectric constant, the Coulomb interaction between an electron and a hole may be strong and the excitons thus tend to be small, of the same order as the size of the unit cell. Molecular excitons may even be entirely located on the same molecule, as in fullerenes. This *Frenkel exciton*, named after Yakov Frenkel, has a typical binding energy on the order of 0.1 to 1 eV. Frenkel excitons are typically found in alkali halide crystals and in organic molecular crystals composed of aromatic molecules, such as anthracene and tetracene.

Wannier–Mott excitons[edit]

In semiconductors, the dielectric constant is generally large. Consequently, electric field screening tends to reduce the Coulomb interaction between electrons and holes. The result is a *Wannier exciton*,[5] which has a radius larger than the lattice spacing. Small effective mass of electrons that is typical of semiconductors also favors large exciton radii. As a result, the effect of the lattice potential can be incorporated into the effective masses of the electron and hole. Likewise, because of the lower masses and the screened Coulomb interaction, the binding energy is usually much less than that of a hydrogen atom, typically on the order of 0.01eV. This type of exciton was named for Gregory Wannier and Nevill Francis Mott. Wannier-Mott excitons are typically found in semiconductor crystals with small energy gaps and high dielectric constants, but have also been identified in liquids, such as liquid xenon. They are also known as *large excitons*.

In single-wall carbon nanotubes, excitons have both Wannier-Mott and Frenkel character. This is due to the nature of the Coulomb interaction between electrons and holes in one-dimension. The dielectric function of the nanotube itself is large enough to allow for the spatial extent of the wave function to extend over a few to several nanometers along the tube axis, while poor screening in the vacuum or dielectric environment outside of the nanotube allows for large (0.4 to 1.0eV) binding energies.

Often there is more than one band to choose from for the electron and the hole leading to different types of excitons in the same material. Even high-lying bands can be effective as femtosecond two-photon experiments have shown. At

Charge-transfer excitons[edit]

An intermediate case between Frenkel and Wannier excitons, *charge-transfer excitons* (sometimes called simply *CT excitons*) occur when the electron and the hole occupy adjacent molecules.[7] They occur primarily in ionic crystals.[8] Unlike Frenkel and Wannier excitons they display a static electric dipole moment.[9]

Surface excitons[edit]

At surfaces it is possible for so called *image states* to occur, where the hole is inside the solid and the electron is in the vacuum. These electron-hole pairs can only move along the surface.

Atomic and molecular excitons[edit]

Alternatively, an exciton may be an excited state of an atom, ion, or molecule, the excitation wandering from one cell of the lattice to another.

When a molecule absorbs a quantum of energy that corresponds to a transition from one molecular orbital to another molecular orbital, the resulting electronic excited state is also properly described as an exciton. An electron is said to be found in the lowest unoccupied orbital and an electron hole in the highest occupied molecular orbital, and since they are found within the same molecular orbital manifold, the electron-hole state is said to be bound. Molecular excitons typically have characteristic lifetimes on the order of nanoseconds, after which the ground electronic state is restored and the molecule undergoes photon or phonon emission. Molecular excitons have several interesting properties, one of which is energy transfer (see Förster resonance energy transfer) whereby if a molecular exciton has proper energetic matching to a second molecule's spectral absorbance, then an exciton may transfer (*hop*) from one molecule to another. The process is strongly dependent on intermolecular distance between the species in solution, and so the process has found application in sensing and *molecular rulers*.

The hallmark of molecular excitons in organic molecular crystals are doublets and/or triplets of exciton absorption bands strongly polarized along crystallographic axes. In these crystals an elementary cell includes several molecules sitting in symmetrically identical positions, which results in the level degeneracy that is lifted by intermolecular interaction. As a result, absorption bands are polarized along the symmetry axes of the crystal. Such multiplets were discovered by Antonina Prikhot'ko[10][11] and their genesis was proposed by Alexander Davydov. It is known as 'Davydov splitting'.[12][13]

Giant oscillator strength of bound excitons[edit]

Excitons are lowest excited states of the electronic subsystem of pure crystals. Impurities can bind excitons, and when the bound state is shallow, the oscillator strength for producing bound excitons is so high that impurity absorption can compete with intrinsic exciton absorption even at rather low impurity concentrations. This phenomenon is generic and applicable both to the large radius (Wannier-Mott) excitons and molecular (Frenkel) excitons. Hence, excitons bound to impurities and defects possess giant

Self-trapping of excitons[edit]

In crystals excitons interact with phonons, the lattice vibrations. If this coupling is weak as in typical semiconductors such as GaAs or Si, excitons are scattered by phonons. However, when the coupling is strong, excitons can be self-trapped.[15][16] **Self-trapping** results in dressing excitons with a dense cloud of virtual phonons which strongly suppresses the ability of excitons to move across the crystal. In simpler terms, this means a local deformation of the crystal lattice around the exciton. Self-trapping can be achieved only if the energy of this deformation can compete with the width of the exciton band. Hence, it should be of atomic scale, of about an electron volt.

Self-trapping of excitons is similar to forming strong-coupling polarons but with three essential differences. First, self-trapped exciton states are always of a small radius, of the order of lattice constant, due to their electric neutrality. Second, there exists a **self-trapping barrier** separating free and self-trapped states, hence, free excitons are metastable. Third, this barrier enables **coexistence of free and self-trapped states** of excitons.[17][18] This means that spectral lines of free excitons and wide bands of self-trapped excitons can be seen simultaneously in absorption and luminescence spectra. It is interesting that while the self-trapped states are of lattice-spacing scale, the barrier has typically much larger scale. Indeed, its spatial scale is about where is effective mass of the exciton, is the exciton-phonon coupling constant, and is the characteristic frequency of optical phonons. Excitons are self-trapped when and are large, and then the spatial size of the barrier is large compared with the lattice spacing. Transforming a free exciton state into a self-trapped one proceeds as a collective tunneling of coupled exciton-lattice system (an instanton). Because is large, tunneling can be described by a continuum theory.[19] The height of the barrier . Because both and appear in the denominator of , the barriers are basically low. Therefore, free excitons can be seen in crystals with strong exciton-phonon coupling only in pure samples and at low temperatures. Coexistence of free and self-trapped excitons was observed in rare-gas solids,[20][21]alkali-halides,[22] and in molecular crystal of pyrene.[23]

Interaction[edit]

Excitons are the main mechanism for light emission in semiconductors at low temperature (when the characteristic thermal energy *kT* is less than the exciton binding energy), replacing the free electron-hole recombination at higher temperatures.

The existence of exciton states may be inferred from the absorption of light associated with their excitation. Typically, excitons are observed just below the band gap.

When excitons interact with photons a so-called polariton (also exciton-polaritons) is formed. These excitons are sometimes referred to as *dressed excitons*.

Provided the interaction is attractive, an exciton can bind with other excitons to form a biexciton, analogous to a dihydrogen molecule. If a large density of excitons is created in a material, they can interact with one another to form an electron-hole liquid, a state observed in k-space indirect semiconductors. Additionally, excitons are integer-spin particles obeying Bose statistics in the low-density limit. In some systems, where the interactions are repulsive, a Bose–Einstein condensed state, called excitonium, is predicted to be the ground state. Some evidence of excitonium has existed since the 1970s, but has often been difficult to discern from a Peierls phase.[24] Exciton condensates have allegedly been seen in a double quantum well systems.[25] In 2017 Kogar et al. found "compelling evidence" for observed excitons condensing in the three-dimensional semimetal 1T-TiSe2[26]