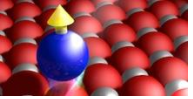
3

Quantum confinement



3. Quantum confinement

Solid State Physics books

Applied nanophotonics

Part I - Basics

S.V. Gaponenko and H. V. Demir

(2018)

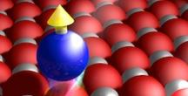
DOI

Fundamental Principles of Quantum Dots

W. J. Parak, L. Manna, Th. Nann

(2010)

DOI: 10.1002/9783527628155.nanotech004



Two approaches to describe electronic states in solids and nanostructures

EPFL

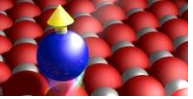
from localized atomic orbitals

tight-binding model

from delocalized electrons in bulk

nearly-free-electron model

electronic band structure



Quantum particles

Whenever the size of a physical system becomes comparable to the wavelength of the particles that interact with such a system, the behavior of the particles is best described by the rules of quantum mechanics, and an electron confined in this structure will behave as a particle in a potential box.

de Broglie wavelength: $\lambda = \frac{h}{p}$

The solutions of the Schrödinger equation are standing waves confined in the potential well and the energies associated with two distinct wavefunctions are, in general, different and discontinuous

The particle energies cannot take on any arbitrary value, and the system exhibits a discrete energy level spectrum

Free electron gas

EPFL

Exercises 3.1 – 3.2

Possible description of electrons in solids (appropriate for some properties only)

The electrons are confined inside the solid, but delocalized (not bound to individual atoms)
The interactions between the electrons, and between the electrons and the crystal potential, are neglected

The energy of a free electron is just its kinetic energy

$$E(k) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 k^2}{2m}$$

$$\boldsymbol{p} = m\boldsymbol{v} = \hbar\boldsymbol{k}$$

$\boldsymbol{p}$ momentum
$\boldsymbol{k}$ wavevector

$$k = \frac{2\pi}{\lambda}$$

λ wavelength

Wavefunctions are plane waves

Three-dimensional systems (bulk material)

The calculation of the energy states for a bulk crystal assumes periodic boundary conditions (mathematical trick to simulate an infinite solid), as opposed to fixed boundary conditions

→ solution of the stationary Schrödinger equation
with boundary conditions, variable separation

$$\psi(x,y,z) \propto \exp(ik_x x)\exp(ik_y y)\exp(ik_z z)$$

$$k_i = \pm n_i \frac{2\pi}{d_i} \qquad n_i \text{ integer}$$

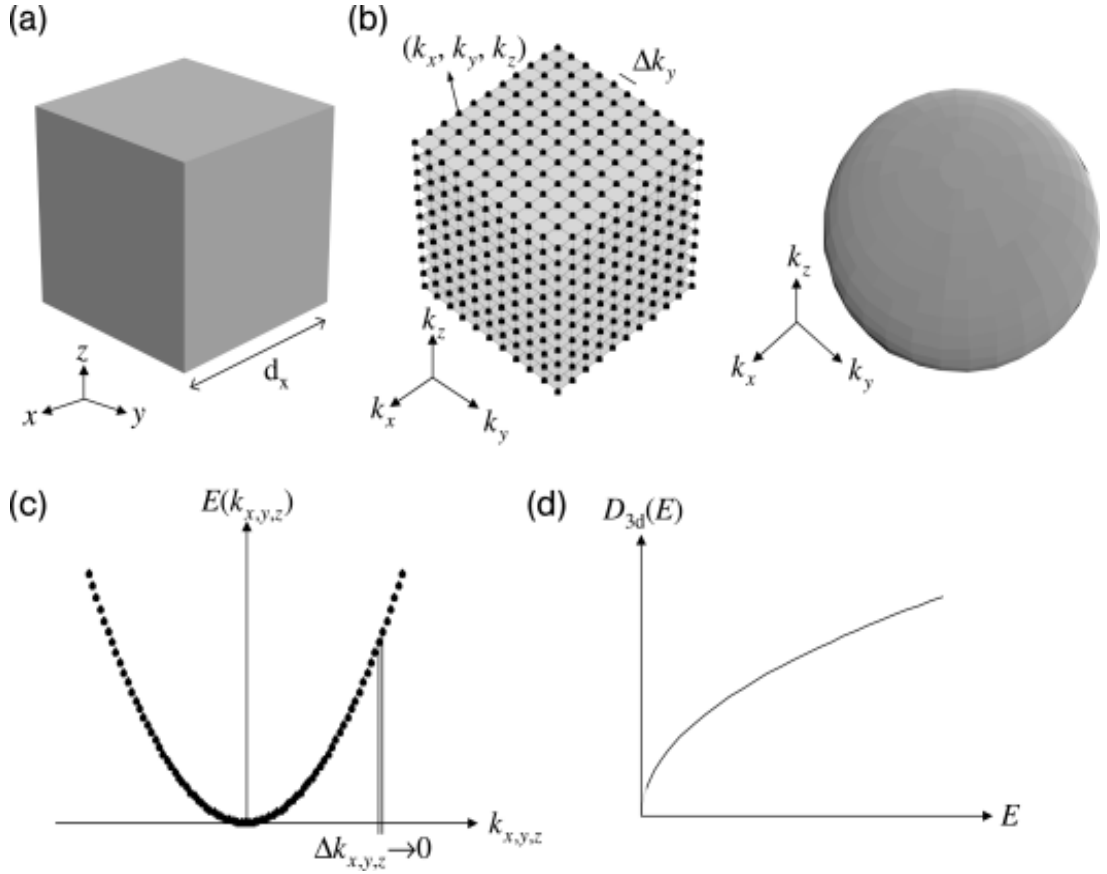
In bulk materials (size d very large), the allowed k values form a quasi-continuum, and are homogeneously distributed in k-space (constant)

N number of states in the solid

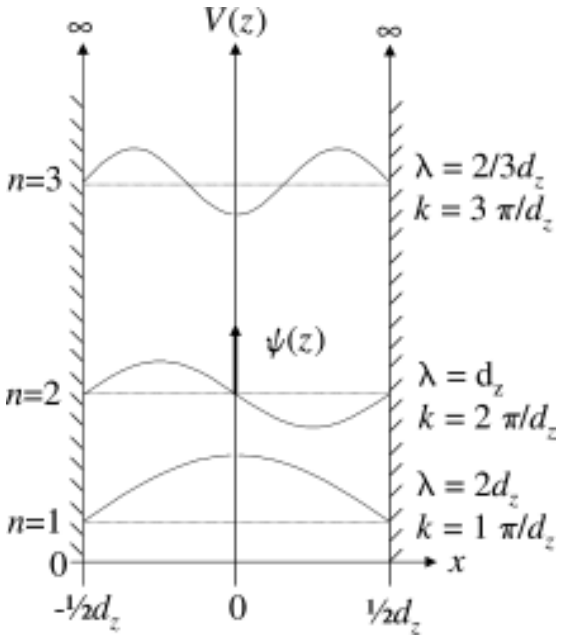
Density of states

$$D_{3d}(E) = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE} \propto E\frac{1}{\sqrt{E}} \propto \sqrt{E}$$

$$\propto k^2 \leftrightarrow E \qquad \propto \frac{1}{\sqrt{E}}$$

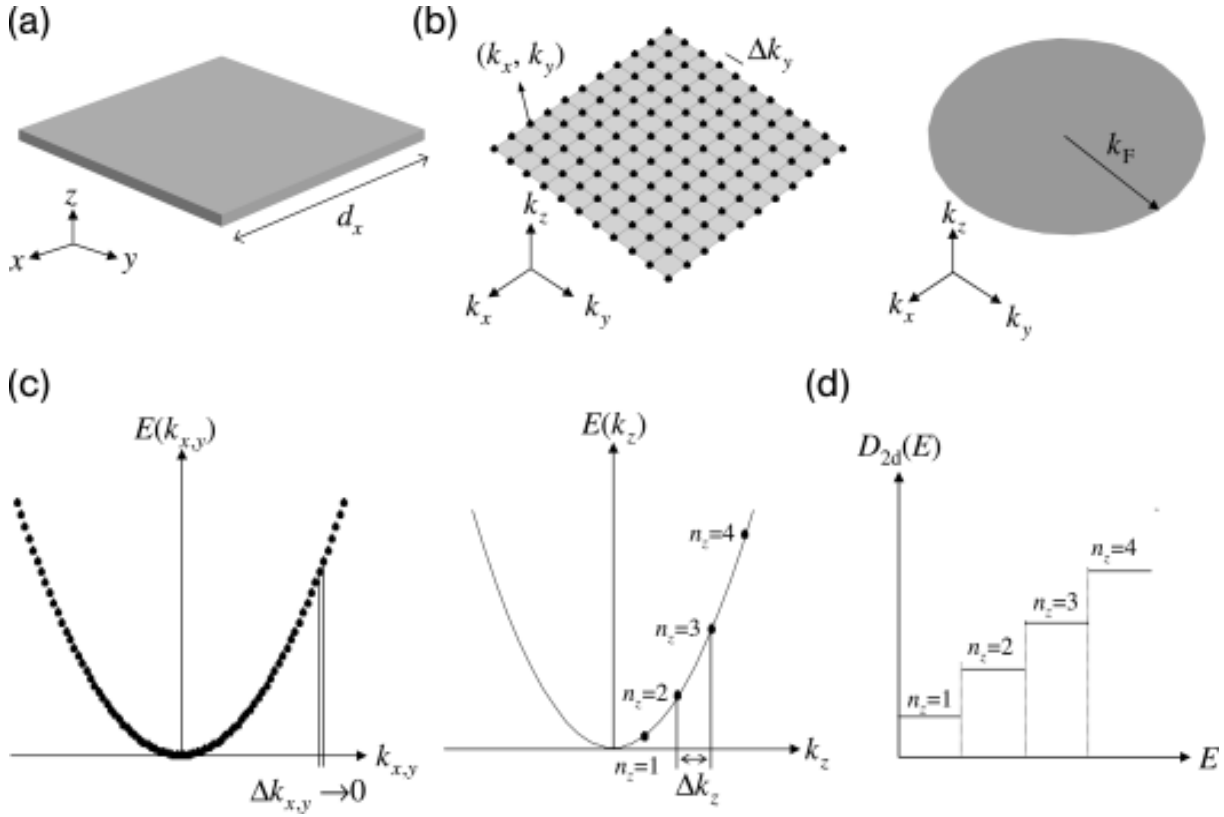


Extended solid along the x-and y-directions, thickness along the z-direction (d_z) very small
Free electrons can still move freely in the xy plane.
Electrons that move in the z-direction are trapped in a box (ideally: infinite potential well)



$$k_z = n_z \frac{\pi}{d_z}$$

$$n_z \text{ integer } > 0$$



Density of states

$$D_{2d}(E) = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE} \propto \sqrt{E}\frac{1}{\sqrt{E}} \propto 1$$

$$\propto k \leftrightarrow \sqrt{E} \qquad \propto \frac{1}{\sqrt{E}}$$

The solid shrinks also along a second (y) dimension.
Electrons can only move freely in the x-direction and their motion along the y- and z-axes is restricted by the edges of the solid

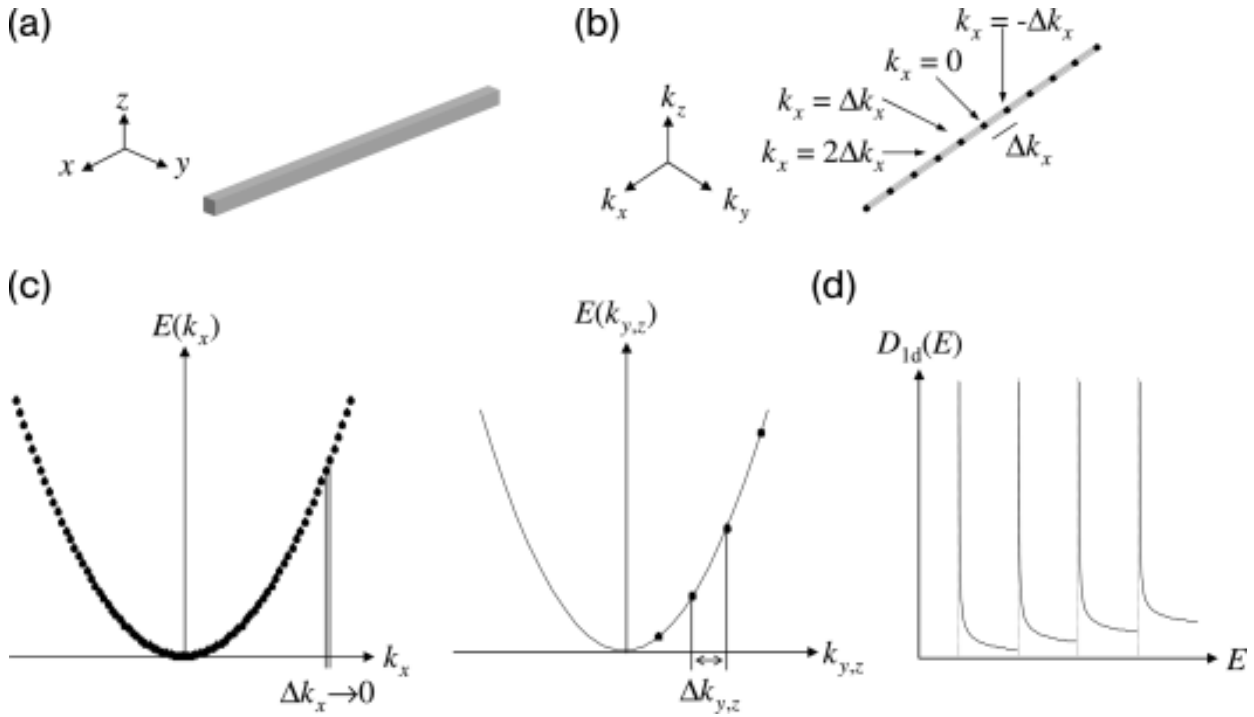
$$k_{y,z} = n_{y,z}\frac{\pi}{d_{y,z}} \qquad n_{y,z} \text{ integer } > 0$$

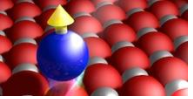
$$k_x = \pm n_x \frac{2\pi}{d_x} \qquad n_x \text{ integer}$$

Density of states

$$D_{1d}(E) = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE} \propto 1\frac{1}{\sqrt{E}} \propto \frac{1}{\sqrt{E}}$$

$\propto 1$ $\qquad$ $\propto \frac{1}{\sqrt{E}}$



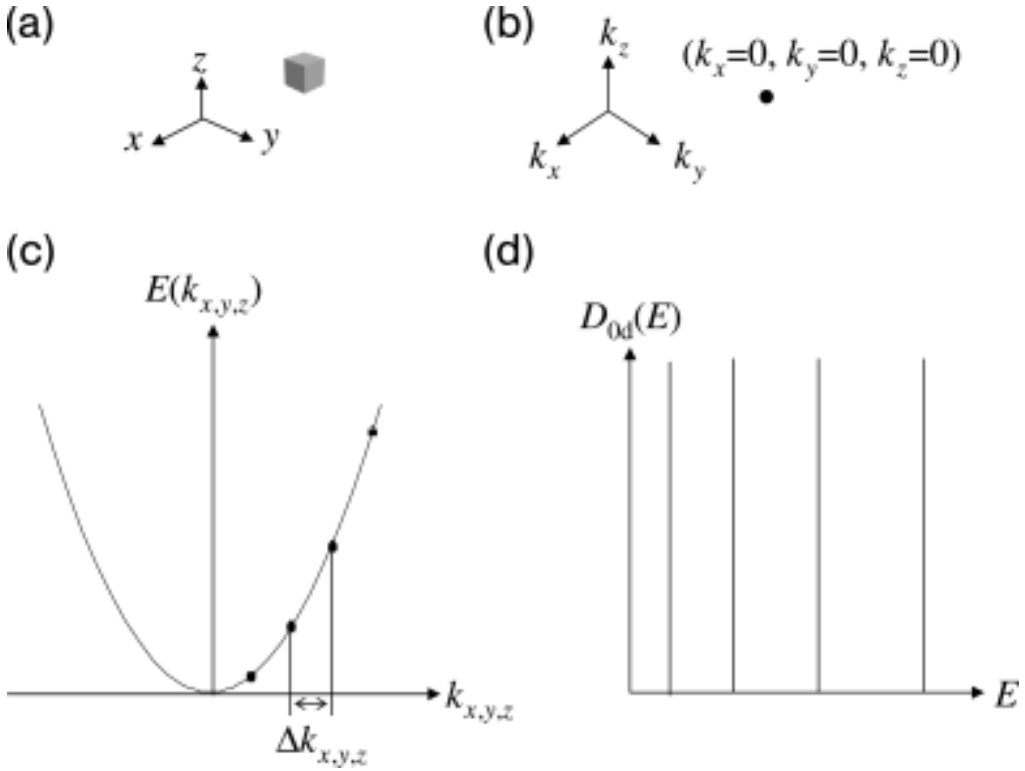


Zero-dimensional systems

The movement of electrons is confined in all three dimensions and there are only discrete (k_x, k_y, k_z)states in the k-space.

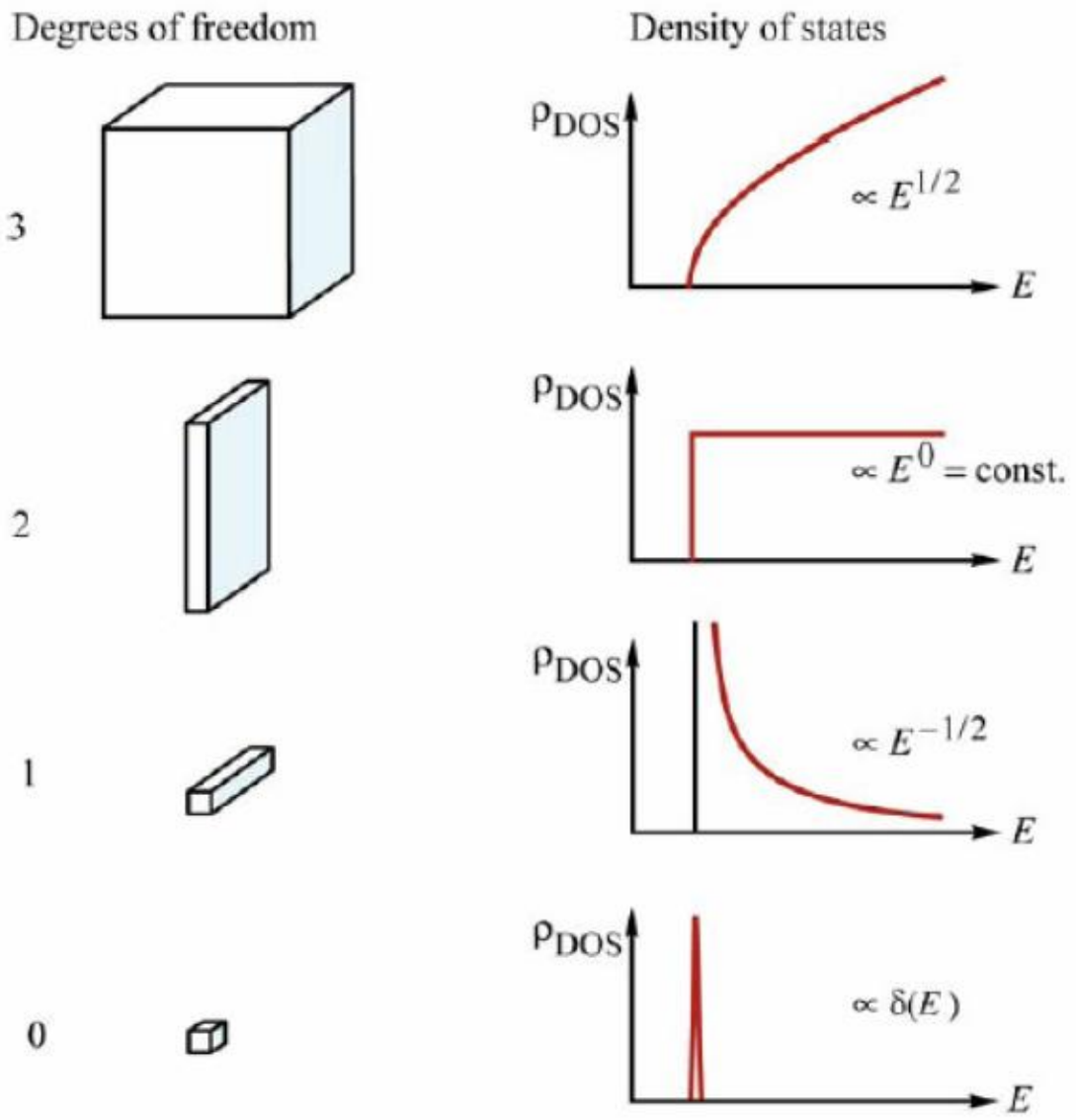
Each individual state in k-space can be represented by a point.

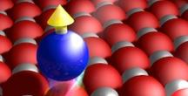
Only discrete energy levels are allowed



Strict dimensionality

Exercise 3.3





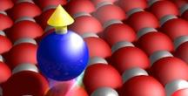
Energies of confined states

The smaller the size, the higher the zero-point energy and the larger the spacing between the energy levels.

Example for the confinement along z direction (thickness d):

$$k_z = n\frac{\pi}{d} \qquad n \text{ integer } > 0$$

$$E_n = \frac{\hbar^2}{2m}k_z^2 = \frac{\hbar^2}{2m}\left(\frac{\pi}{d}\right)^2 n^2 = \frac{h^2}{8md^2}n^2$$



Quantum world: same scale for all materials?

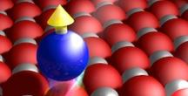
de Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{m^* v}$

m^* : effective mass
the properties of electrons in solids can be described replacing the free electron mass by an effective mass m^* which partially takes into account the effect of the interactions of the electrons with the crystal potential

$E(k) = \frac{\hbar^2 k^2}{2m^*}$

the effective mass is inversely proportional to the curvature of the energy band:
small curvature (flat parabola) ⇔ higher effective mass
large curvature (narrow parabola) ⇔ lower effective mass

affects the electron wavelength
→
affects the scale at which quantum size effects are relevant



Quantum world: metals vs semiconductors

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

$m_e = 9.1 \cdot 10^{-31}$ kg

$h = 6.6 \cdot 10^{-34}$ J s

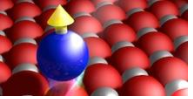
$v \approx 10^6$ m s^{-1}

typical effective mass values:

in metals: $\frac{m^*}{m_e} \sim 0.5 - 1 \quad \rightarrow \quad \lambda \sim 1 - 2$ nm

in semiconductors (electrons and holes) : $\frac{m^*}{m_e} \sim 0.01 - 0.1 \quad \rightarrow \quad \lambda \sim 10 - 100$ nm

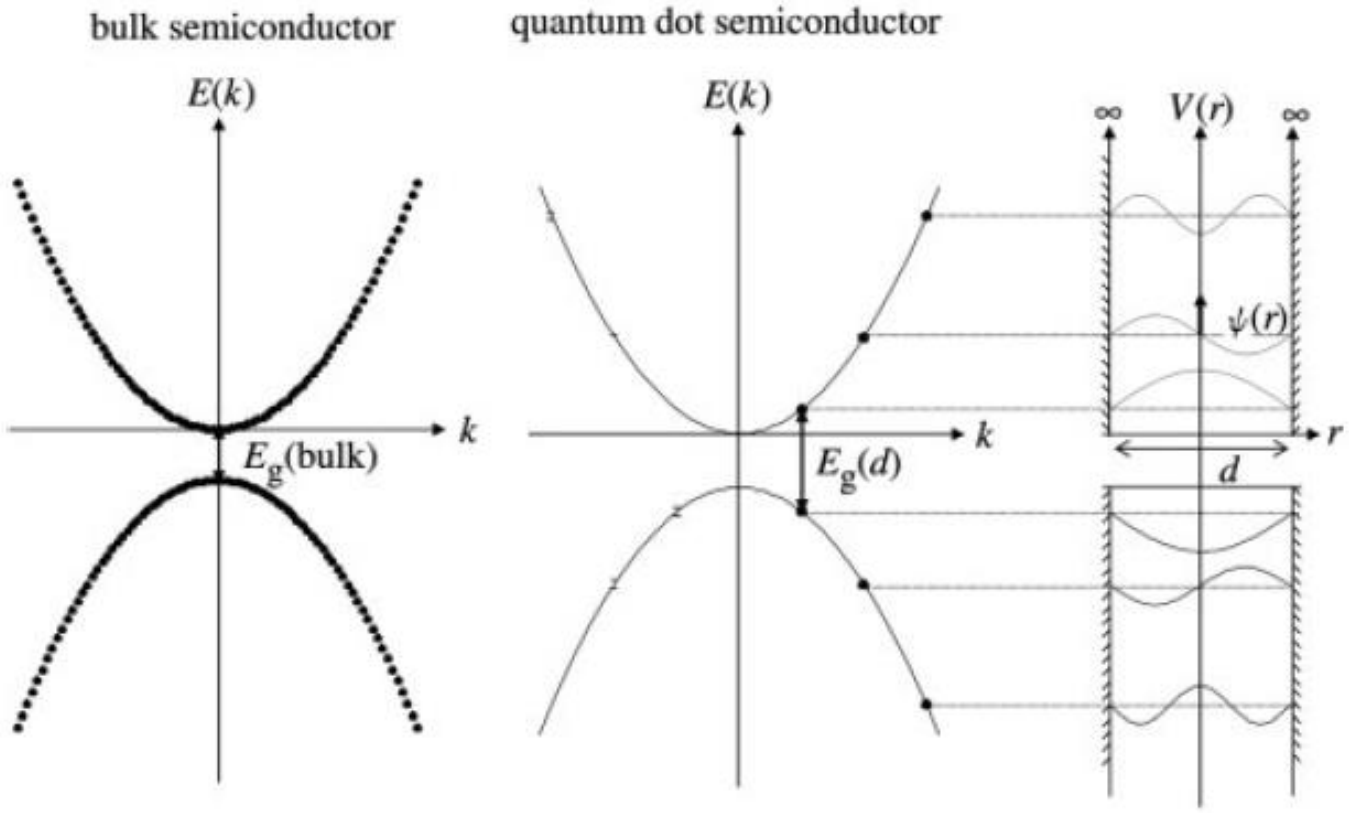
the quantum effects are relevant up to different sizes		
metals	:	nanometer
semiconductors	:	tens of nanometers



Semiconductor quantum dots

The electronic properties of semiconductors are strongly related to the transitions between the edges of the valence band and the conduction band

The energy gap in a quantum dot is always larger than the gap in the corresponding bulk material



Exercise 3.4

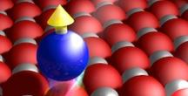
The electronic spectrum of a QD can be derived to first approximation using the particle-in-a-box model. This involves carrier confinement inside an infinite three-dimensional quantum well, whose width d is smaller than the de Broglie wavelength of the carriers.

Cubic box: the overall zero-point energy is simply the sum of the individual zero-point energies for each degree of freedom

$$E_{well,(cube)} = 3E_{well,1D} = \frac{3}{8}\frac{h^2}{md^2}$$

Spherical box, the Schrödinger equation can be solved by introducing spherical coordinates and by separating the equation in a radial part and a part containing the angular momentum. The lowest energy level (with angular momentum = 0) is

$$E_{well,(\mathrm{sphere})} = \frac{1}{2}\frac{h^2}{md^2}$$



Semiconductor quantum dots

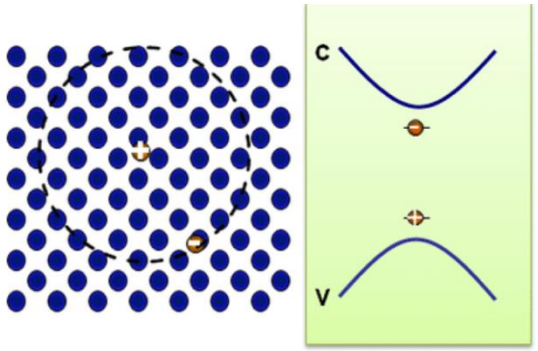
Confinement must be considered for both bands:

$$E_{well} = \frac{1}{2}\frac{h^2}{\mu d^2}$$

μ is the reduced mass of electron and hole

Quantum dot energy gap: $E_{g,(dot)} = E_{g(bulk)} + E_{well}$

A third term, that reduces the apparent gap, must be included: when exciting an electron to the conduction band, an exciton (electron-hole pair bound by Coulomb interaction) is formed. This happens also in bulk.



Exciton in bulk

In bulk, energy and radius of the excitons can be determined with an hydrogenic model taking into account the effective masses and the dielectric constant of the material

When reducing the size, the exciton gets more confined → the Colomb interaction increases, and the determinant distance is the size of the quantum dot.

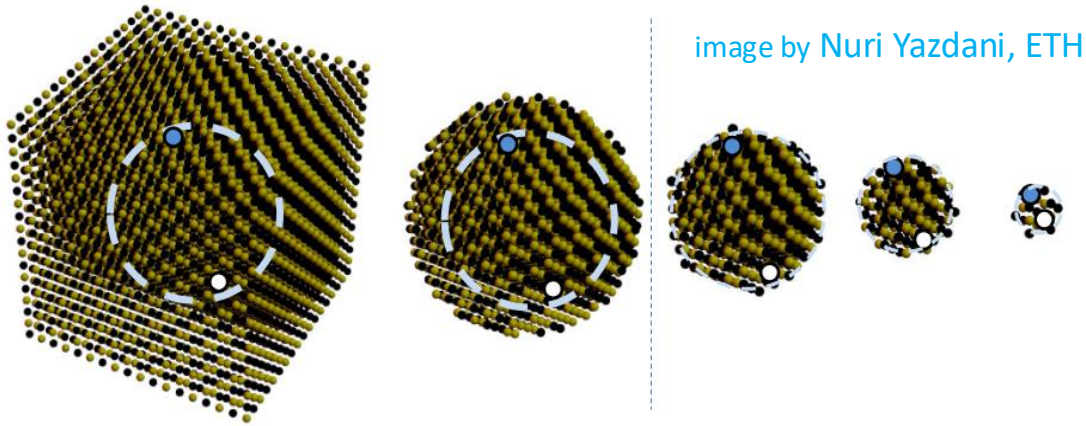
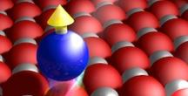


image by Nuri Yazdani, ETH

Coulomb interaction

$$E_{Coul} \propto -\frac{e^2}{\varepsilon_0 \varepsilon_r d}$$



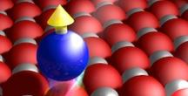
Semiconductor quantum dots

$$E_{g,(dot)} = E_{g(bulk)} + E_{well} + E_{Coul}$$

The confinement energy is always a positive term and thus the energy of the gap is always raised with respect to the bulk situation.

On the other hand, the Coulomb interaction is always attractive for an electron–hole pair system and therefore reduced the energy ($E_{Coul} < 0$)

Because of the $1/d^2$ dependence, the quantum confinement effect becomes the predominant term for very small quantum dot sizes, although the Coulomb energy is also affected by the confinement

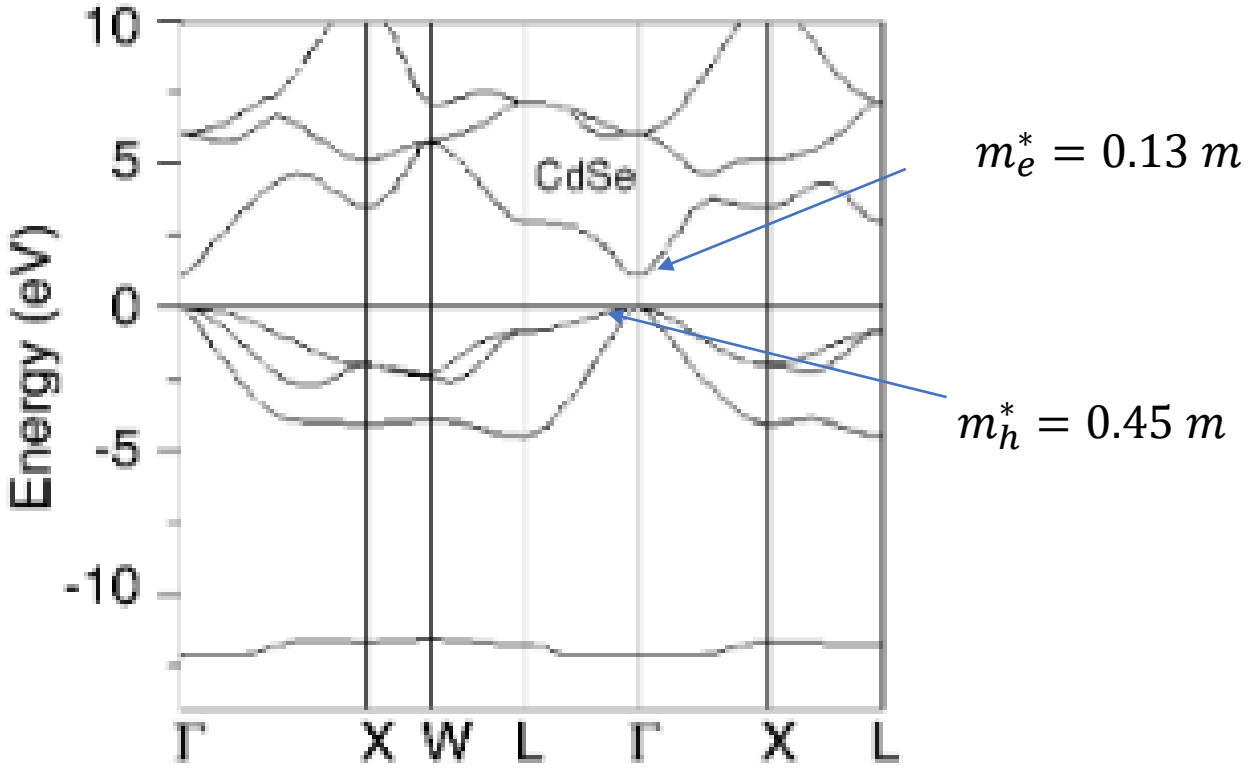


Some properties of CdSe

CdSe (cadmium selenide, II-VI semiconductor)

$E_{g(bulk)} =$ 1.74 eV @ RT

$\varepsilon_r = 10.3$



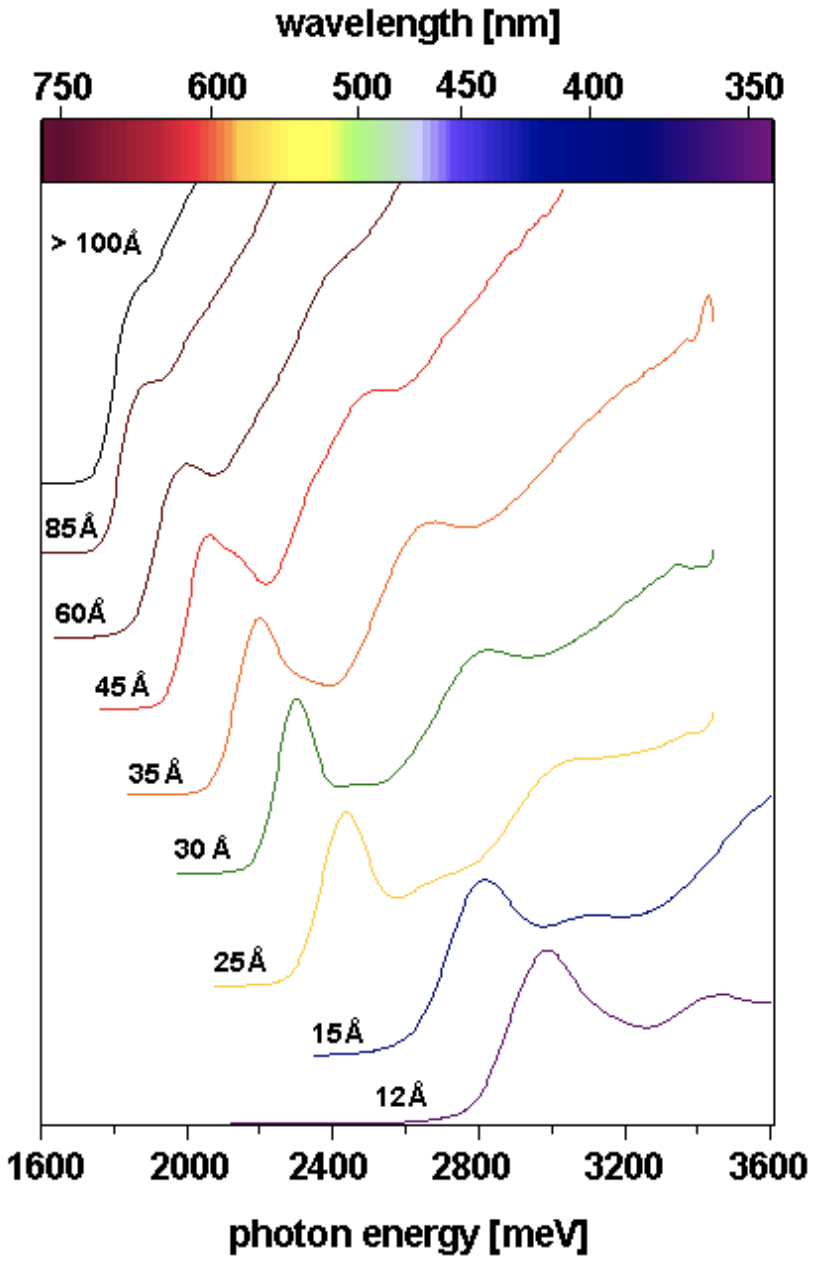
CdSe quantum dots

Exercises 3.5 – 3.6

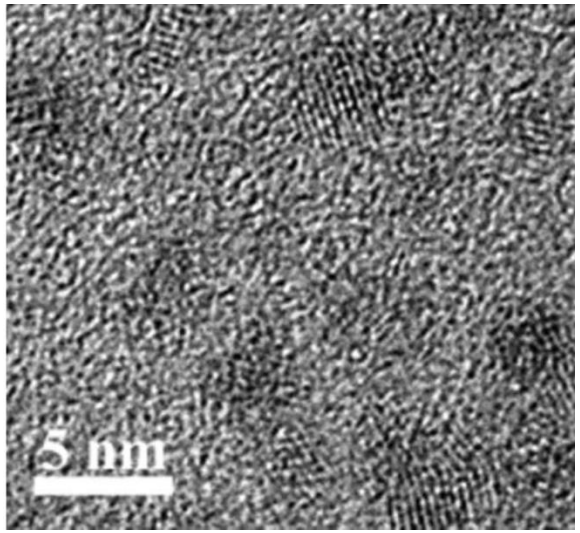
Size-dependence of optical absorption spectra recorded from CdSe nanocrystals with diameters ranging between 1.2 and 8.5 nm.

$$E = \frac{hc}{\lambda}$$

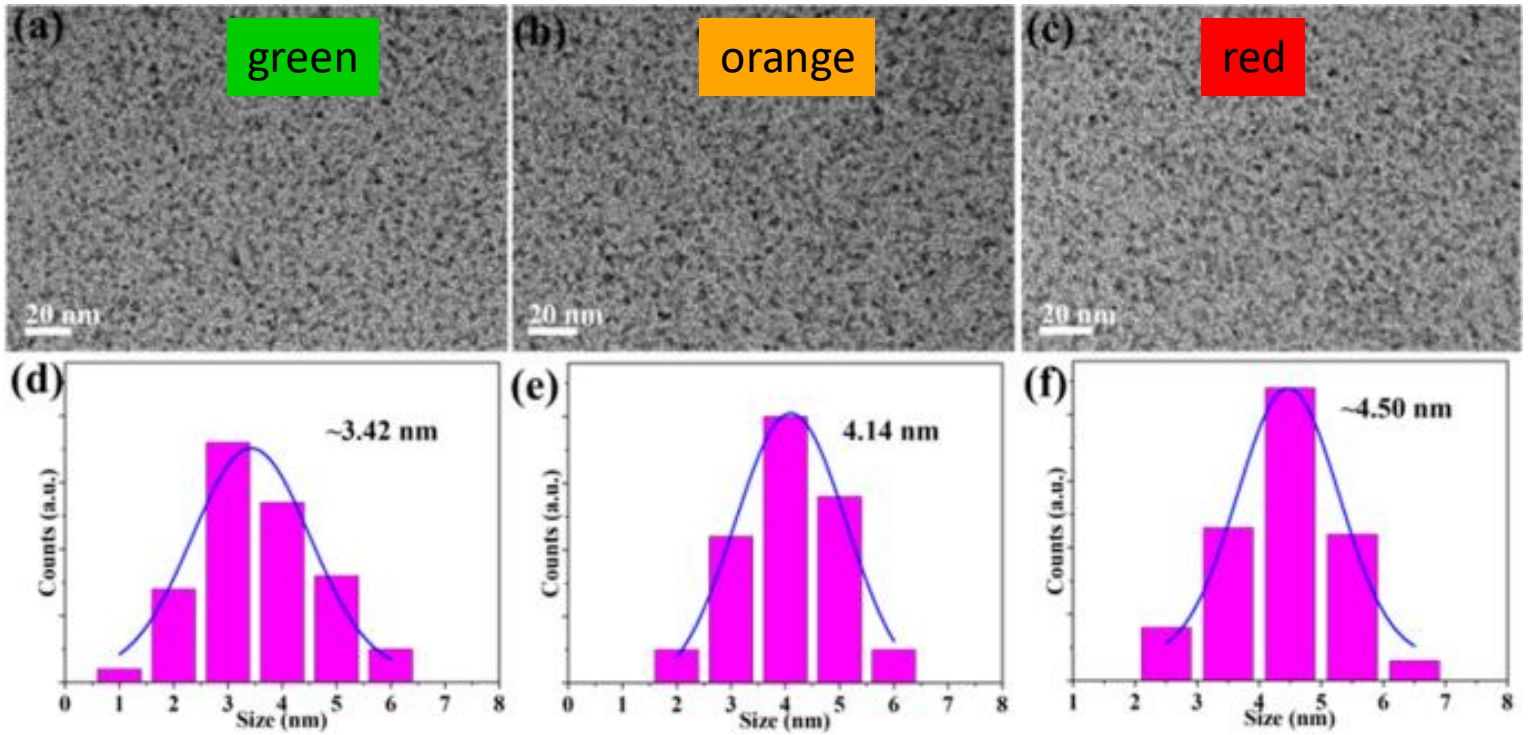
$$E(\text{eV}) = \frac{1240}{\lambda\ (\text{nm})}$$



CdSe quantum dots

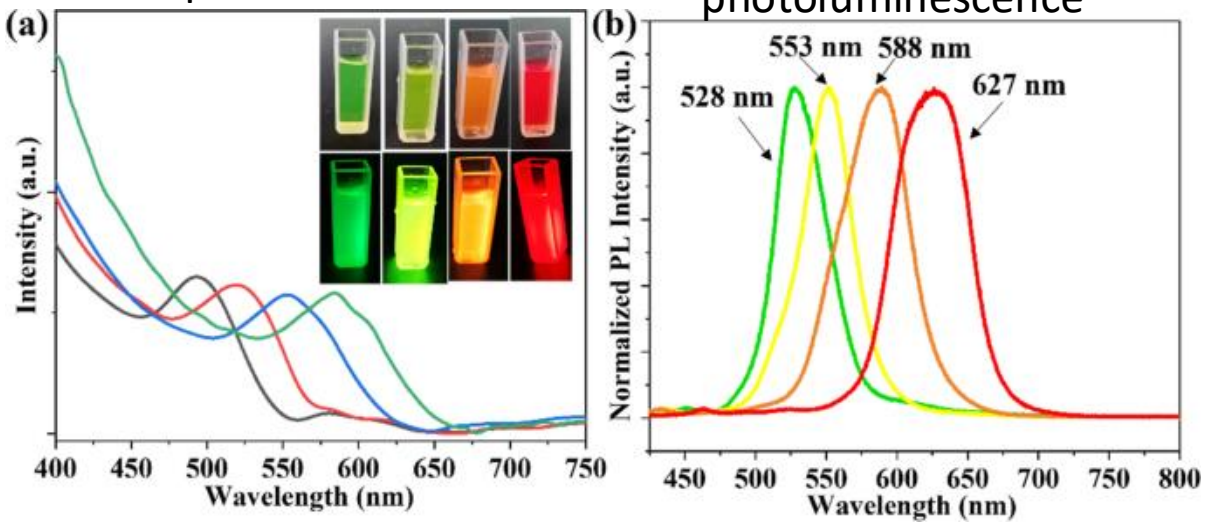


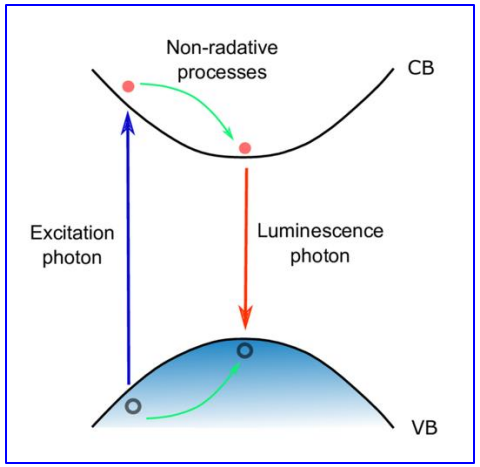
TEM images



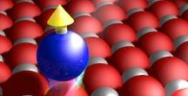
absorption

photoluminescence



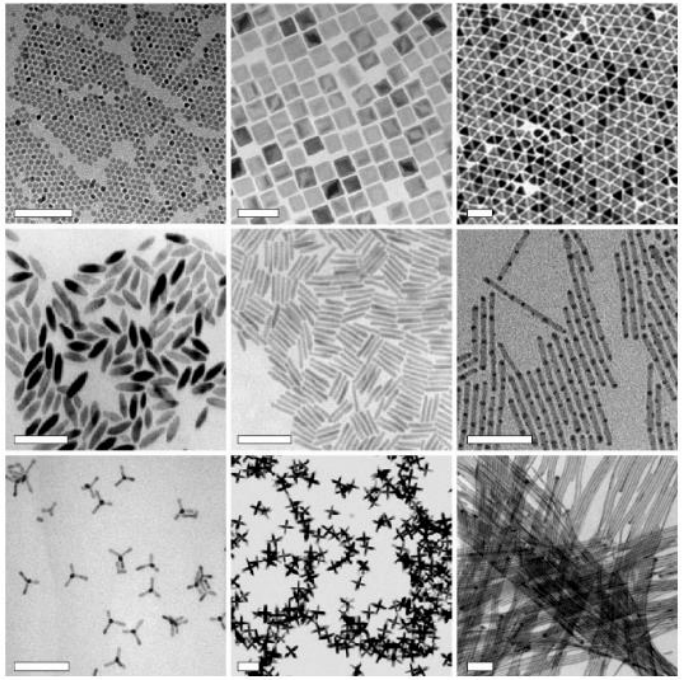


DOI: 10.1007/s12596-023-01556-5
J. Opt. 53, 3829 (2024)

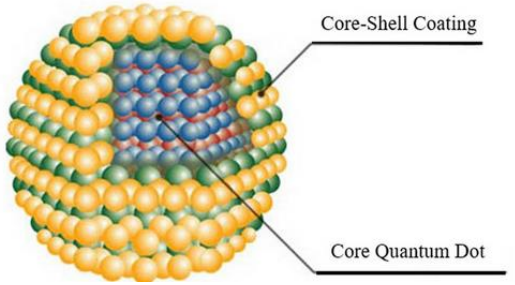


Semiconductor quantum dots

shape
sphere
cube
pyramidal
tetrahedral
platelet
rod
….



structure (colloidal)
simple
core/shell
core/double shell



materials
Cd chalcogenides
Pb chalcogenides
II-VI semiconductors

III-V more difficult for colloidal synthesis, ok for growth

Nobel Prize in Chemistry in 2023

production
colloidal synthesis
self-assembly
growth (embedded in bulk material)

applications
optical (markers)
optoelectronic
- LED
- flexible screens
- solar cells

field effect transistors
…

Transmission Electron Microscope (TEM)

Abbe diffraction limit for a microscope
λ wavelength
n refraction index
α semi-angle

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2\ NA}$$

Use other particles instead of photons ?

de Broglie wavelength $$\lambda = \frac{h}{\sqrt{2\ m\ E}}$$

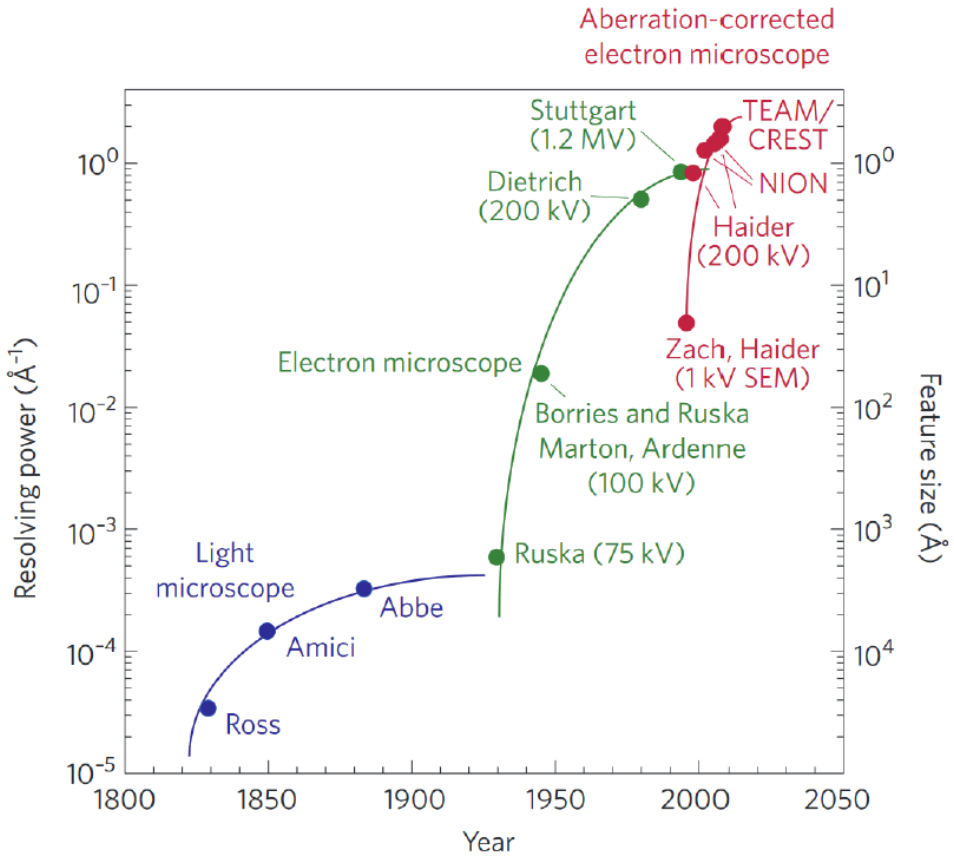
relativistic $$\lambda = \frac{h}{\sqrt{2\ m_0\ E\left(1 + \frac{E}{2m_0c^2}\right)}}$$

Electrons

High electron energy $\mathrm{E} = 100\ \mathrm{keV} \rightarrow \lambda = 0.0375\ \text{Å}$

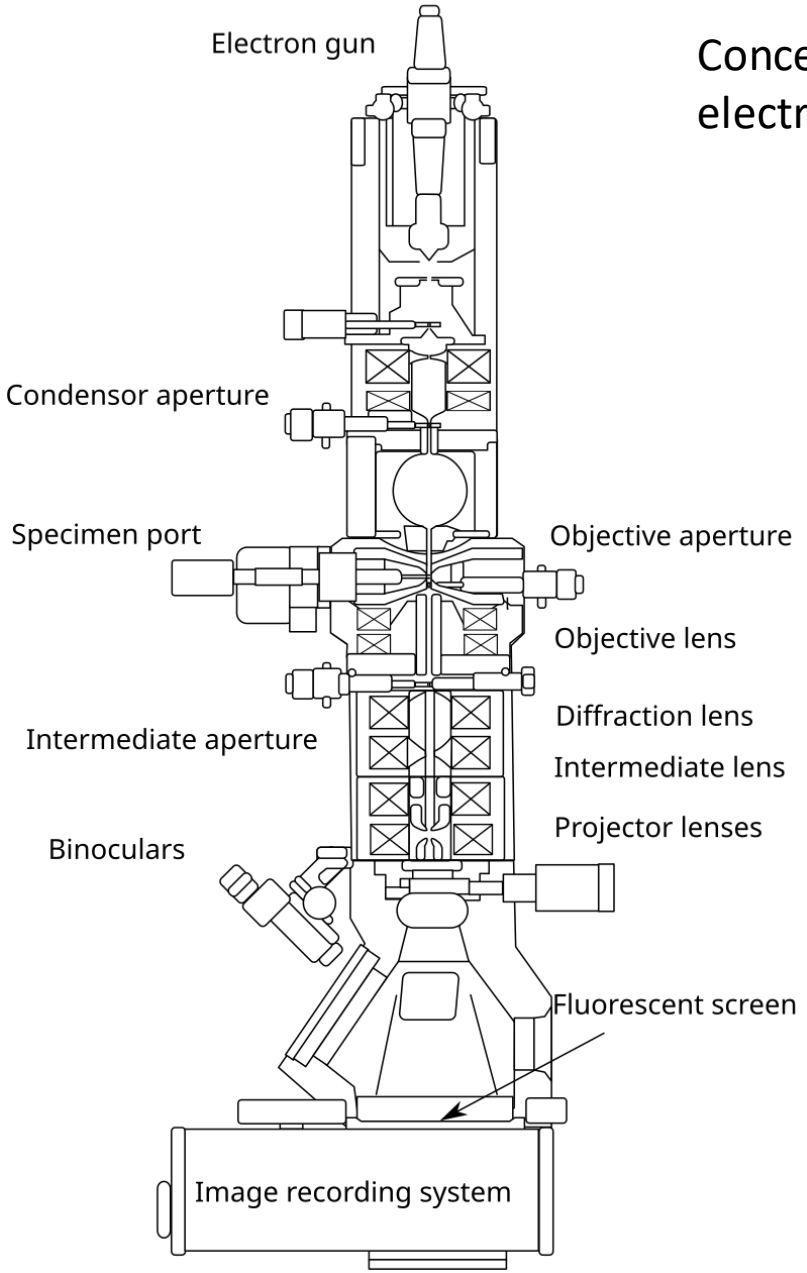
Theoretical resolution about hundred thousands times better than that of light.

In HR-TEM today the resolution reaches 50 pm.



Nature Materials **8,** 263 (2009)

Transmission Electron Microscope (TEM)



Conceptually identical to an optical microscope where electrons are used in place of photons

In practice

Due to the limited penetration depth of electrons in solids, the samples should be very thin: the acceptable thickness is 10-100 nm for conventional microscopes with accelerating voltages of 50-200 keV.

The electron beam loses part of its intensity due to scattering. The loss is greater for thicker regions or regions with species of higher atomic number. The thicker regions and the regions of higher atomic number appear dark.

With high-resolution TEM, images showing the atomic structure can be obtained. For complex systems, numerical image simulations are required for the reliable interpretation of the image features in terms of atomic structure.