

ET-1039: Nanotechnology

Chapter I: Fundamentals of solid state

1. Introduction
2. Atoms and light
 - Some basic properties and units
 - Wave function
 - Heisenberg uncertainty principle
2. Wave function of matter
 - Schrödinger equation
 - Tunnel effect
3. Energy bands in solids
 - Conductors, semiconductors and insulators
 - Intrinsic and extrinsic semiconductors
 - p-n junction

References:

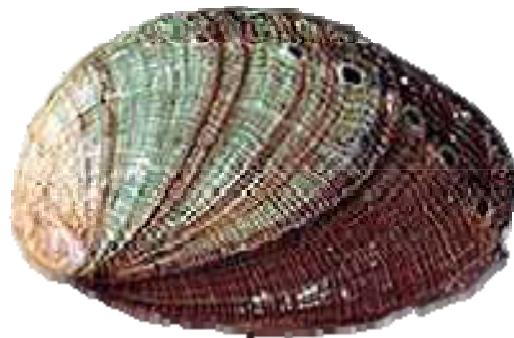
- N. W. Ashcroft, N. Mermin **Solid State Physics** 2nd ed. Holt Rinehart & Winston, 2002.
- Y. M. Galperin. *Introduction to modern solid state physics*. <http://folk.uio.no/yurig/fys448/f448pdf.pdf>
- A.M. Criado Pérez, F. Frutos Rayego. *Introducción a los fundamentos físicos de la informática*. Paraninfo, Madrid, 1999.
- Sze, S. M. *Physics of Semiconductor Devices*. 2nd ed.; John Wiley and Sons: New York, 1981.

I Fundamentals of solid state

I.1 Introduction

The nanoworld

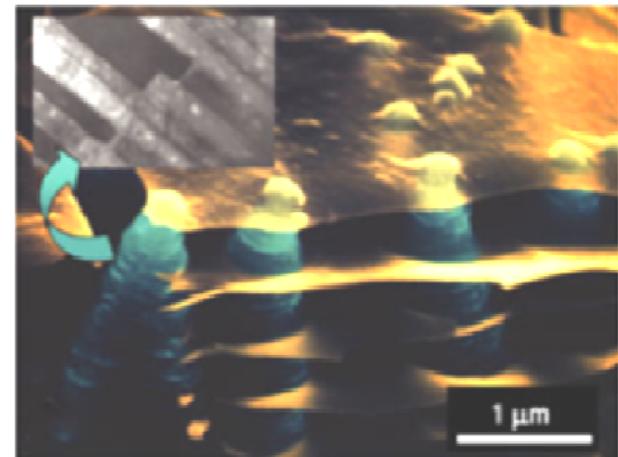
Dimensions 1 - 100s nm



Abalone (g. *Haliotis*) Orella de mar



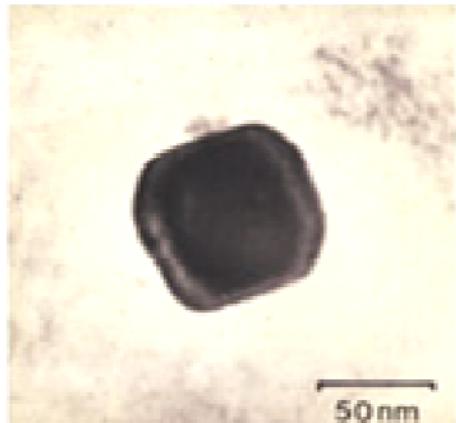
Scanning electron microscopy (SEM) image of a growth edge of abalone (*Haliotis rufescens*) displaying aragonite (calcium carbonate) platelets (blue) separated by organic film (orange) that eventually becomes nacre. Inset: transmission electron microscope (TEM) image.



I Fundamentals of solid state

I.1 Introduction

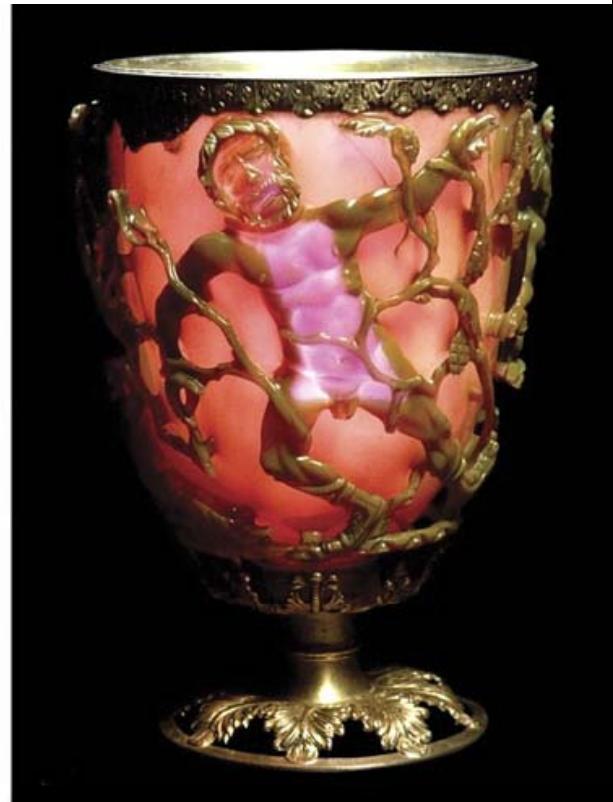
The nanoworld



Licurgo's cup (s IV aC). Silver and gold nanoparticles



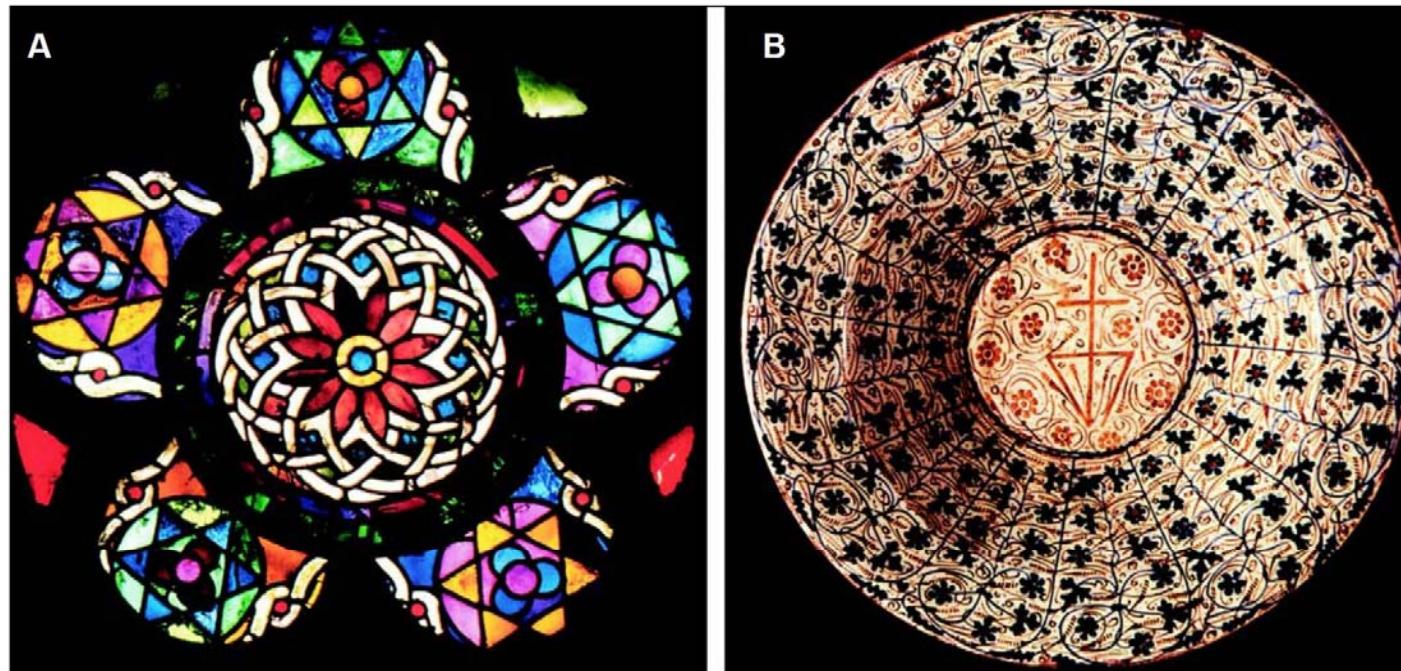
Reflected light



Transmited light

I Fundamentals of solid state

I.1 Introduction



(A) Stained glass at Monasteri de Santes Creus (Cister s. XIII aC)
(B) Maises ceramic plate (~ s. XI aC). Metallic reflections and iridescence were obtained using metelic nanoparticles or films (Pérez-Arantegui et al. 2001).

There's plenty of room at the bottom (R. Feynman)

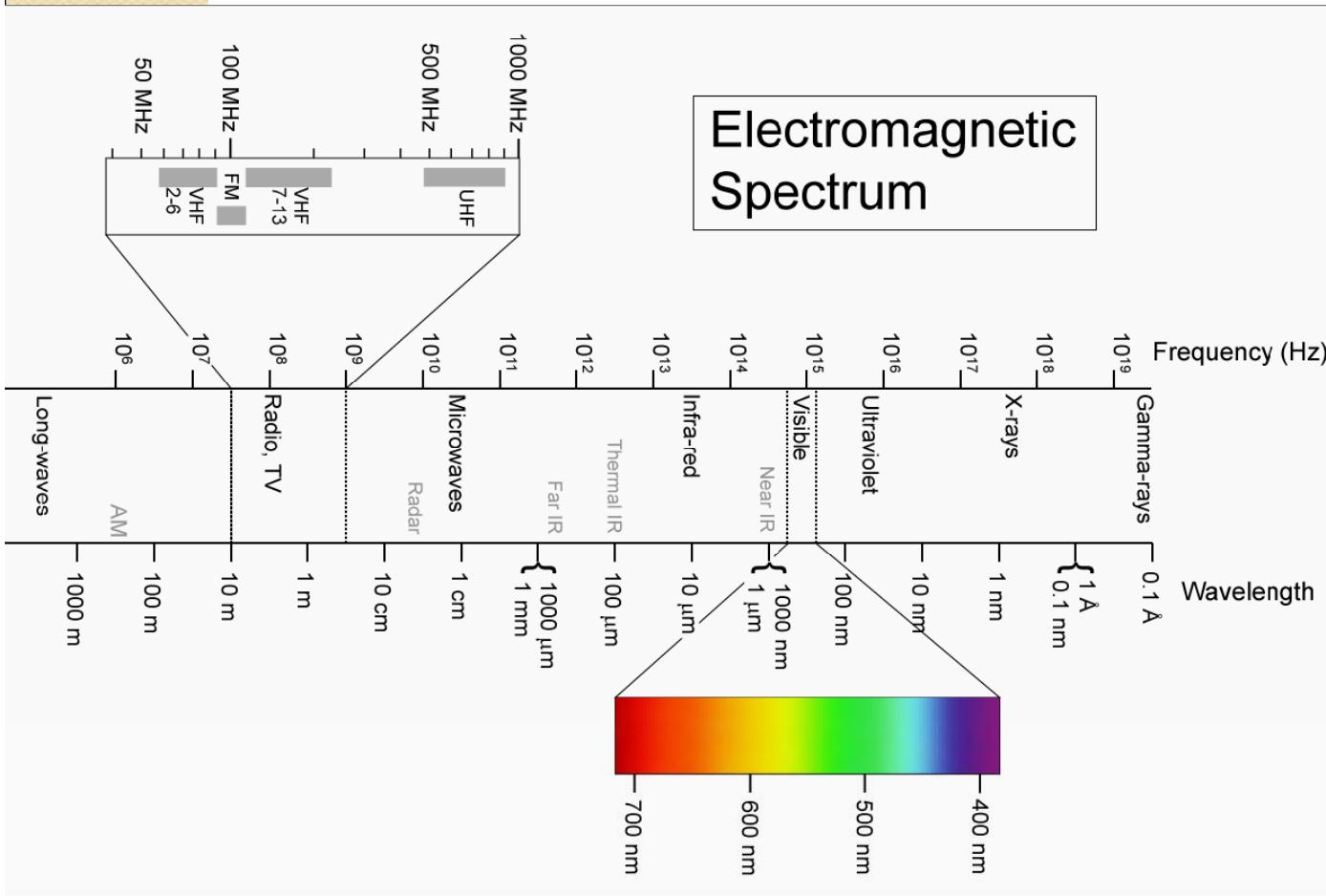
<https://www.youtube.com/watch?v=4eRCygdW--c>

<http://muonray.blogspot.ie/2012/12/richard-feynman-theres-plenty-of-room.html>

I Fundamentals of solid state

I.I Atoms and light

Electromagnetic spectrum



$$\nu = \frac{c}{\lambda}$$

$$E = h\nu = h \frac{c}{\lambda}$$

$h = 6.63 \cdot 10^{-34} \text{ J}\cdot\text{s}$:
Planck's constant .

$c = 3 \cdot 10^8 \text{ m}\cdot\text{s}^{-1}$:
light speed in vacuum
 ν (or f): frequency (Hz)
 λ : wave length (nm)

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

$\hbar = h/2p = 1.1 \cdot 10^{-34} \text{ J}\cdot\text{s}$
Reduced Plank const. or
Dirac constant

$$E = \hbar\omega$$

ω angular frequency

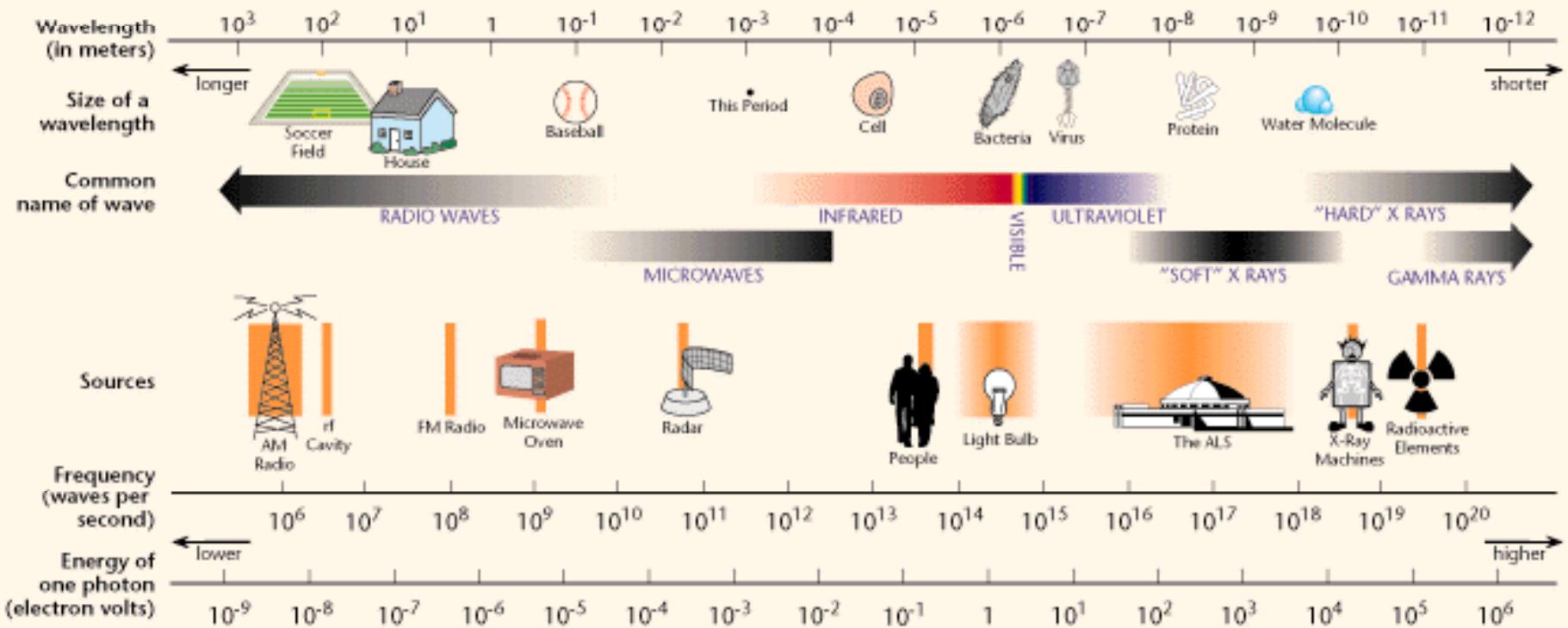
I Fundamentals of solid state

I.I Atoms and light

Electromagnetic spectrum

$$E = h\nu = h \frac{c}{\lambda}$$

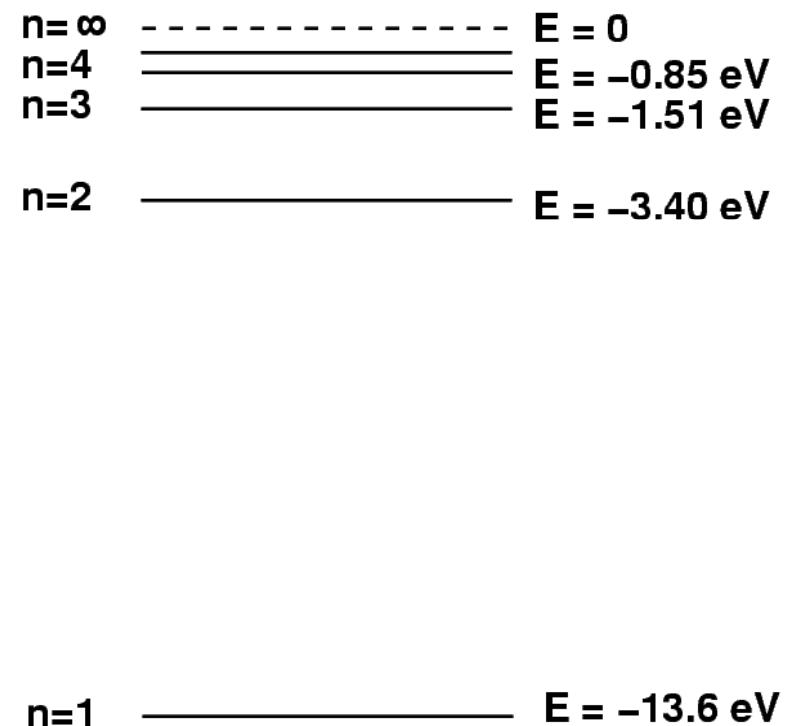
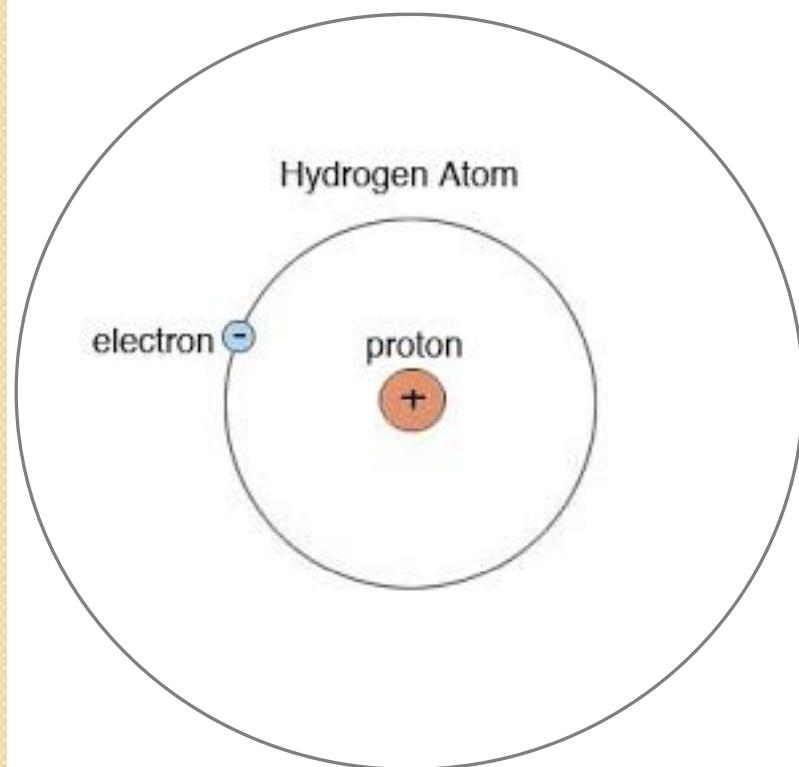
THE ELECTROMAGNETIC SPECTRUM



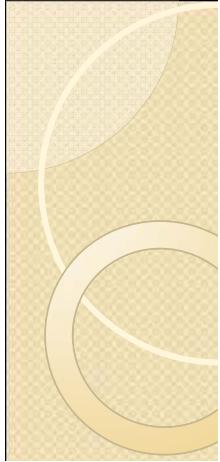
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I.I Atoms and light

Energy levels in Hydrogen Atom



$$1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$$

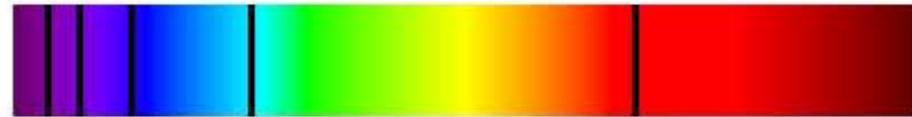


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I.I Atoms and light

Energy of photons

Hydrogen Absorption Spectrum



Hydrogen Emission Spectrum



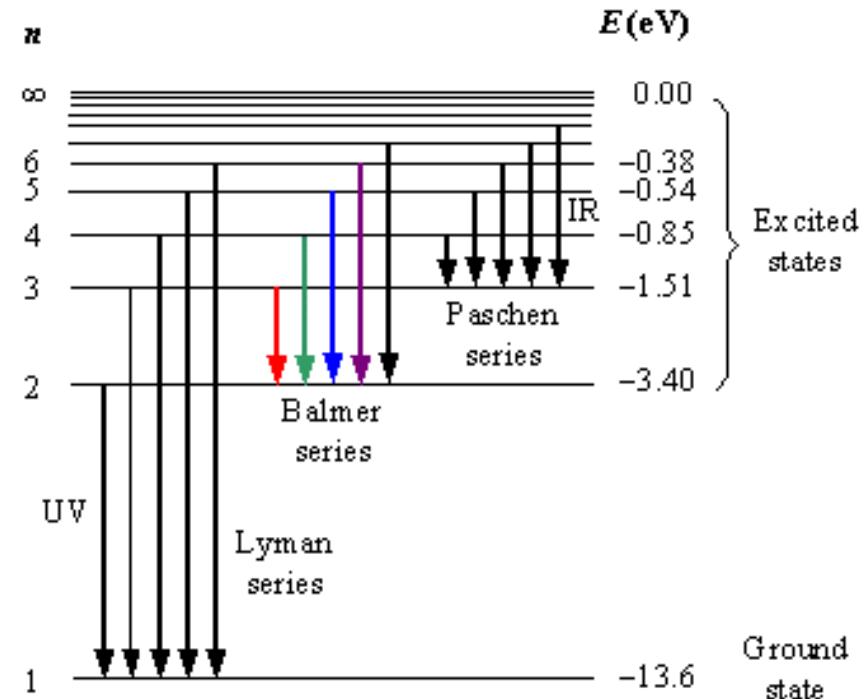
400nm

700nm

$$E = h\nu$$

H Alpha Line
656nm
Transition N=3 to N=2

$h = 6.63 \cdot 10^{-34} \text{ J}\cdot\text{s}$: Planck's constant
 ν (or f): frequency (Hz)

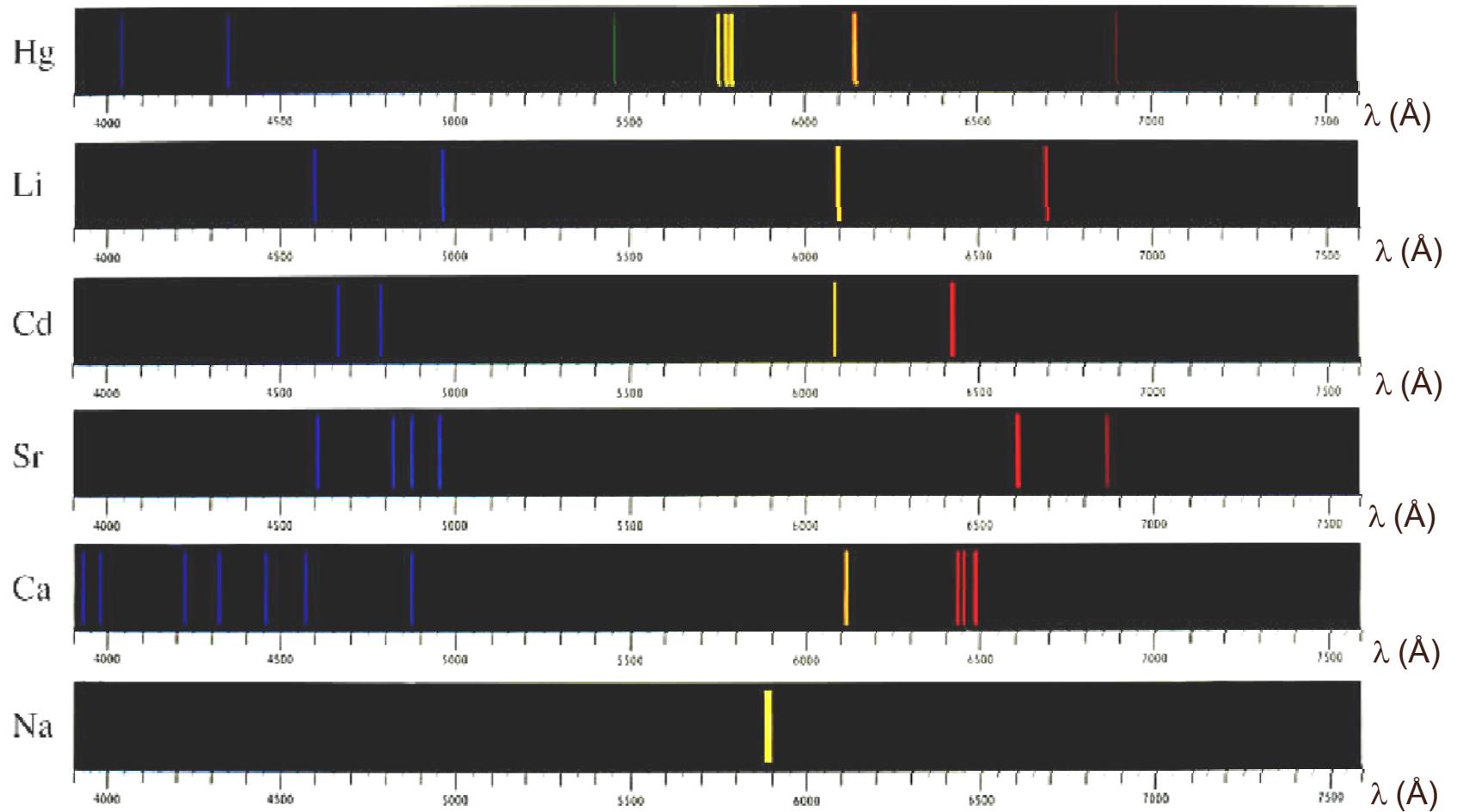


Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated

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I.I Atoms and light

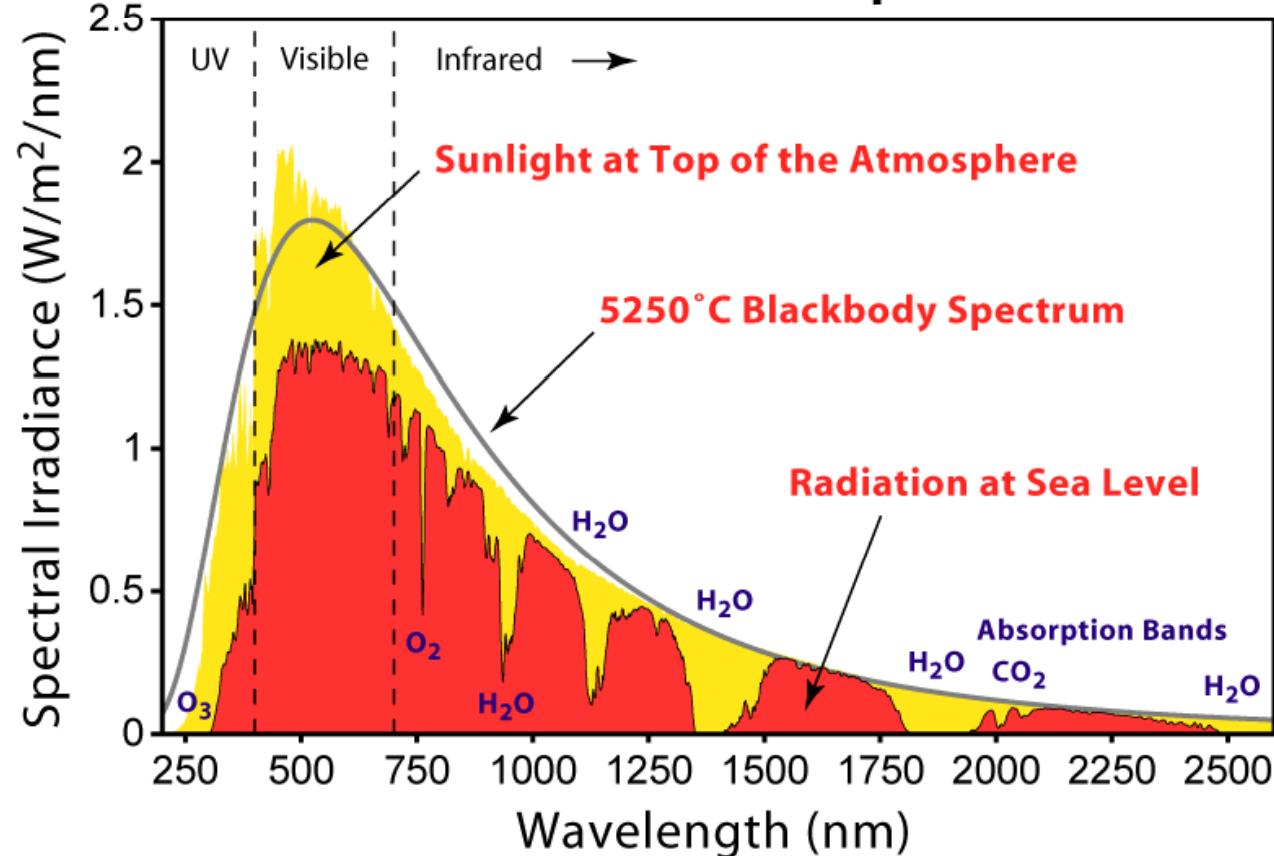
Energy of photons



I Fundamentals of solid state

I.I Atoms and light

Solar Radiation Spectrum $E = h\nu = h \frac{c}{\lambda}$



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I.I Atoms and light

Plank's law black body radiation:

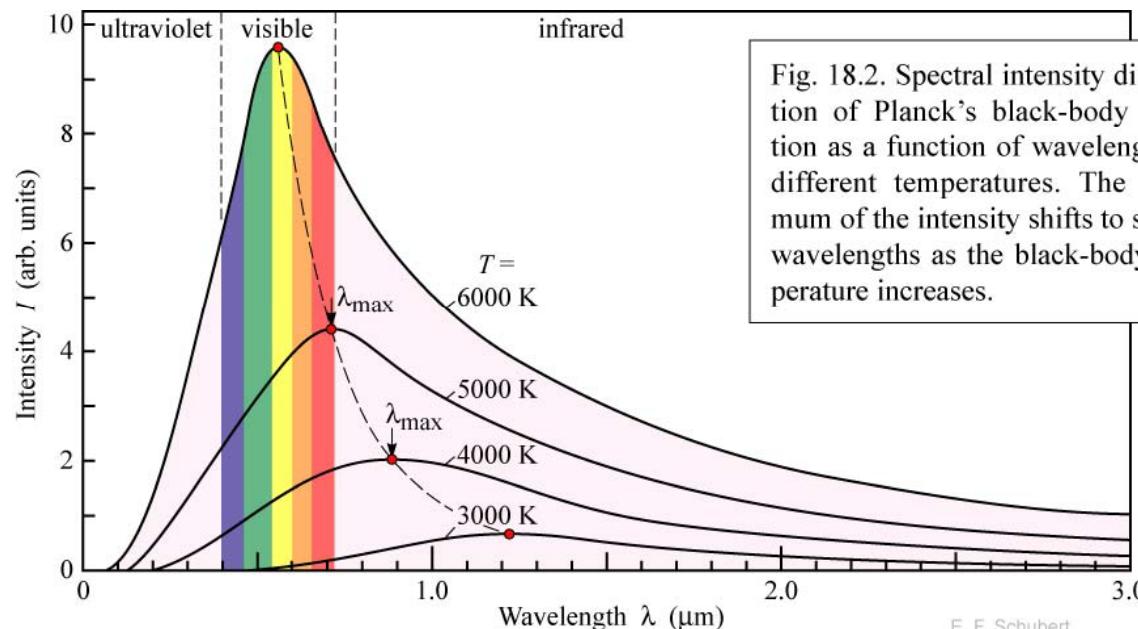


Fig. 18.2. Spectral intensity distribution of Planck's black-body radiation as a function of wavelength for different temperatures. The maximum of the intensity shifts to shorter wavelengths as the black-body temperature increases.

E. F. Schubert

Light-Emitting Diodes (Cambridge Univ. Press)
www.LightEmittingDiodes.org

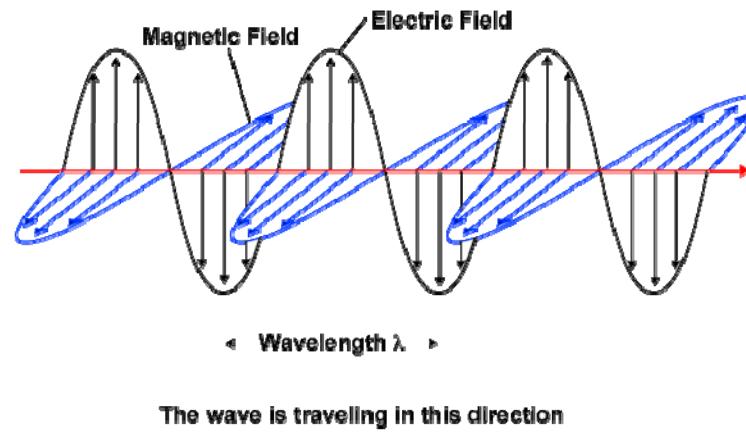
Planck, Max. "On the Law of Distribution of Energy in the Normal Spectrum". *Annalen der Physik* 4: 553 (1901)
<http://weelookang.blogspot.com.es/2010/06/ejs-open-source-java-applet-blackbody.html>

I Fundamentals of solid state

I.I Atoms and light

Light as a wave

Electromagnetic Waves



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Wave function of light in vacuum

$$\nabla^2 \Psi(E, B, x, t) = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \Psi(E, B, x, t)$$

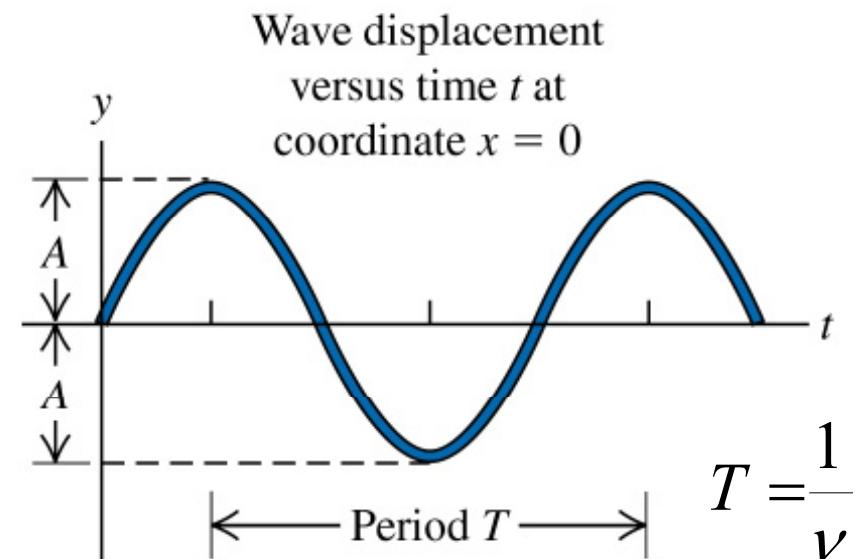
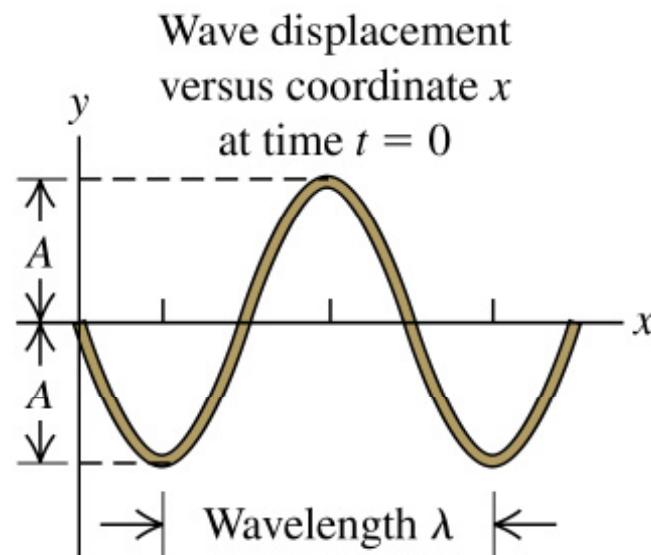
I Fundamentals of solid state

I.I Atoms and light

Wave function for electric field

$$E(x, t) = E_0 \cos[kx - \omega t + \phi_0]$$

With $k = \frac{2\pi}{\lambda}$ the wave number and ϕ_0 the phase.



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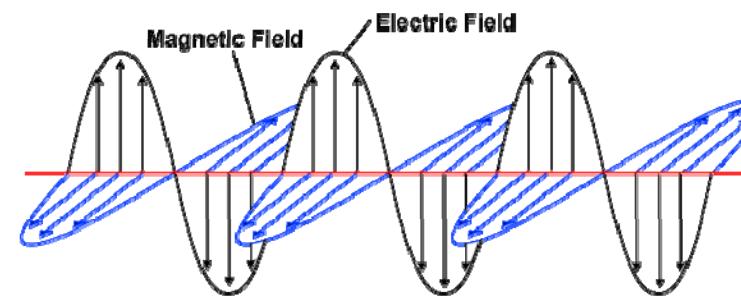
I.I Atoms and light

Wave function in general media

$$\nabla^2 \Psi = \frac{1}{v^2} \frac{\partial^2}{\partial t^2} \Psi$$

$$v = \frac{c}{n} = v \cdot \lambda = \frac{\omega}{k}$$

Electromagnetic Waves



The wave is traveling in this direction

With $n = \sqrt{\mu_r \epsilon_r}$ the refractive index of the medium and

μ_r and ϵ_r the relative permeability and permittivity of the medium

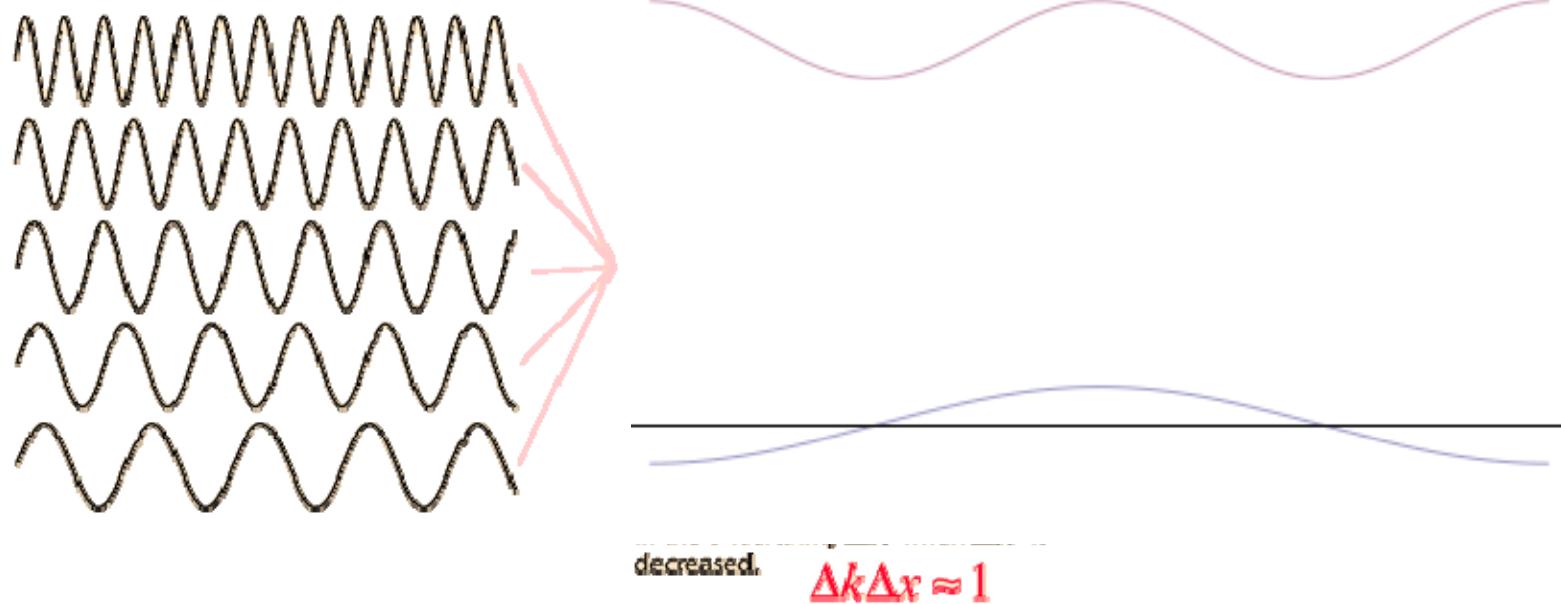
The lineal moment of a light wave is defined as $p = \hbar \cdot k = E / c$

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I.I Atoms and light

Wave superposition and wave packet

$$\Psi_{\Sigma} = \sum a_i \Psi_i$$



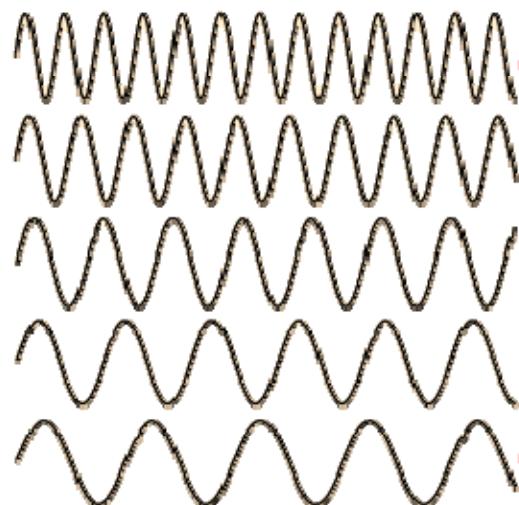
Heisenberg's uncertainty principle: $\Delta p \cdot \Delta x \geq \hbar / 2$

I Fundamentals of solid state

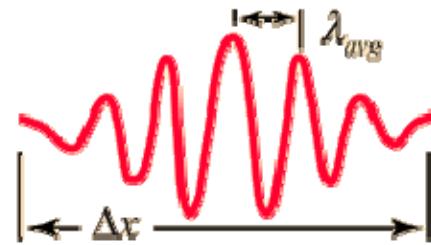
I.I Atoms and light

Wave superposition and wave packet

$$\Psi_{\Sigma} = \sum a_i \Psi_i$$



Adding several waves of different wavelength together will produce an interference pattern which begins to localize the wave.



But that process spreads the wave number k values and makes it more uncertain. This is an inherent and inescapable increase in the uncertainty Δk when Δx is decreased.

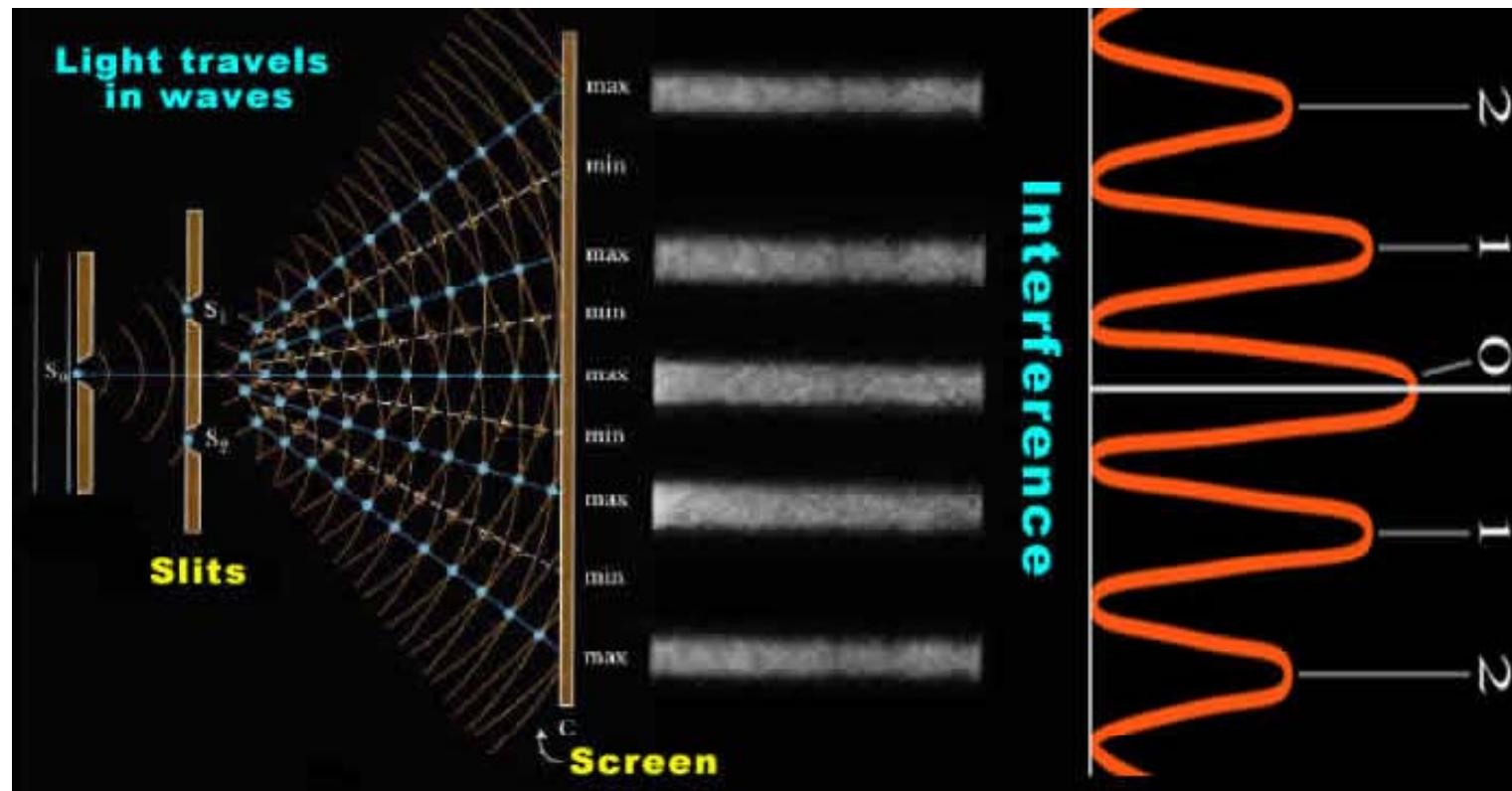
$$\Delta k \Delta x \approx 1$$

Heisenberg's uncertainty principle: $\Delta p \cdot \Delta x \geq \hbar / 2$

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I.I Atoms and light

Diffraction (Young, 1806)



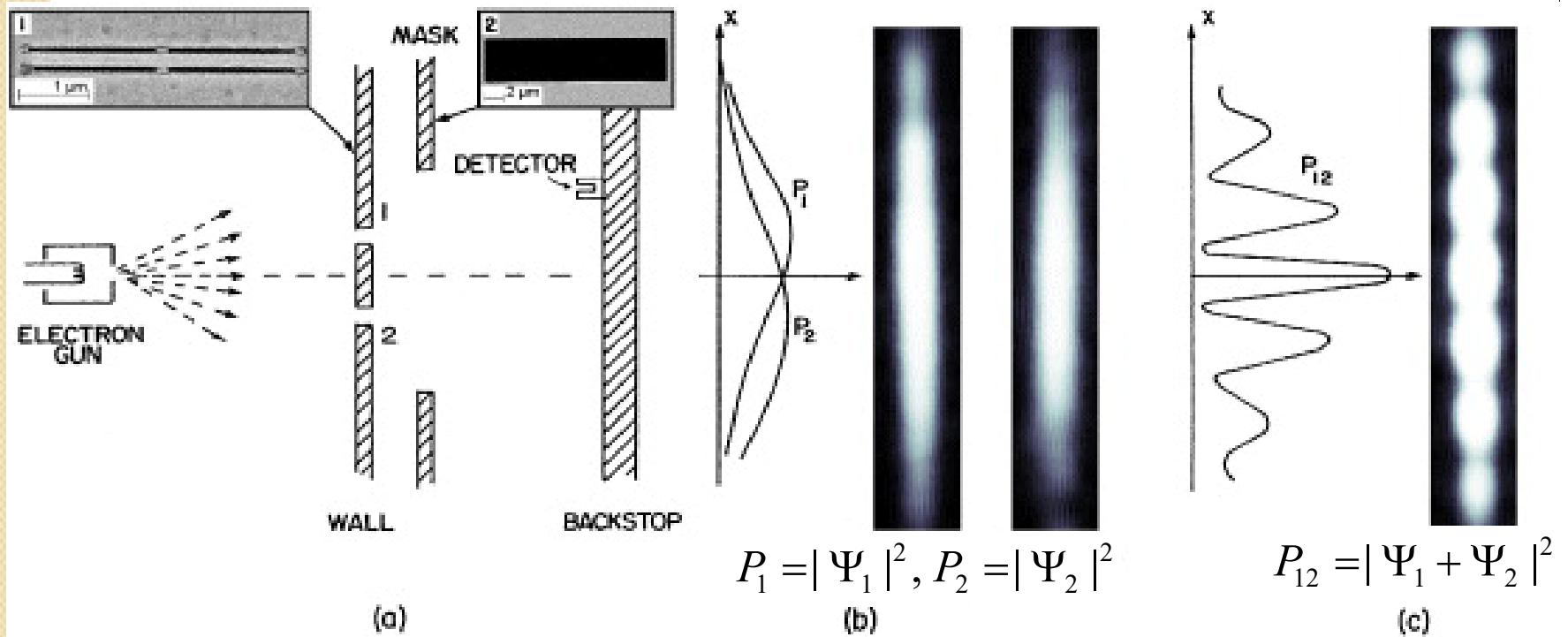
https://www.youtube.com/watch?v=6Q4_nl0ICao

I Fundamentals of solid state

I.I Atoms and light

Matter as a wave

Theory de Broglie 1924
Experiments Thomson, Davisson



slits are 62 nm wide \times 4 μm tall and separated by 272 nm

Mask may block individual slits..... or none

The Feynman Lectures on Physics, vol III, Richard P Feynman, Robert B Leighton and Matthew Sands. Ed. The Perseus Books Group. 2011.

I Fundamentals of solid state

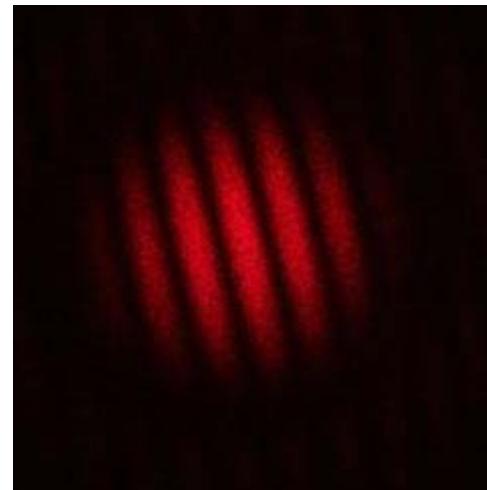
I.I Atoms and light

Matter as a wave

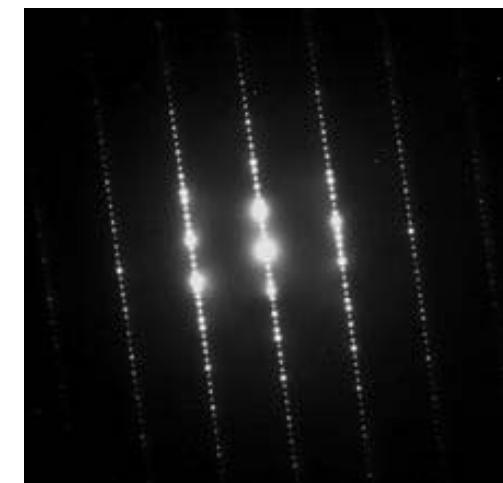
Theory: de Broglie, 1924

Experimental demonstration: Thomson, Davisson and Germer, 1927

Nobel prize: 1937



Light difraction pattern

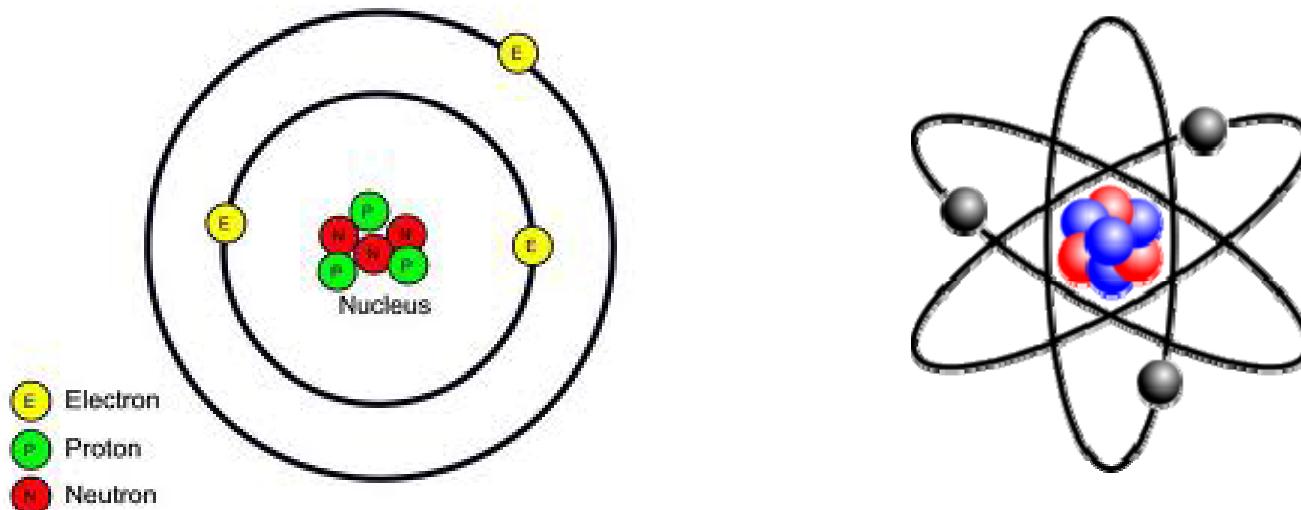


electron difraction pattern

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I.2 Wave function of matter

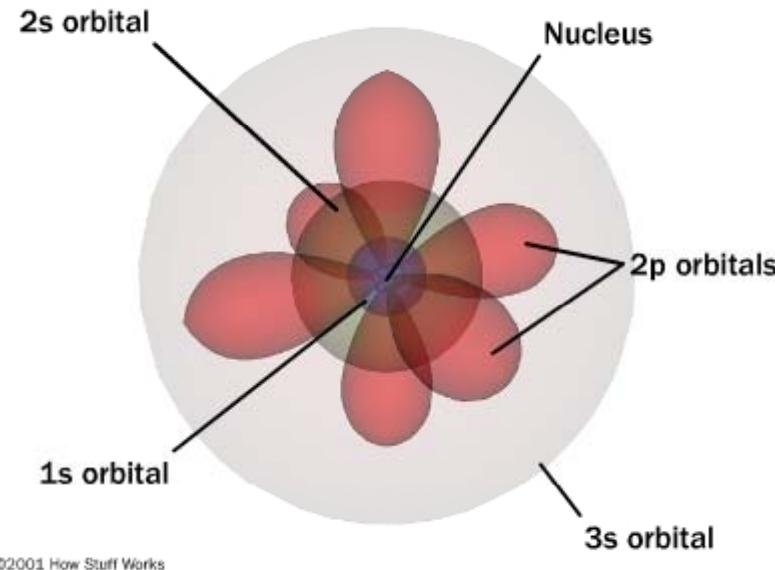
Shape of orbitals



I Fundamentals of solid state

I.2 Wave function of matter

Shape of orbitals



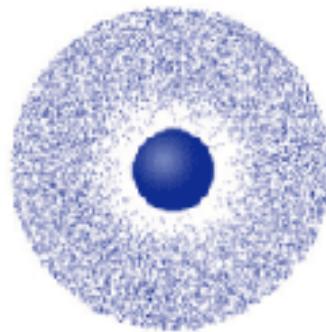
$$P = |\Psi|^2$$

I Fundamentals of solid state

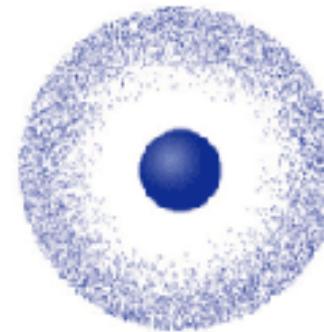
I.2 Wave function of matter

Shape of orbitals

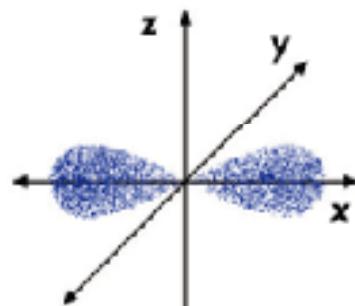
$|\Psi|^2$ = probability density function



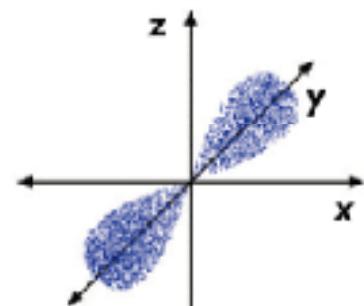
Orbital 1s



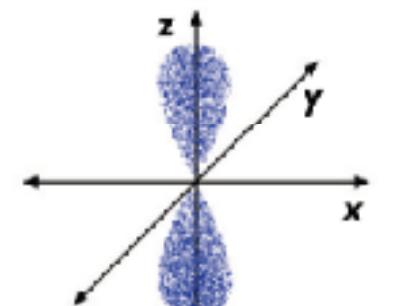
Orbital 2s



Orbital 2p_x



Orbital 2p_y



Orbital 2p_z

I Fundamentals of solid state

I.2 Wave function of matter

General Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \Psi(r,t) = \hat{H} \Psi(r,t)$$



With \hat{H} the Hamiltonian

Schrödinger Equation for a non relativistic particle in a potential V

$$i\hbar \frac{\partial}{\partial t} \Psi(r,t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r,t) \right) \Psi(r,t)$$

Remembre the laplacian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$



I Fundamentals of solid state

I.2 Wave function of matter

Test General Schrödinger Equation

$$i\hbar \frac{\partial}{\partial t} \Psi(r, t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(r, t) \right) \Psi(r, t)$$

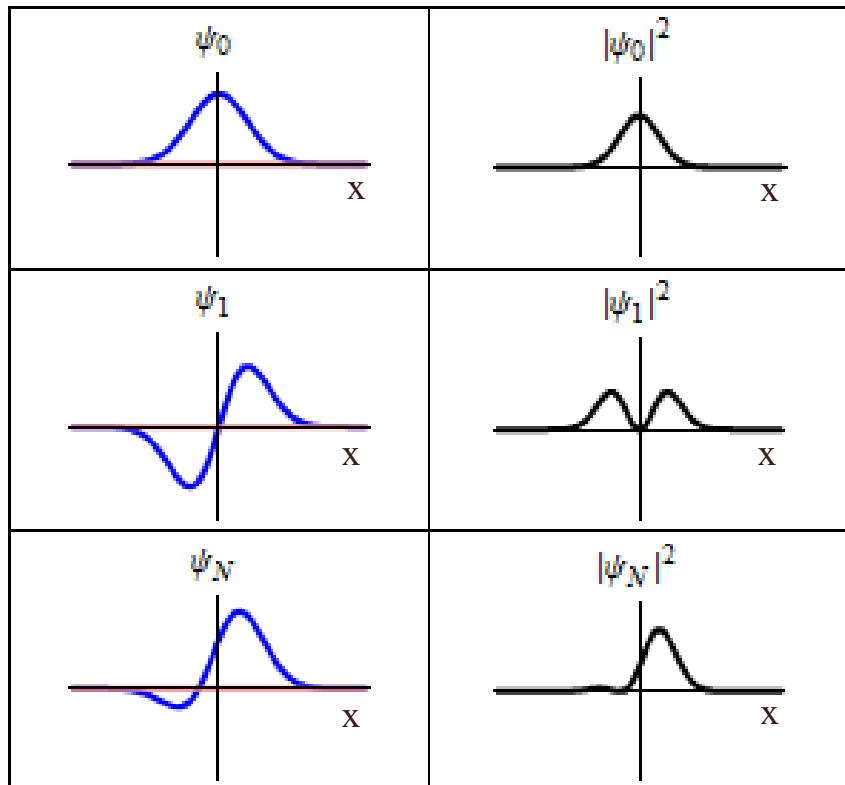
With a unidimensional wave propagating to the right

$$\Psi(x, t) = A \sin(kx - \omega t)$$

I Fundamentals of solid state

I.2 Wave function of matter

Stationary states of energy E accomplish



$$E \Psi(r, t) = \hat{H} \Psi(r, t)$$

Standing wave

Standing wave

Non standing wave

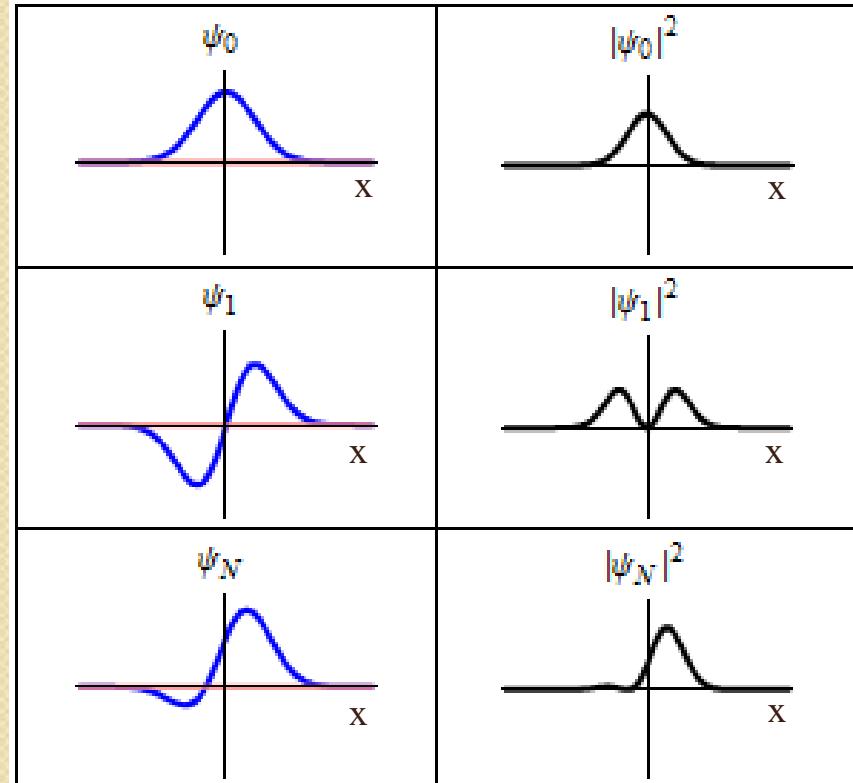
Left: The real part (blue) and imaginary part (red) of the wavefunction. Right: The probability of finding the particle at a certain position.



I Fundamentals of solid state

I.2 Wave function of matter

Stationary states of energy E accomplish



Left: The real part (blue) and imaginary part (red) of the wavefunction. Right: The probability of finding the particle at a certain position.

$$\Psi(x, t) = A \sin(kx - \omega t)$$

$$\Psi'(x, t) = A \sin(kx + \omega t)$$

Total wave

$$\begin{aligned}\Psi_T &= \Psi(x, t) + \Psi'(x, t) = \\ &= A \sin(kx - \omega t) + A \sin(kx + \omega t) \\ &= 2A \sin(kx) \cos(\omega t)\end{aligned}$$

When Ψ_T is zero?



I Fundamentals of solid state

I.3 Energy bands in solids

Electron in an infinite well

Schrödinger equation

$$\frac{\hbar^2}{2m} \nabla^2 \Psi - V \Psi - i\hbar \frac{\partial}{\partial t} \Psi = 0$$

$$\frac{\hbar^2}{2m} \left[\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right] - V \Psi - i\hbar \frac{\partial}{\partial t} \Psi = 0$$

In one dimension and stationary conditions reduces to

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \Psi = 0$$

I Fundamentals of solid state

I.3 Energy bands in solids

Electron in an infinite well

Inside the well

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

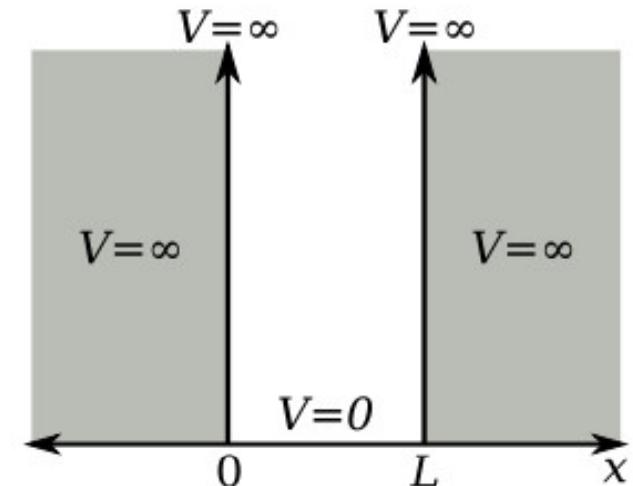
With solution

$$\Psi(x) = A \sin(kx)$$

Where A is constant and

$$k^2 = \frac{2mE}{\hbar^2} \rightarrow \hbar^2 k^2 = p^2 = 2mE$$

As $\Psi = 0$ in $x=0$ and $x=L$ $k = n \frac{\pi}{L}$ with n integer number



I Fundamentals of solid state

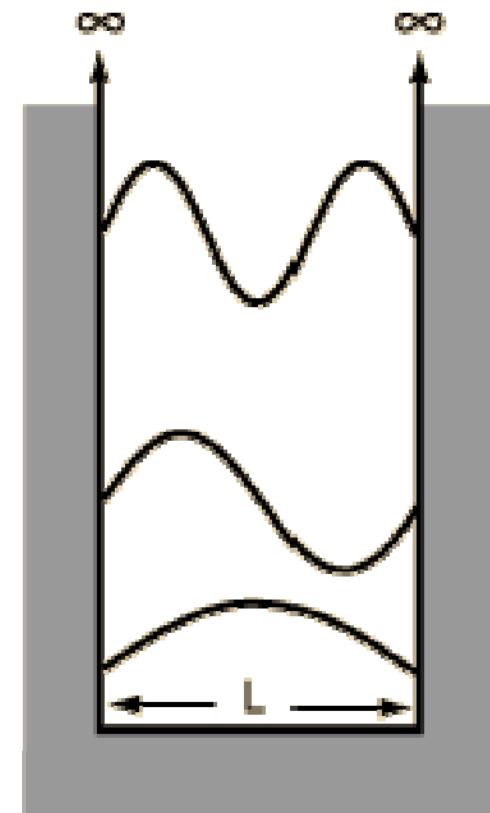
I.3 Energy bands in solids

Electron in an infinite well

$$E = \frac{n^2 \hbar^2}{8mL^2} \quad k = n \frac{\pi}{L}$$

Energy and wave number (moment) are quantized (by quantum number n) and only certain wave functions are allowed

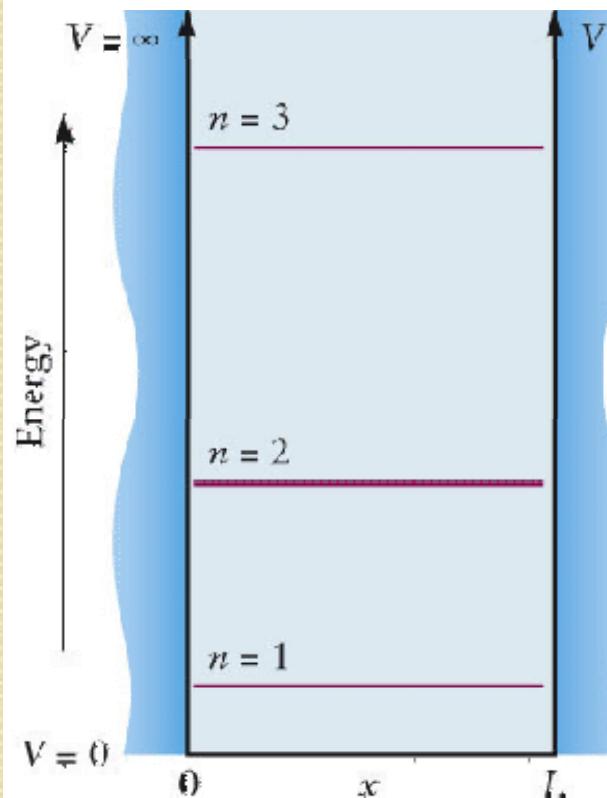
$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(n \frac{\pi}{L} x\right)$$



I Fundamentals of solid state

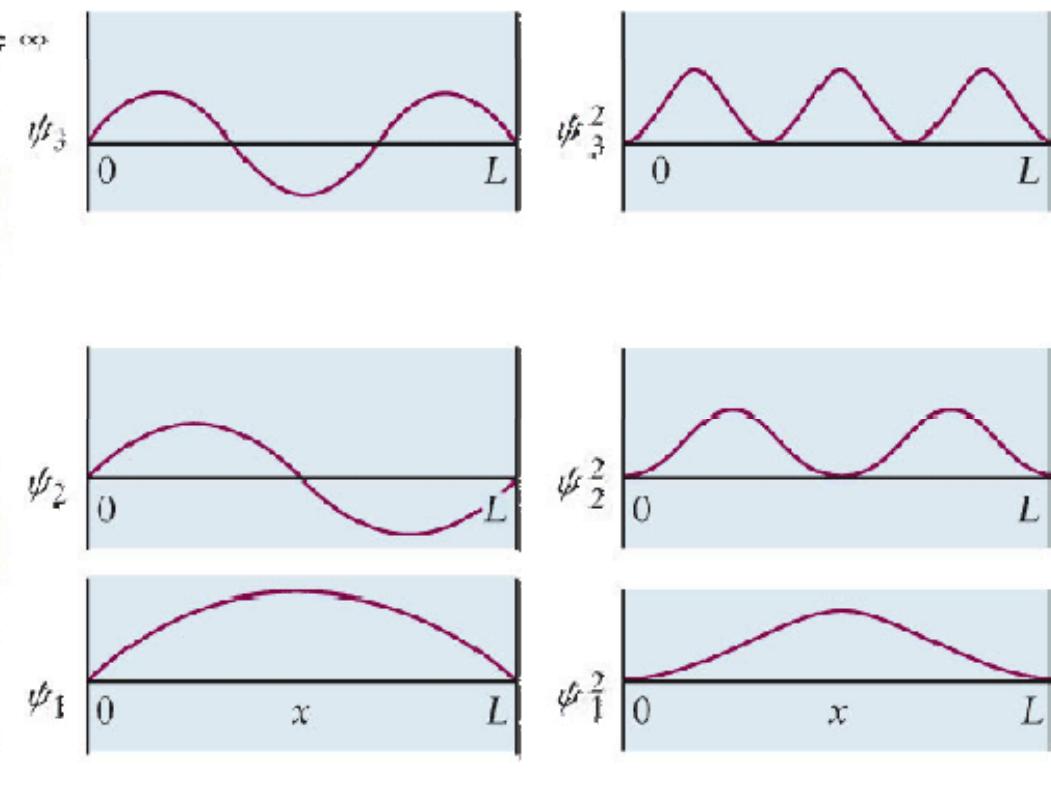
I.3 Energy bands in solids

Electron in an infinite well



(a) Energy levels

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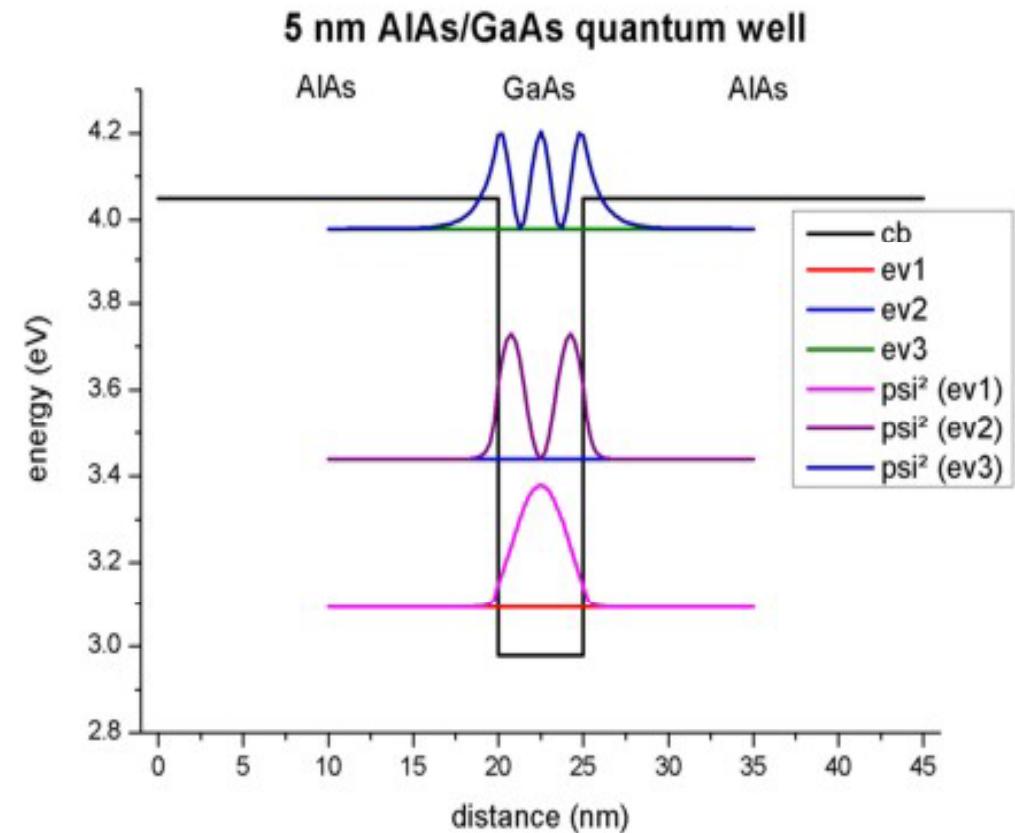
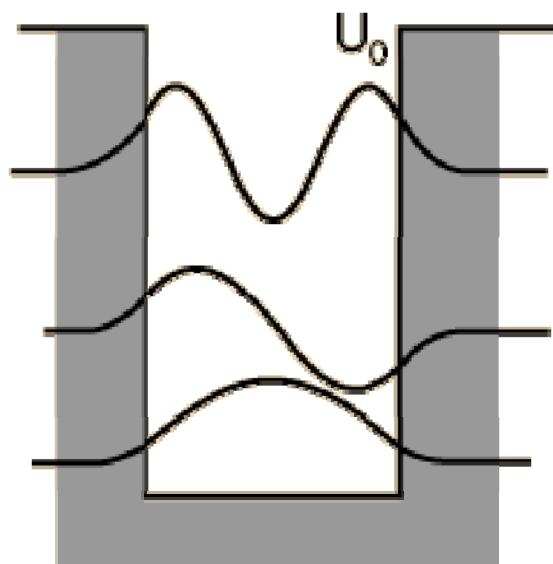
(b) Wave functions

(c) Probabilities

I Fundamentals of solid state

I.3 Energy bands in solids

Electron in a **not** infinite well



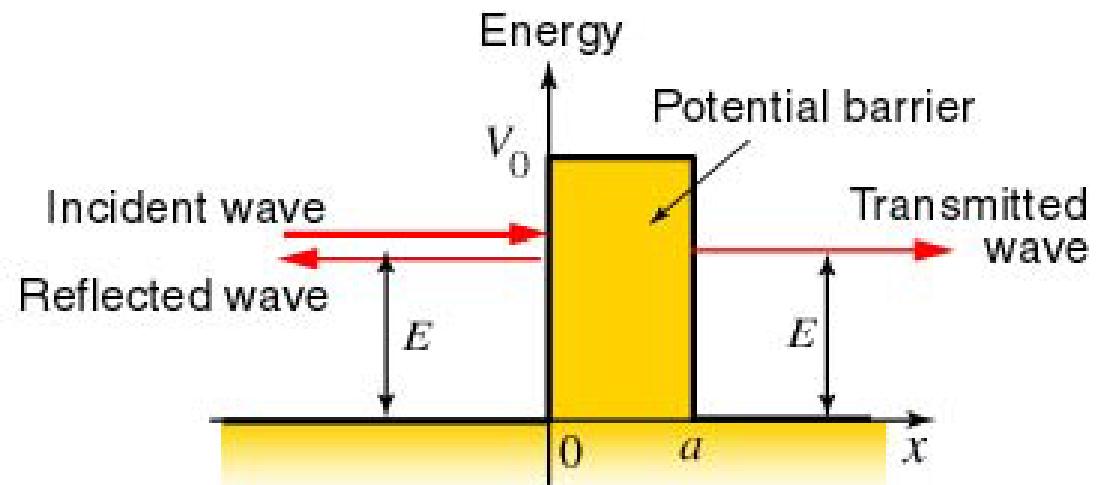
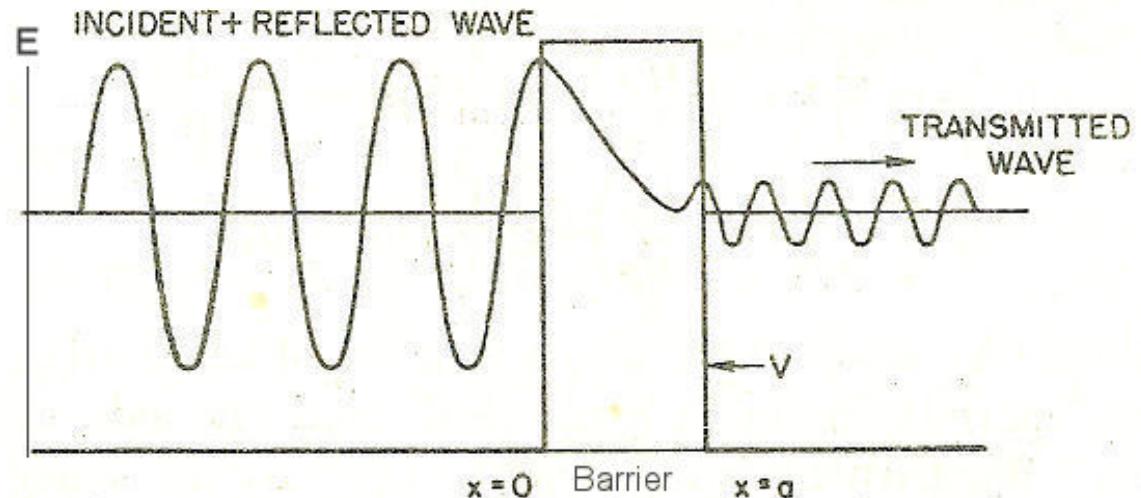
I Fundamentals of solid state

I.2 Wave function of matter

Tunnel effect

Matter has a not null probability of crossing the barrier despite its lower energy.

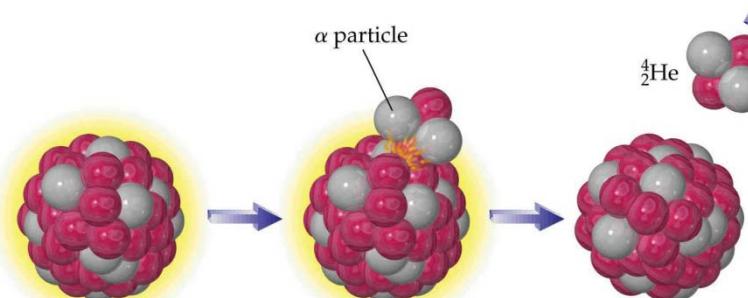
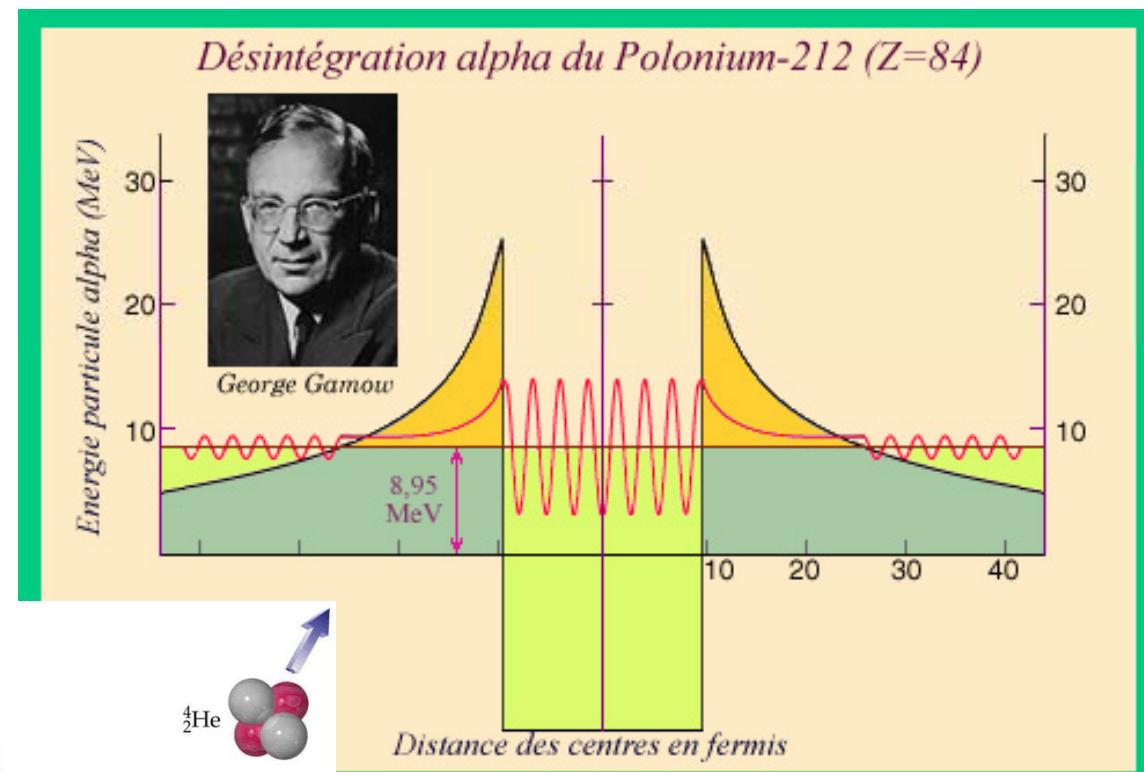
This effect may not occur in classical mechanics in which energy need to be larger than potential to overcome the barrier.



I Fundamentals of solid state

I.2 Wave function of matter

Tunnel effect

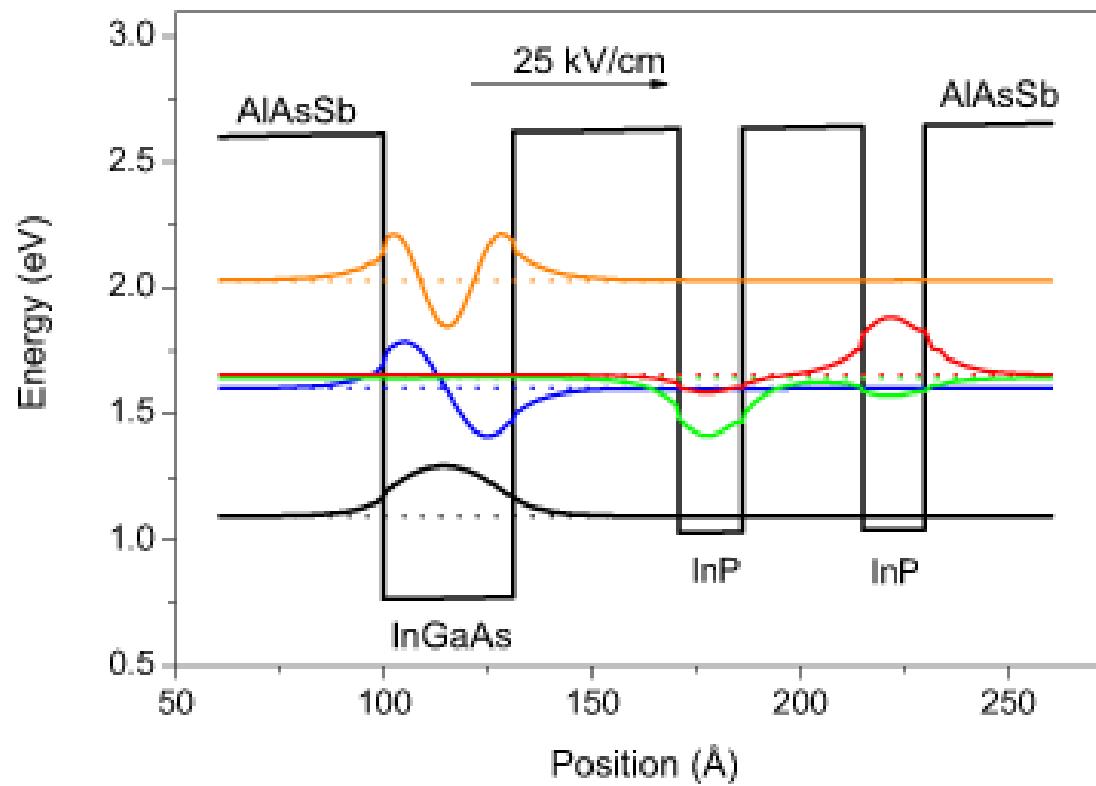


Alfa particle escapes the potential well generated by the nuclear forces

I Fundamentals of solid state

I.3 Energy bands in solids

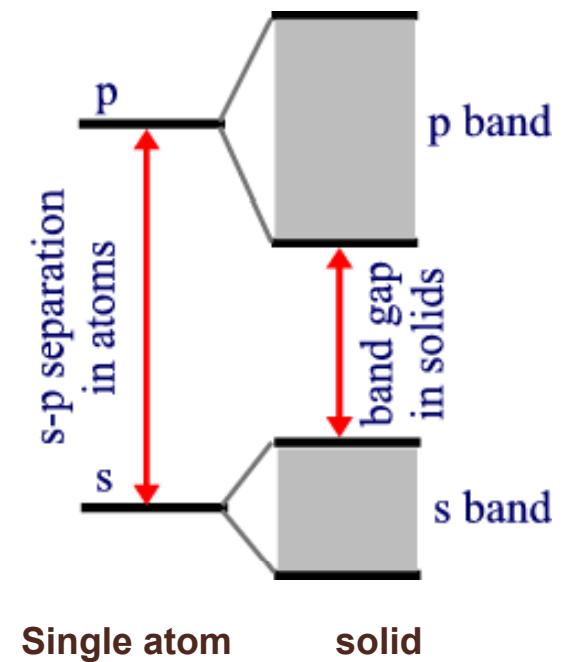
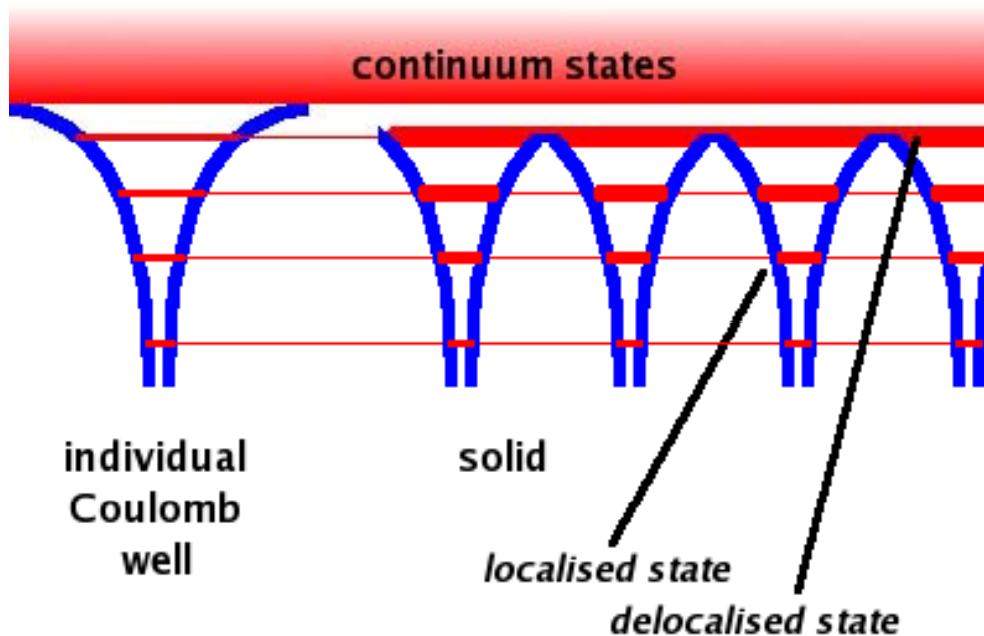
Electron in a **not** infinite well



I Fundamentals of solid state

I.3 Energy bands in solids

Bands in solids

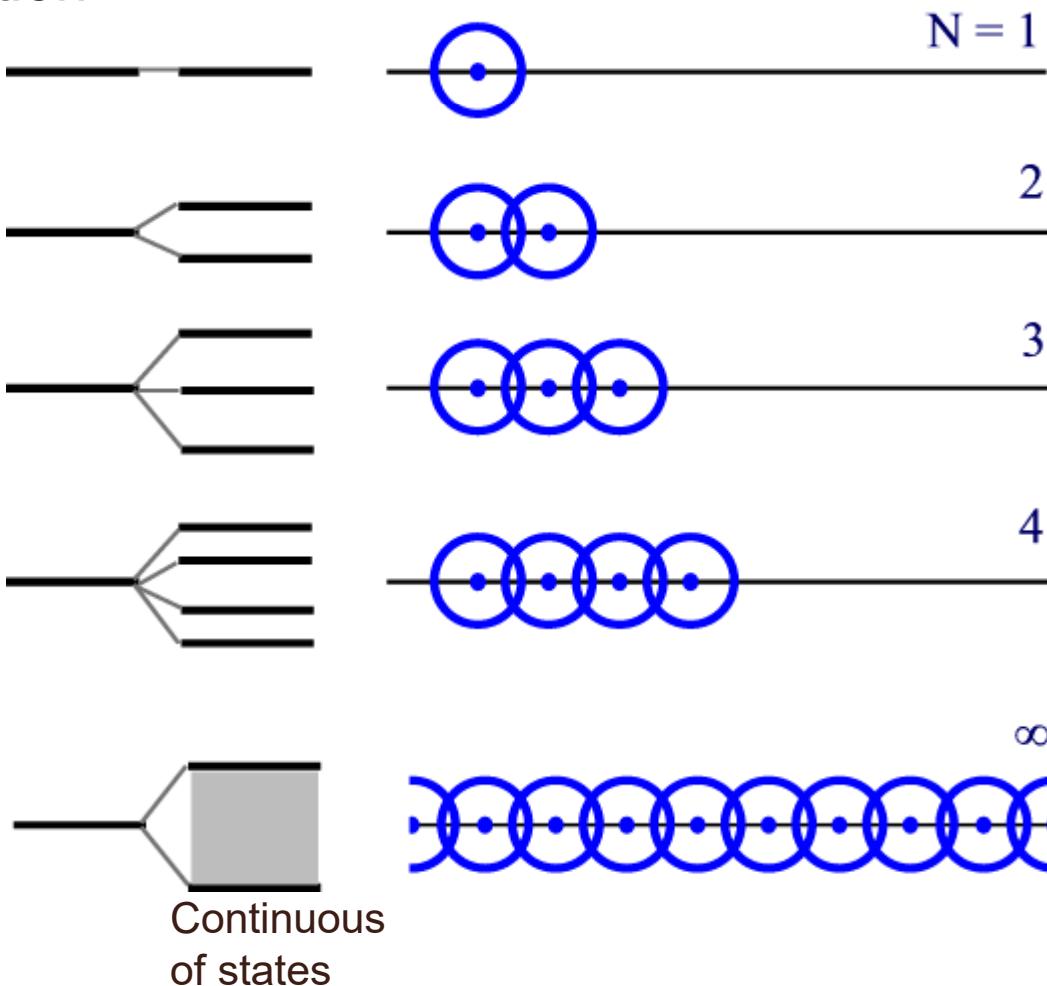


Energy levels widens as a consequence of electron interactions in the crystalline network

I Fundamentals of solid state

I.3 Energy bands in solids

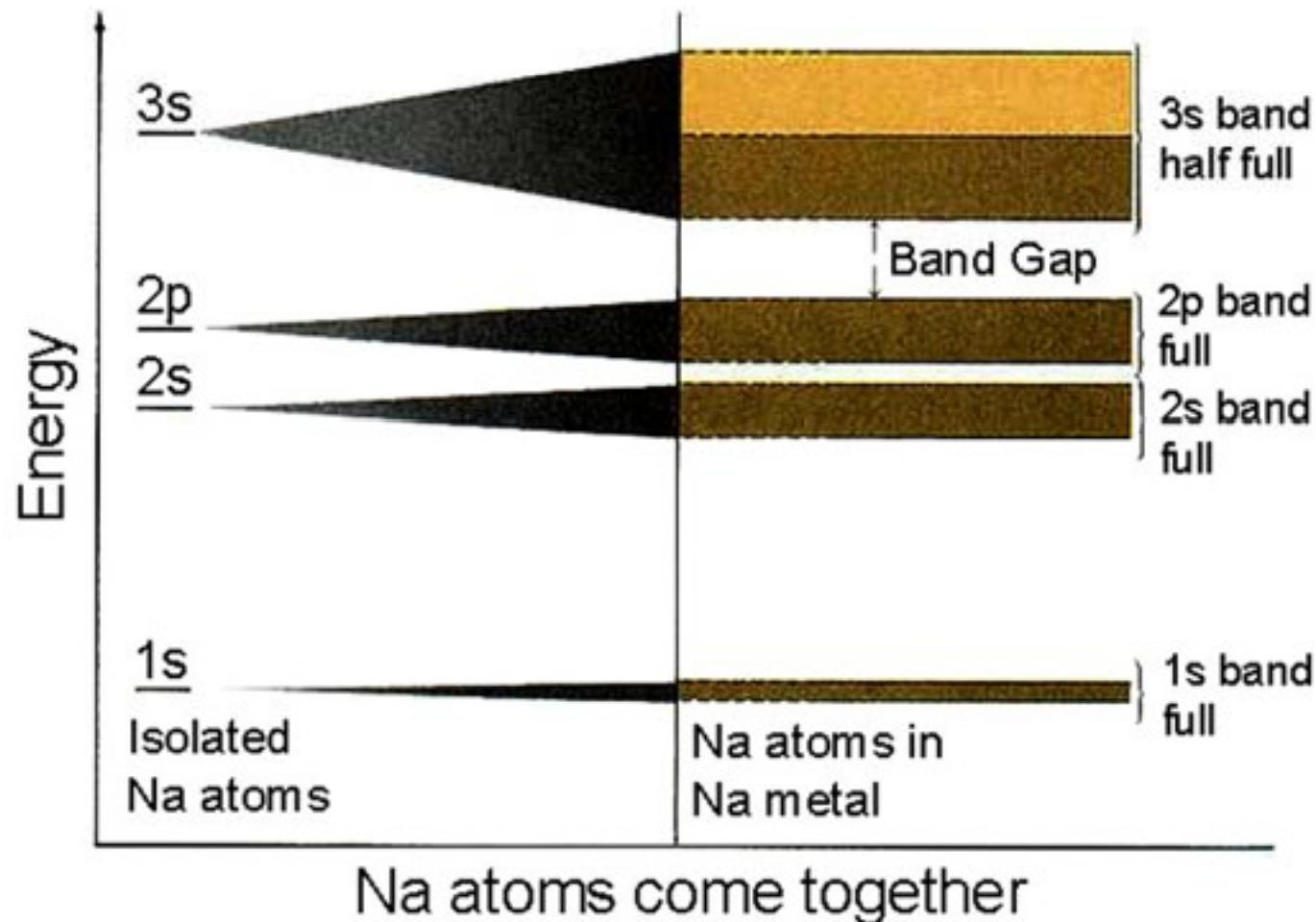
Band formation



I Fundamentals of solid state

I.3 Energy bands in solids

Band formation

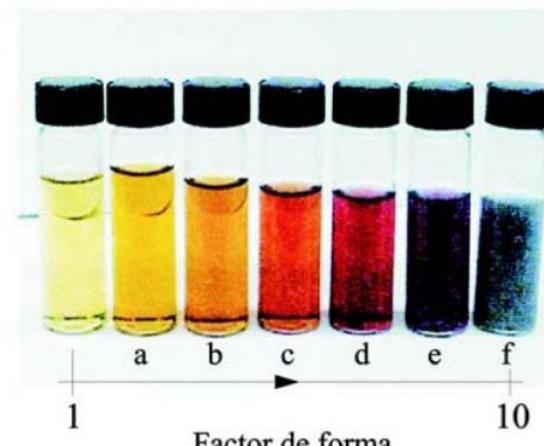
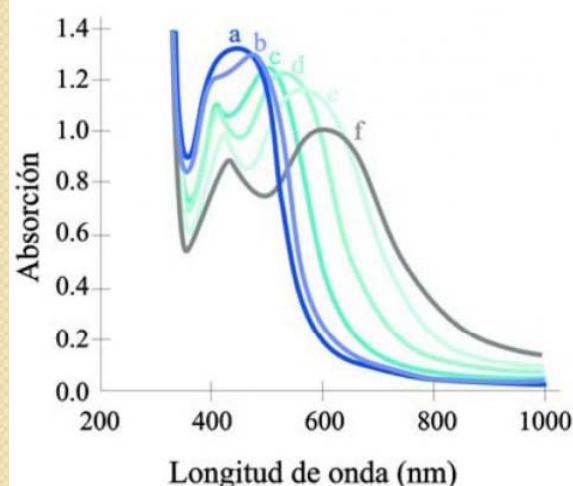
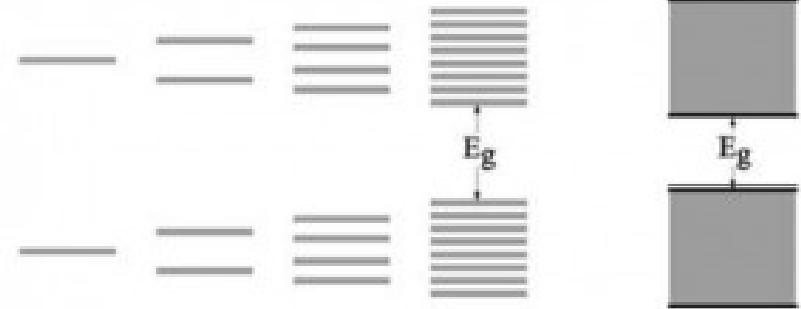


I Fundamentals of solid state

I.3 Energy bands in solids

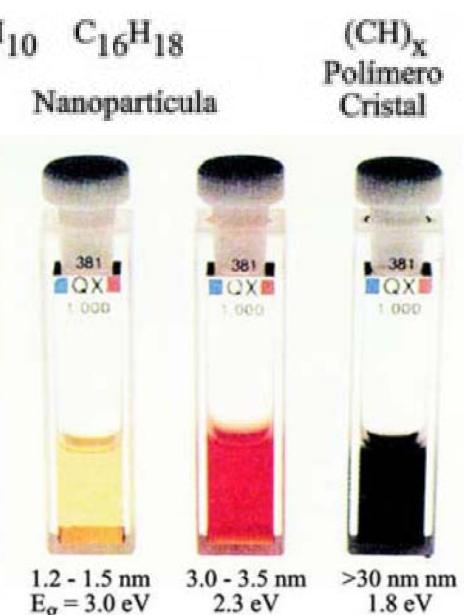
Colour change in solids

Change in electronic energy levels when single molecules form large polymers



Color depends on shape silver nanocilindres in aquoeus solution. Left tube contains 4nm esferic nanoparticles.

<http://www.madrimasd.org/blogs/ingenieriamateriales/2012/04/20/380/>



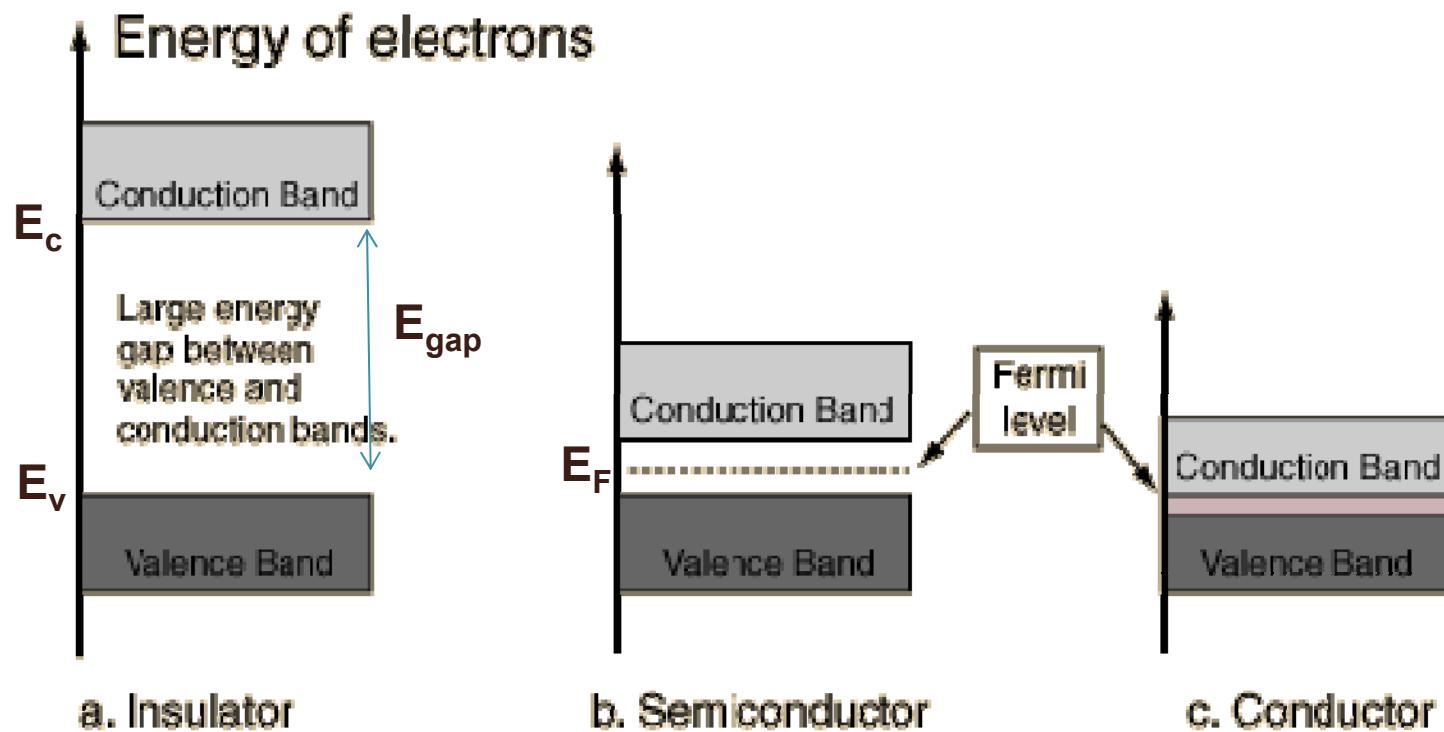
Fluorescence of CdSe nanocolloids

I Fundamentals of solid state

I.3 Energy bands in solids

Solids classification

Looking exclusively on the external electronic bands, materials are classified in:



I Fundamentals of solid state

I.3 Energy bands in solids

Fermi Level

It is the equilibrium energy level of electrons (holes) in materials. it is equivalent to electrochemical potential in electrochemistry and physical-chemistry.

Allows estimating the number of electrons in conduction band and of holes in valence band

$$n = N_c \exp\left[\frac{E_{Fn} - E_c}{k_B T} \right]$$

$k_B = 1.38 \cdot 10^{-23} \text{ J}\cdot\text{K}^{-1}$ is
Boltzmann constant

$$p = N_v \exp\left[\frac{E_v - E_{Fp}}{k_B T} \right]$$

I Fundamentals of solid state

I.3 Energy bands in solids

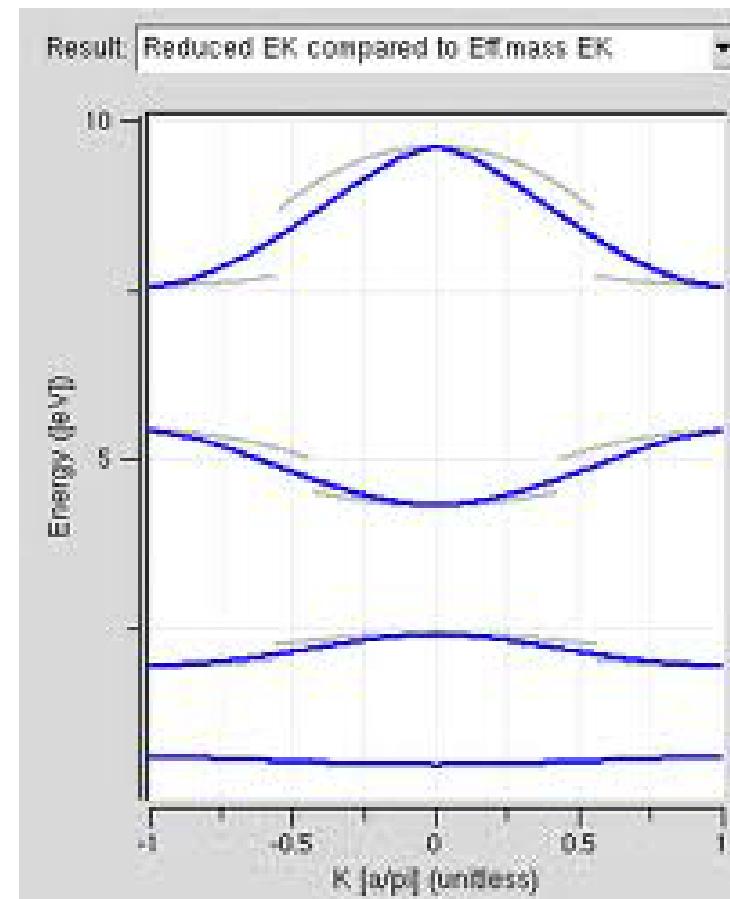
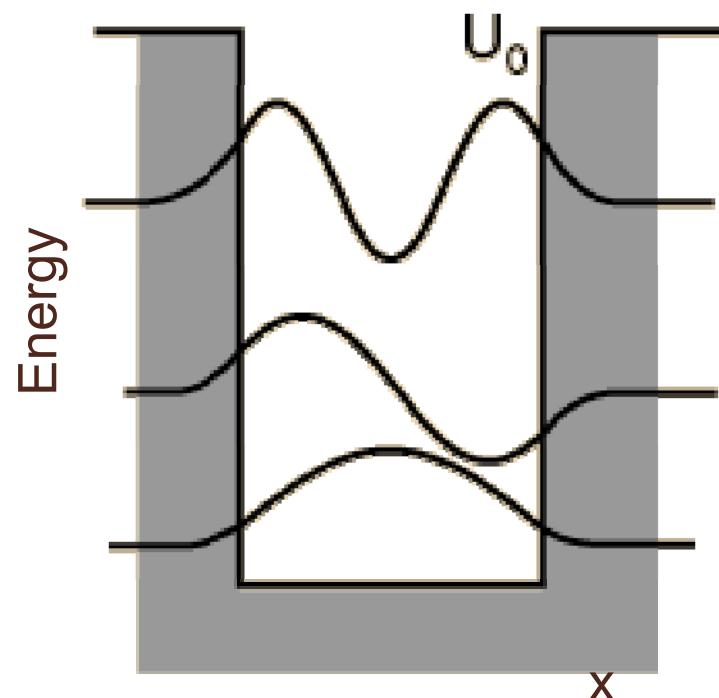
Electron and hole movement



I Fundamentals of solid state

I.3 Energy bands in solids

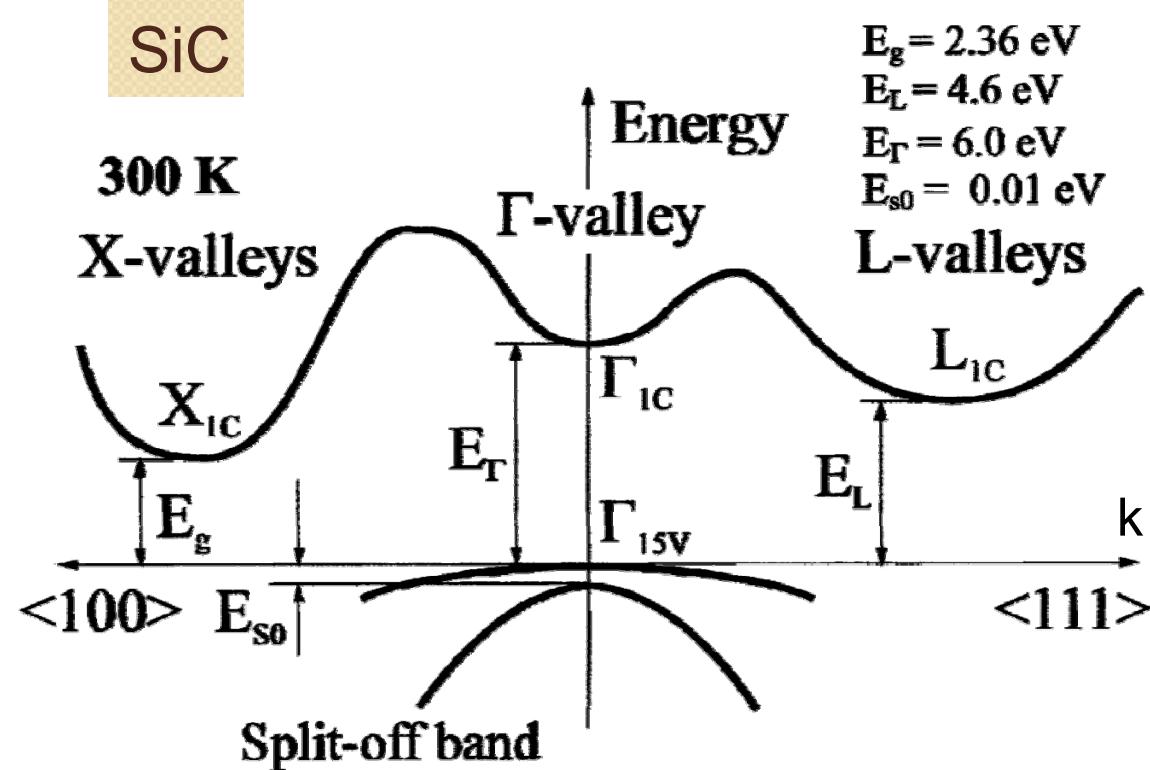
Direct and indirect semiconductors



I Fundamentals of solid state

I.3 Energy bands in solids

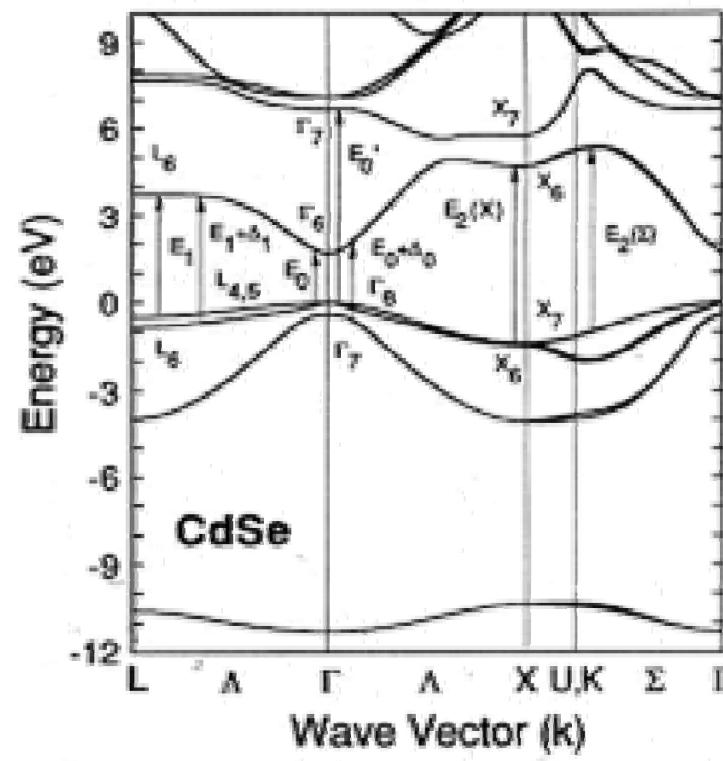
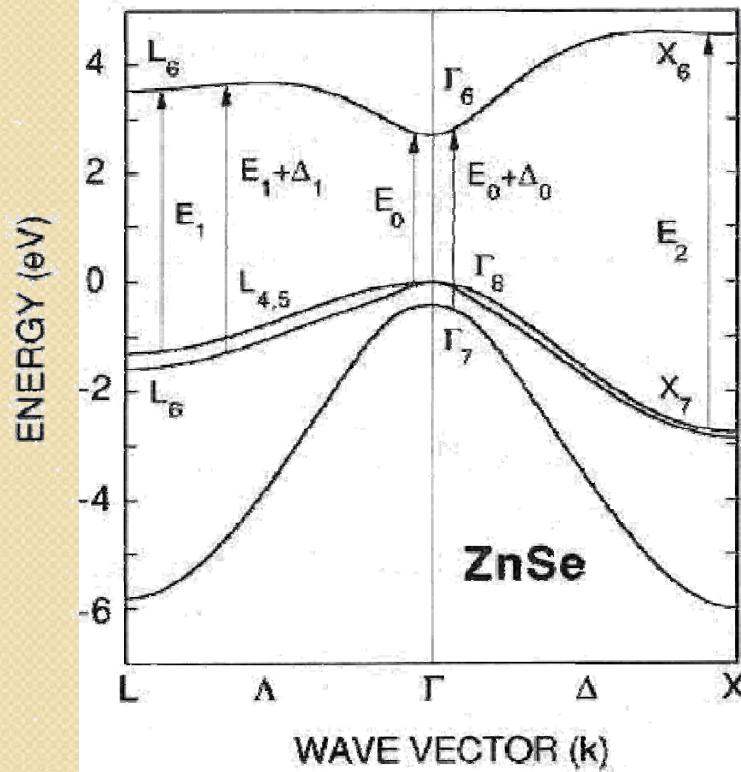
Direct and indirect semiconductors



I Fundamentals of solid state

I.3 Energy bands in solids

Direct and indirect semiconductors

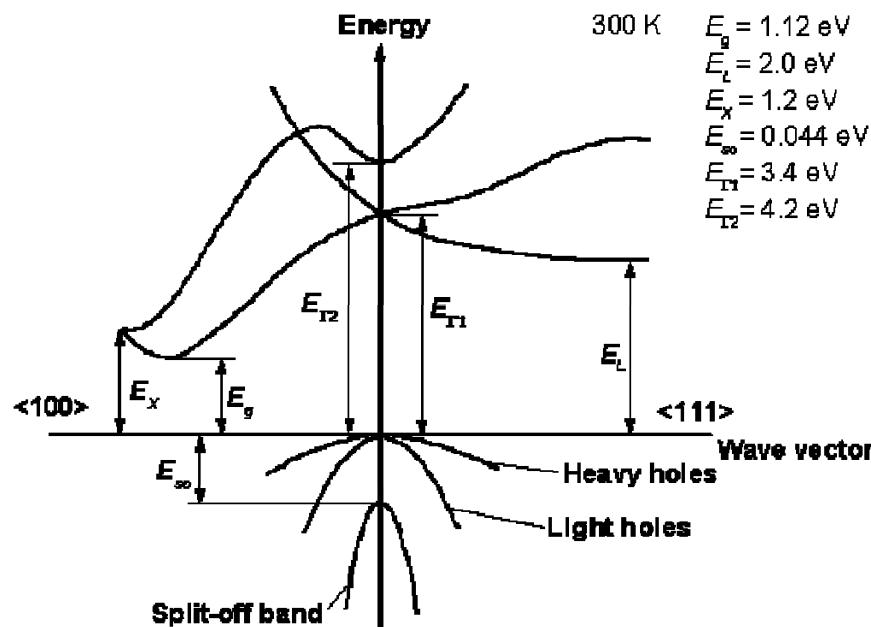


I Fundamentals of solid state

I.3 Energy bands in solids

Direct and indirect semiconductors

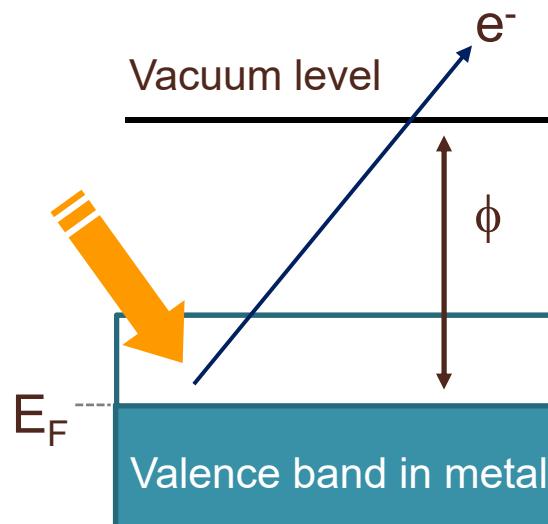
Si



I Fundamentals of solid state

I.3 Energy bands in solids

Work Function in a metal



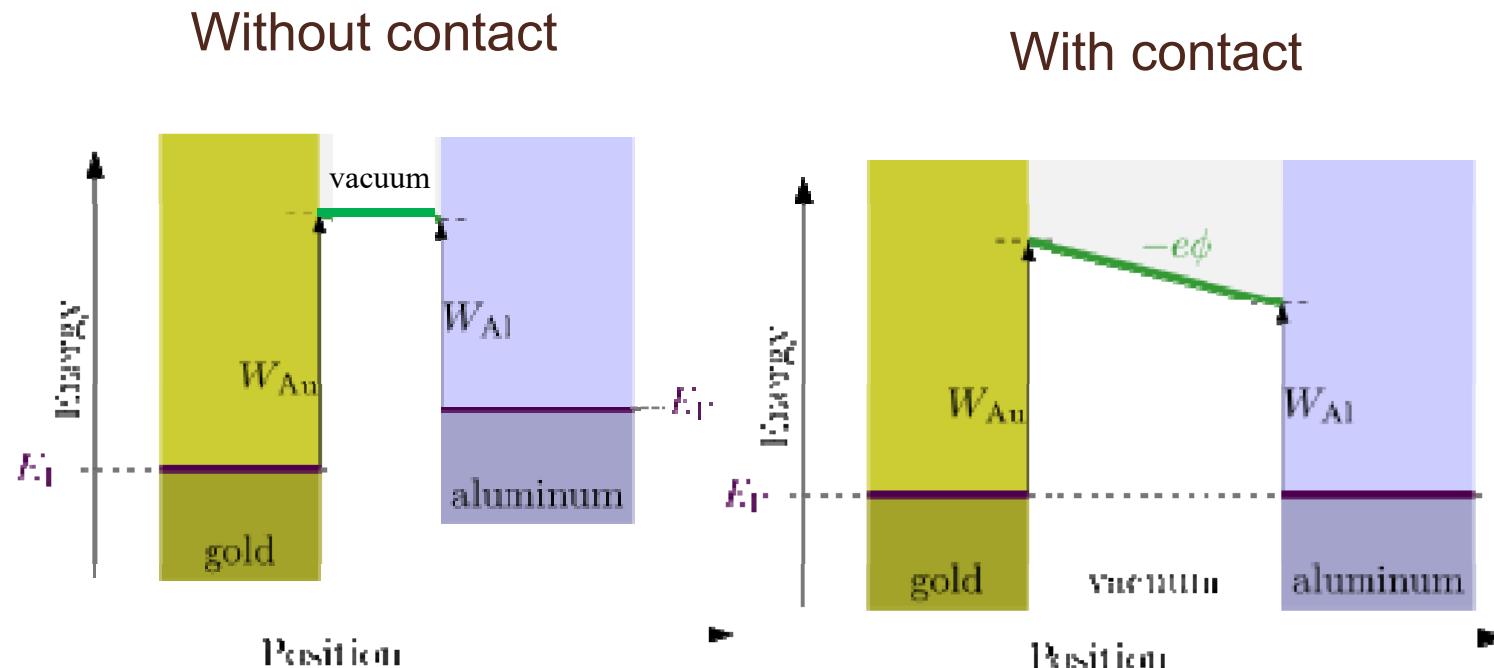
Photoelectric effect

Metal	Work Function eV*
Li	2.9
Na	2.4
K	2.3
Cs	1.9
Ba	2.5
Ca	2.9
Nb	2.3
Zr	4.05
Mg	3.66
Al	4.2
Cu	4.6
Ag	4.64
Zn	3.6
Sc	3.5

I Fundamentals of solid state

I.3 Energy bands in solids

Work Function in metals



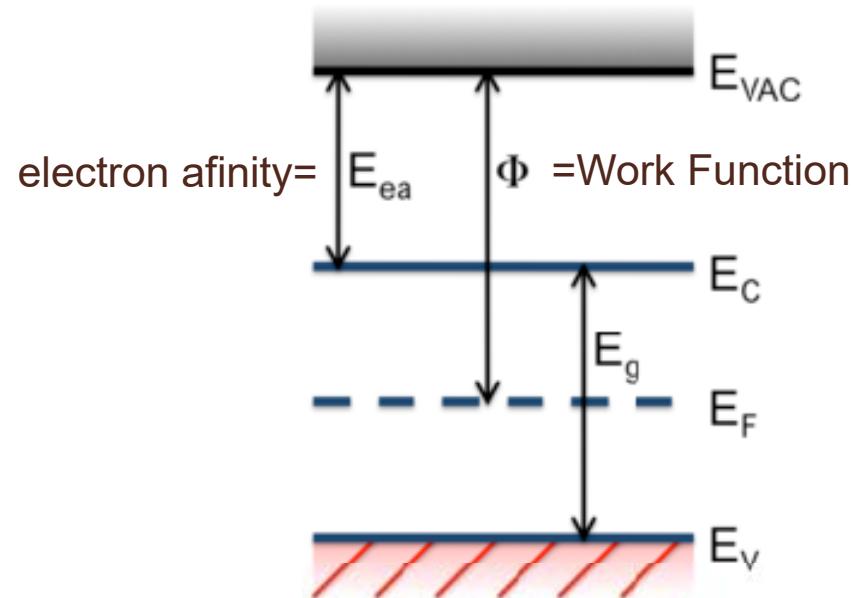
Potential may be generated at the contact.
If the potential is dependent of Temperature → Thermopair

I Fundamentals of solid state

I.3 Energy bands in solids

Work Function and electron affinity

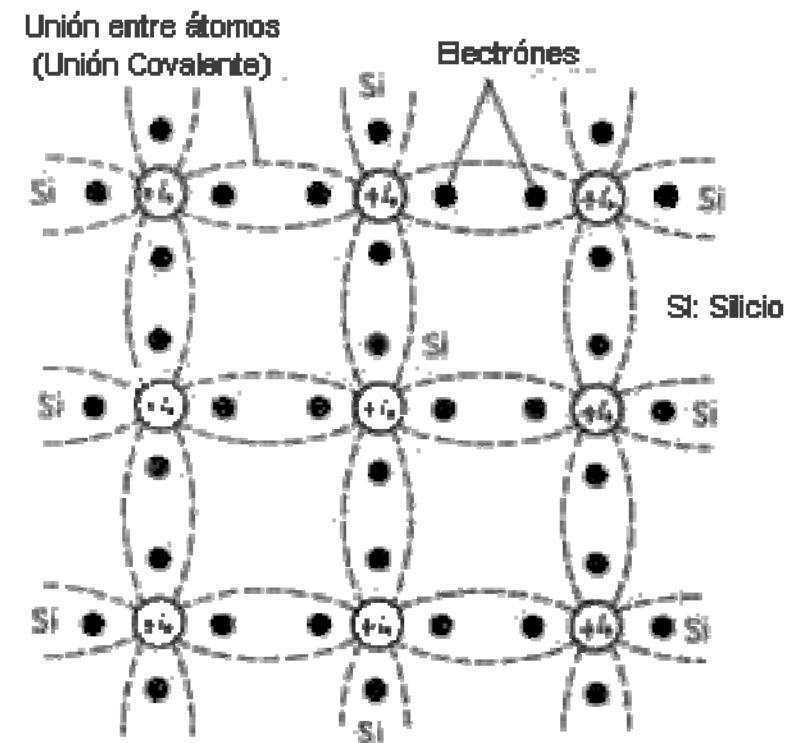
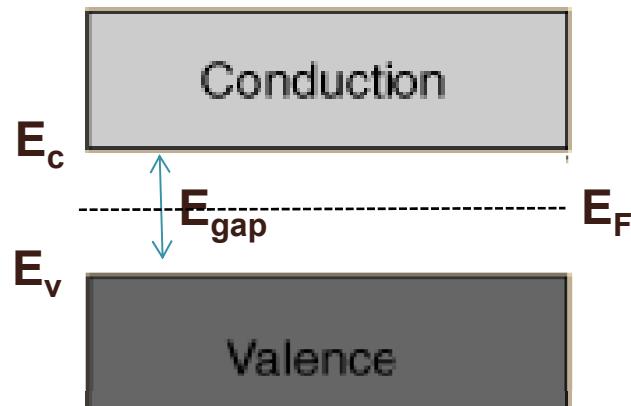
For semiconductors



I Fundamentals of solid state

I.3 Energy bands in solids

Intrinsic (undoped) semiconductors

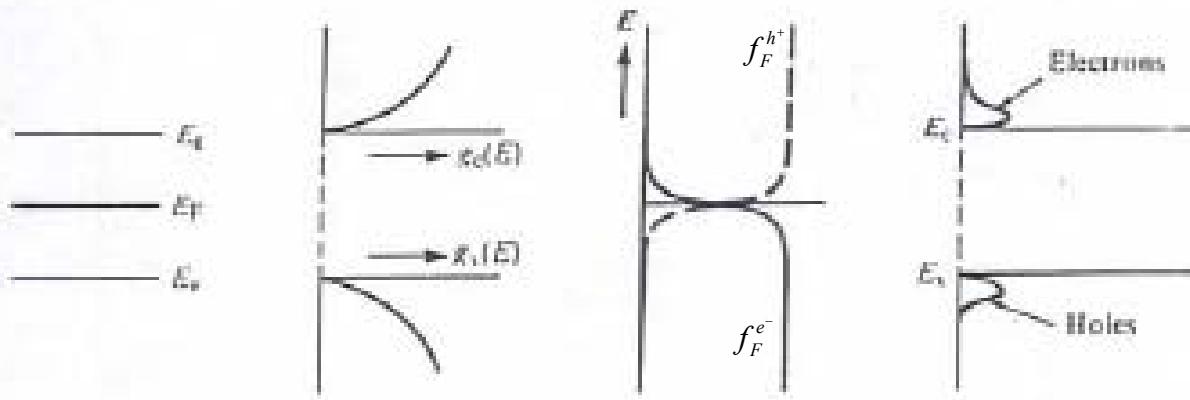


I Fundamentals of solid state

I.3 Energy bands in solids

Intrinsic (undoped) semiconductors

The Fermi level of an intrinsic semiconductor is placed in the middle of the gap.



$$f_F^{e^-}(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$$

$$n = \frac{N_c}{e^{(E_C-E_F)/kT} + 1} \approx N_c e^{-(E_C-E_F)/kT}$$

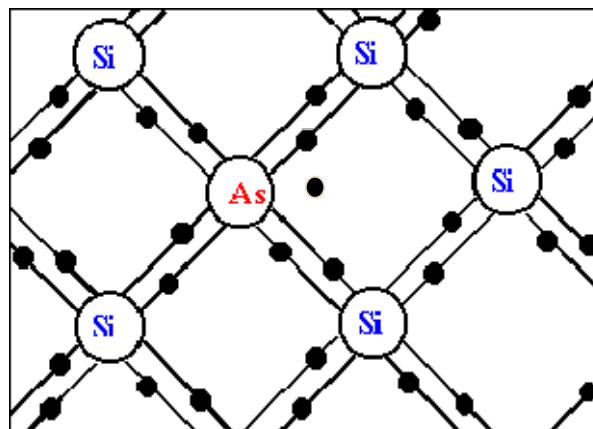
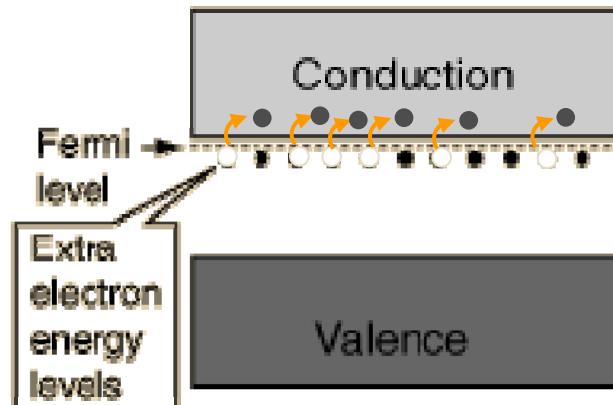
$$f_F^{h^+}(E) = \frac{1}{e^{-(E-E_F)/kT} + 1}$$

$$p = \frac{N_v}{e^{-(E_V-E_F)/kT} + 1} \approx N_v e^{(E_C-E_F)/kT}$$

I Fundamentals of solid state

I.3 Energy bands in solids

Extrinsic (doped) semiconductors



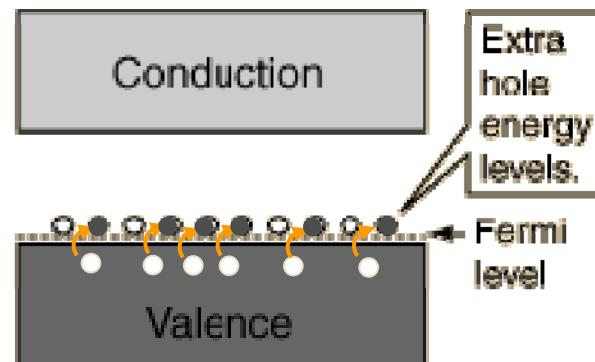
0	2	He			
IIA	IVA	VIA	VIA	VIA	0
5	6	7	8	9	10
B	C	N	O	F	Ne
13	14	15	16	17	18
Al	Si	P	S	Cl	Ar
31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
49	50	51	52	53	54
In	Sn	Sb	Te	I	Xe
81	82	83	84	85	86
Tl	Pb	Bi	Po	At	Rn

Tipus n: Substituïsc un àtom de Si per un altre amb més electrons a la capa de valència (impuresa donadora)

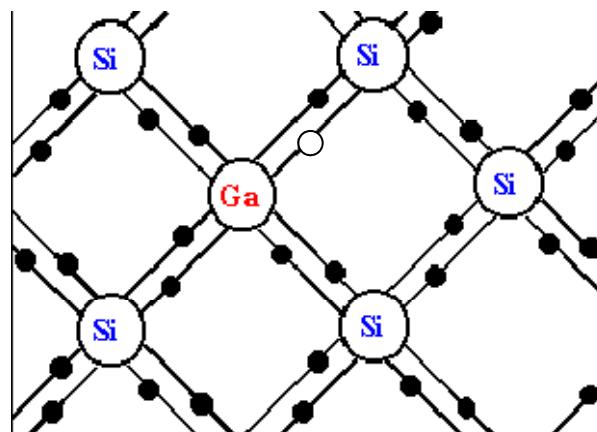
I Fundamentals of solid state

I.3 Energy bands in solids

Extrinsic (doped) semiconductors



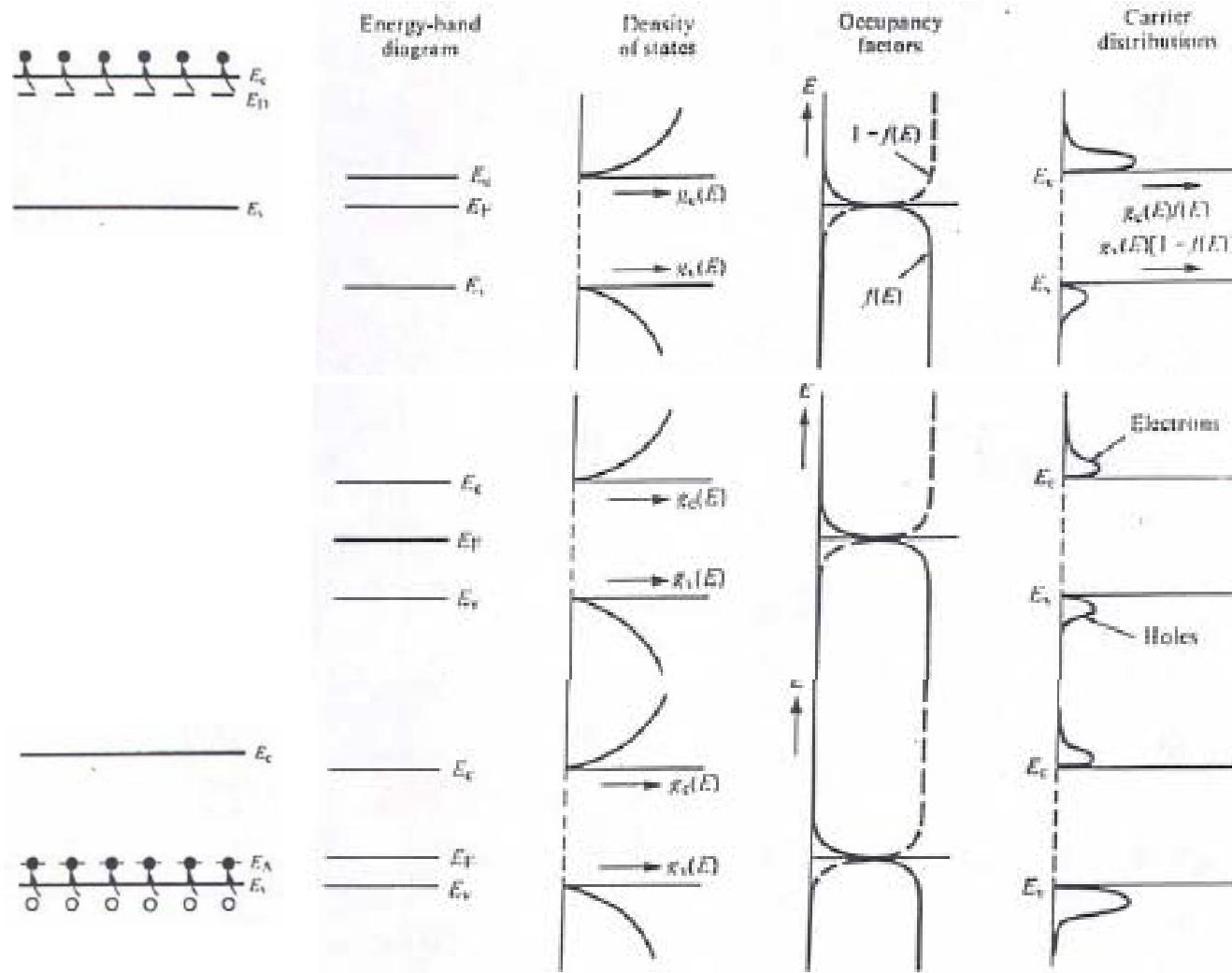
0	2	He			
III	IV	V	VI	VIIA	0
5	6	7	8	9	10
B	C	N	O	F	Ne
13	14	15	16	17	18
Al	Si	P	S	Cl	Ar
31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
49	50	51	52	53	54
In	Sn	Sb	Te	I	Xe
81	82	83	84	85	86
Tl	Pb	Bi	Po	At	Rn



Tipus p: Substituis un àtom de Si per un altre amb menys electrons a la capa de valència (impuresa acceptora)

I Fundamentals of solid state

I.3 Energy bands in solids



n-type

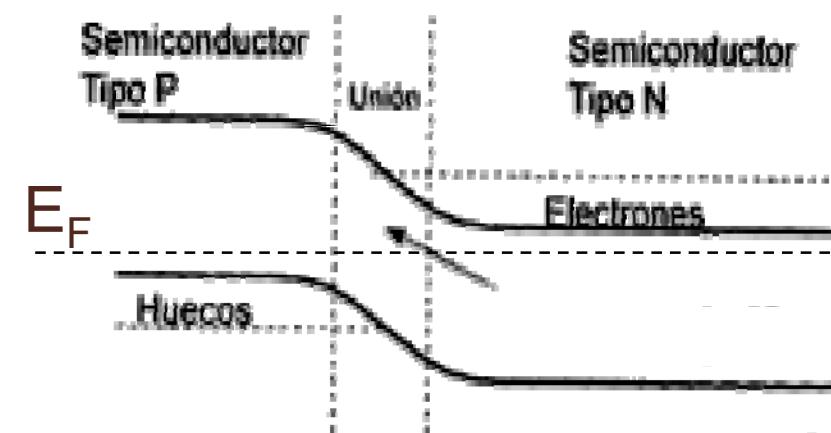
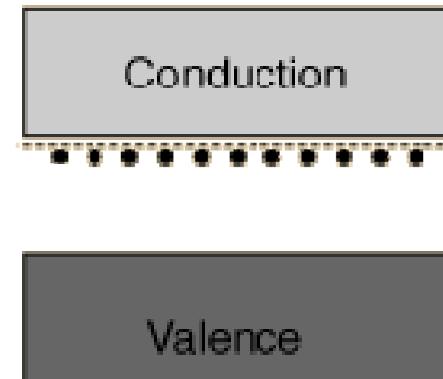
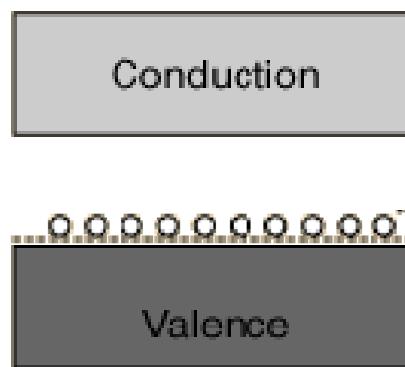
Intrinsic

p-type

I Fundamentals of solid state

I.3 Energy bands in solids

p-n junction

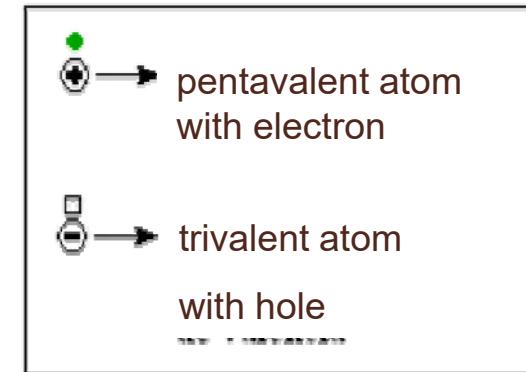
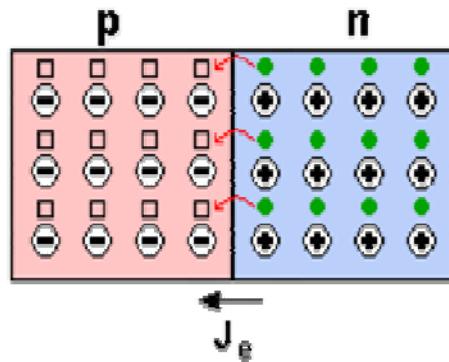


I Fundamentals of solid state

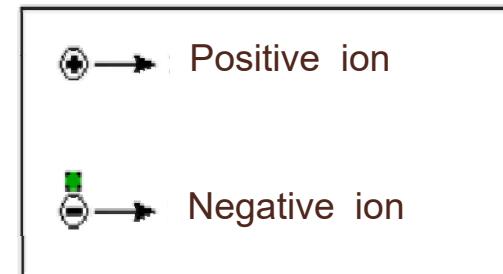
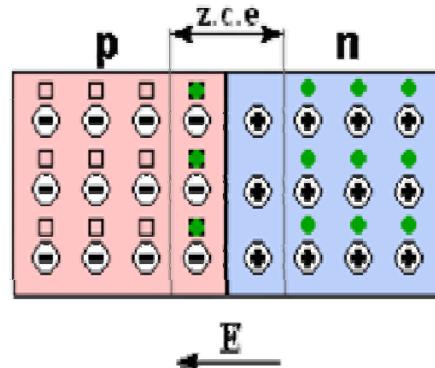
I.3 Energy bands in solids

p-n junction

$$J_n = qD \frac{\partial n}{\partial x}$$



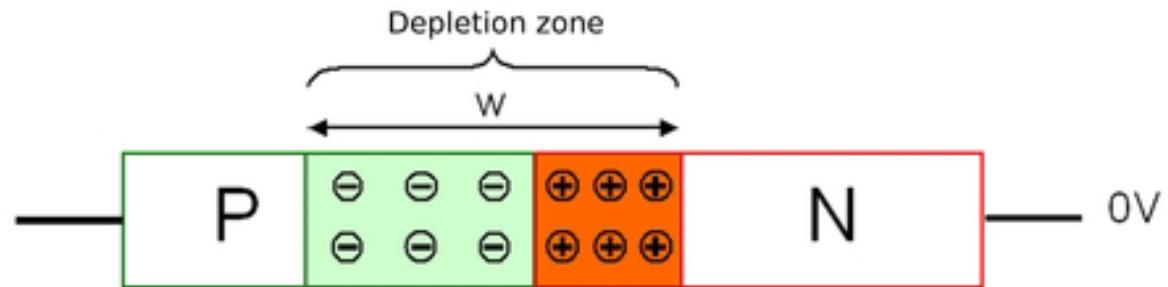
$$J_n = qn\mu E$$



I Fundamentals of solid state

I.3 Energy bands in solids

p-n junction



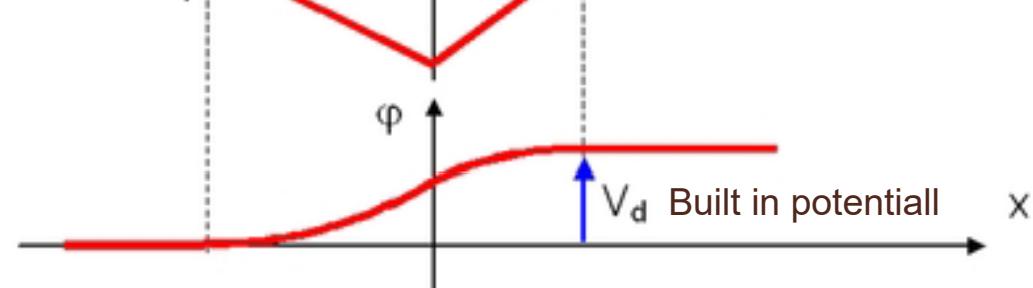
Charge distribution



Electric field



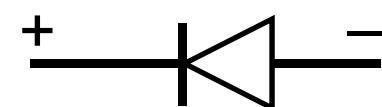
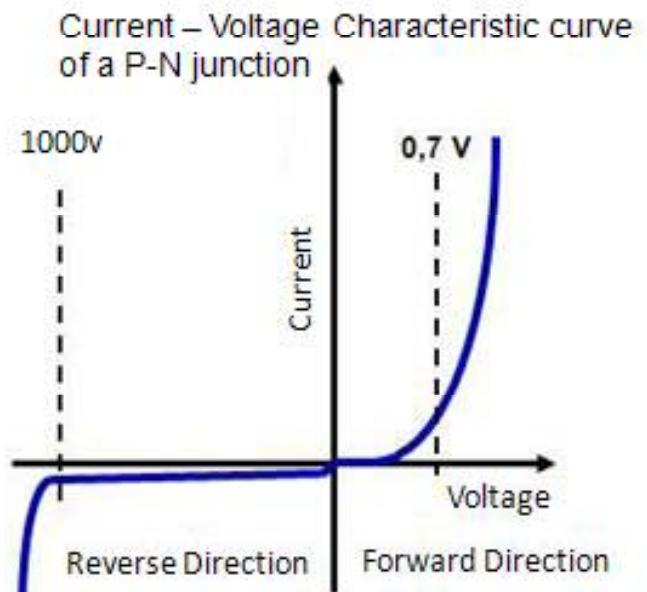
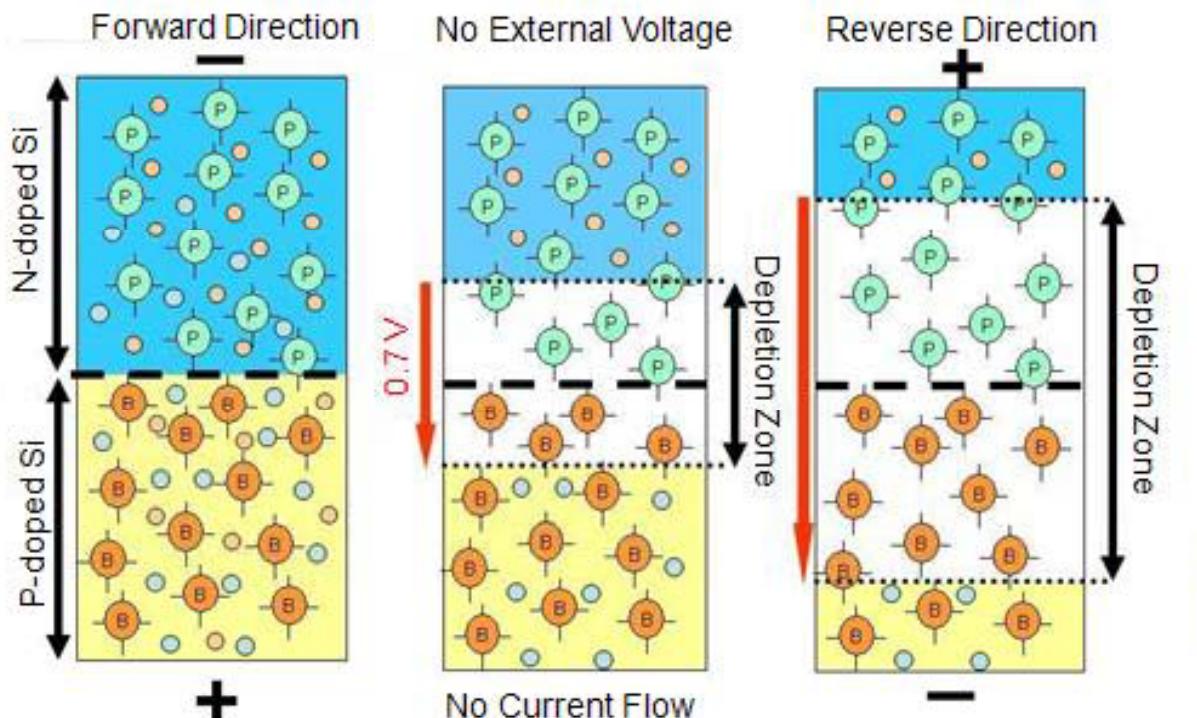
Potential



I Fundamentals of solid state

I.3 Energy bands in solids

p-n junction

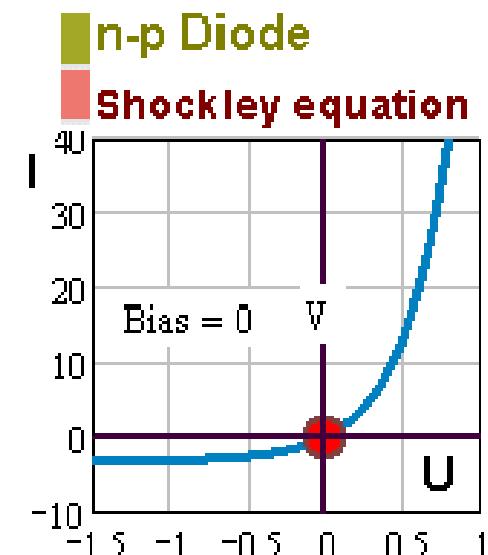
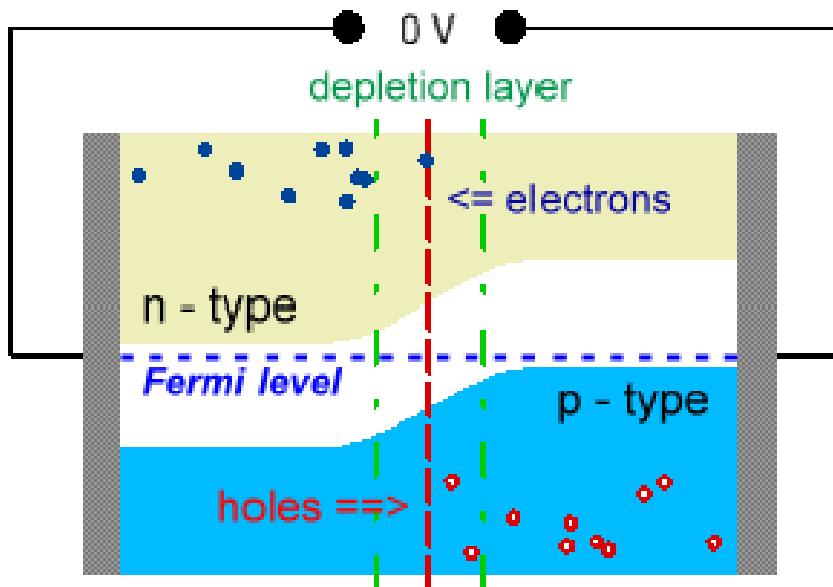


$$J = J_0 \left[e^{\frac{q}{mkT}V} - 1 \right]$$

I Fundamentals of solid state

I.3 Energy bands in solids

p-n junction



I Fundamentals of solid state

I.3 Energy bands in solids

p-n junction

