Course 2

Wednesday, 10 September 2025 09:51

EE557Cours 2 -...

Equal opportunity makes us brighter
Diversity is our strength
Listen and dare to speak up
Look out for each other
Kindness brings serenity
Together we go further
EPFL

EE-557
Semiconductor devices I
Energy bang gap and band diagrams

Génie Electrique et Electronique
Master program
Prof. Elison Matioli

Outline of the lecture

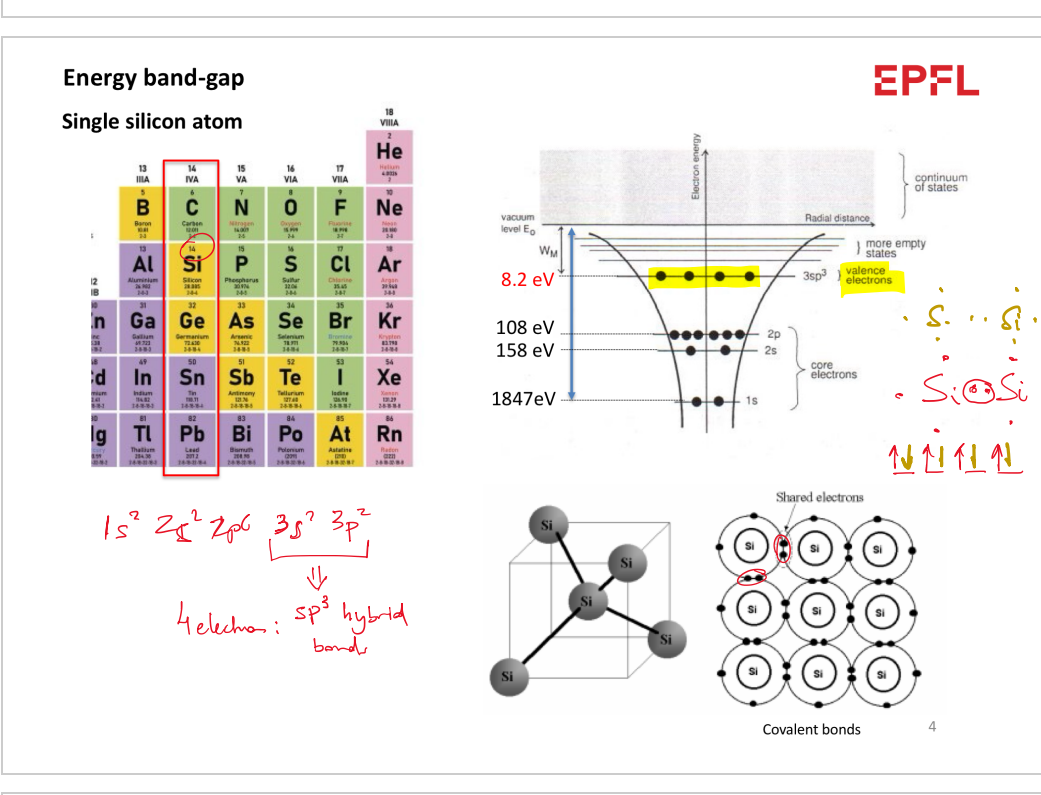
1. Introduction
2. Energy gap and energy bands
3. Important bits of knowledge

References:

- J. A. del Alamo, course materials for 6.720J Integrated Microelectronic Devices, Spring 2007. MIT OpenCourseWare (http://ocw.mit.edu/)
- C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 2005

Key questions

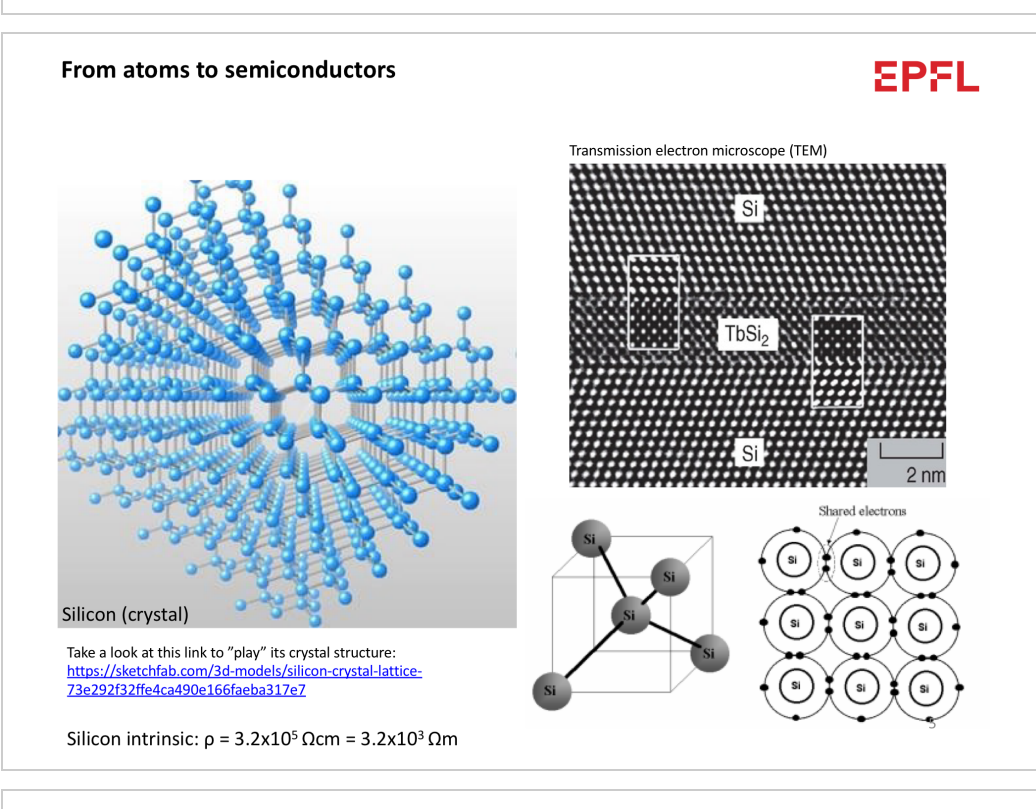
- What is a semiconductor?
- What is an energy band gap?
- How do we treat electrons in a solid?
- How do atoms arrange themselves? And the consequences…
- How do electrons arrange themselves (in energy) in an electronic system?



Energy band-gap

Single silicon atom

Electron energy
continuum of states
vacuum level E0
Radial distance
WM
more empty states
8.2 eV
3sp3
valence electrons
108 eV
158 eV
2p
2s
core electrons
1847eV
1s
Shared electrons
Covalent bonds
1s² 2s² 2p⁶ 3s² 3p²
4 electrons: sp³ hybrid bond

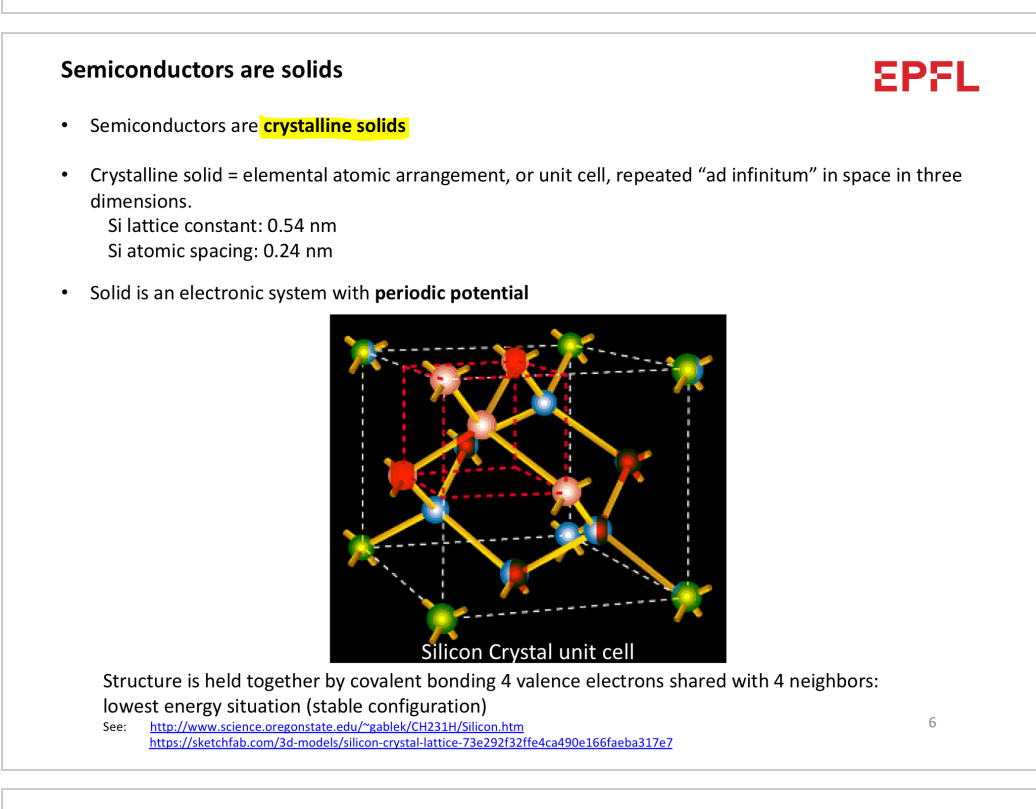


From atoms to semiconductors

Transmission electron microscope (TEM)
Si
TbSi2
Si
2 nm
Silicon (crystal)

Take a look at this link to "play" its crystal structure: https://sketchfab.com/3d-models/silicon-crystal-lattice-73e292f32ffe4ca490e166faeba317e7

Silicon intrinsic: $\rho = 3.2\times10^5\ \Omega\text{cm} = 3.2\times10^3\ \Omega\text{m}$



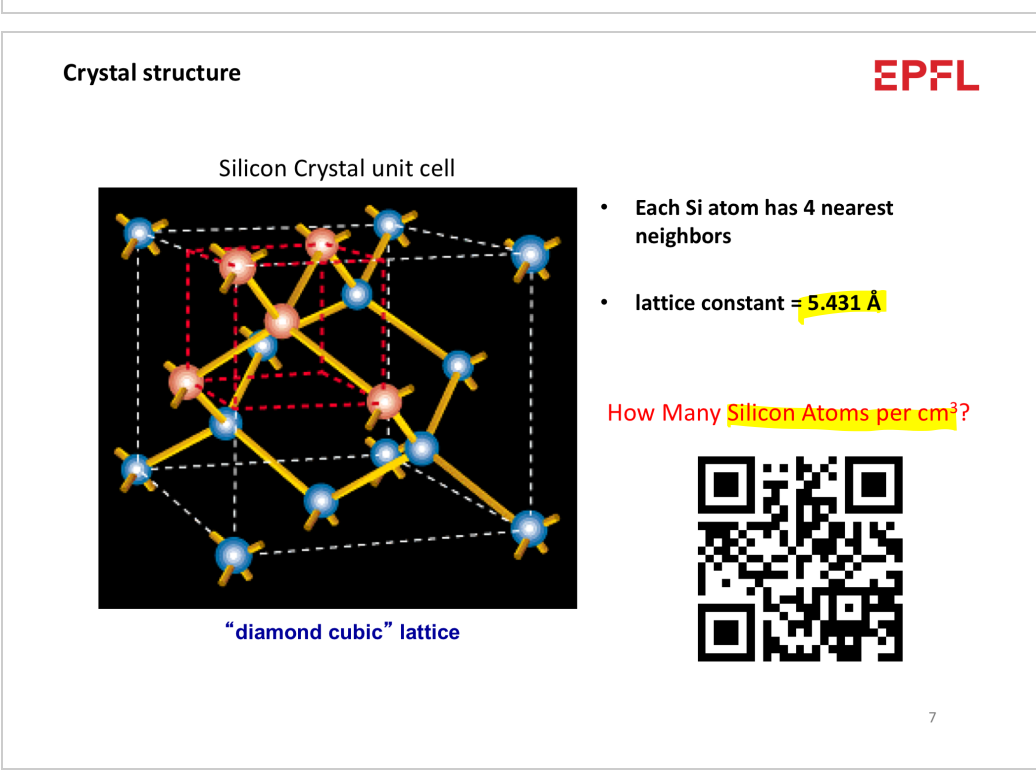
Semiconductors are solids

- Semiconductors are **crystalline solids**
- Crystalline solid = elemental atomic arrangement, or unit cell, repeated "ad infinitum" in space in three dimensions.
  Si lattice constant: 0.54 nm
  Si atomic spacing: 0.24 nm
- Solid is an electronic system with **periodic potential**

Silicon Crystal unit cell

Structure is held together by covalent bonding 4 valence electrons shared with 4 neighbors: lowest energy situation (stable configuration)

See: http://www.science.oregonstate.edu/~gablek/CH231H/Silicon.htm
https://sketchfab.com/3d-models/silicon-crystal-lattice-73e292f32ffe4ca490e166faeba317e7



Crystal structure

Silicon Crystal unit cell

"diamond cubic" lattice

- **Each Si atom has 4 nearest neighbors**
- **lattice constant = 5.431 Å**

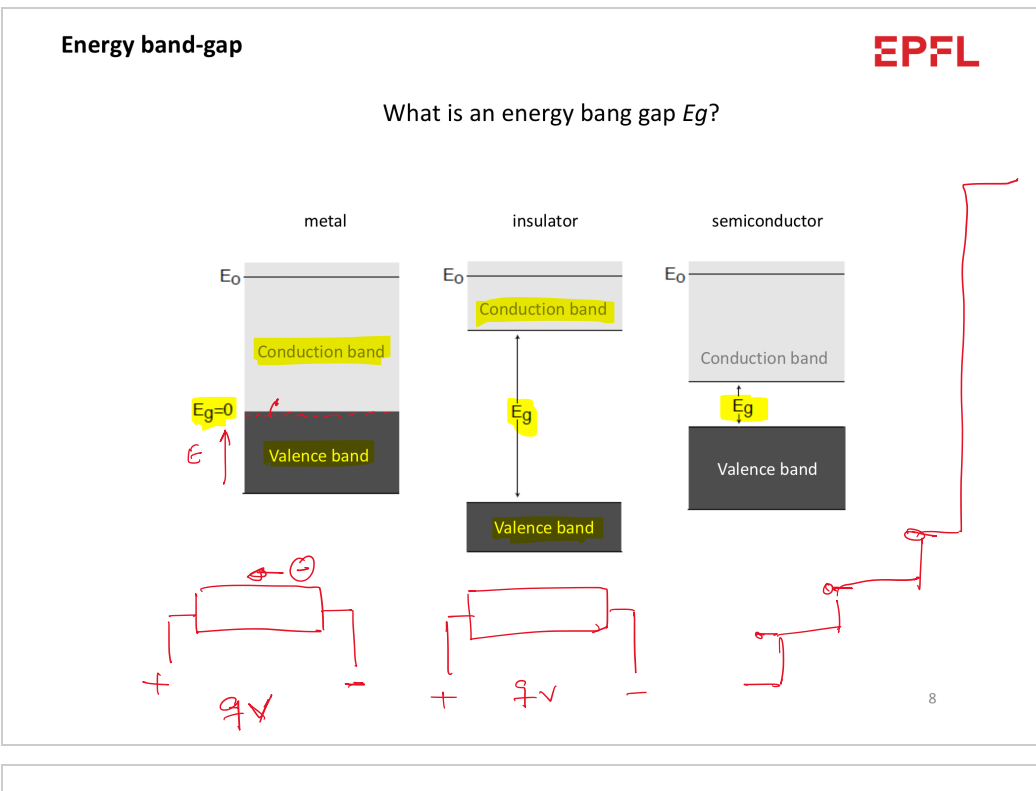
How Many Silicon Atoms per cm³?

# atoms

corners: $8\times 1/8$: 1
faces: $6\times 1/2$: 3
Inside: 4 : 4
$\} \; 8$

Volume: $(5.431\times10^{-10}\,\text{m})^3 = (5.431\times10^{-8})^3 = 1.6\times10^{-22}\,\text{cm}^3$

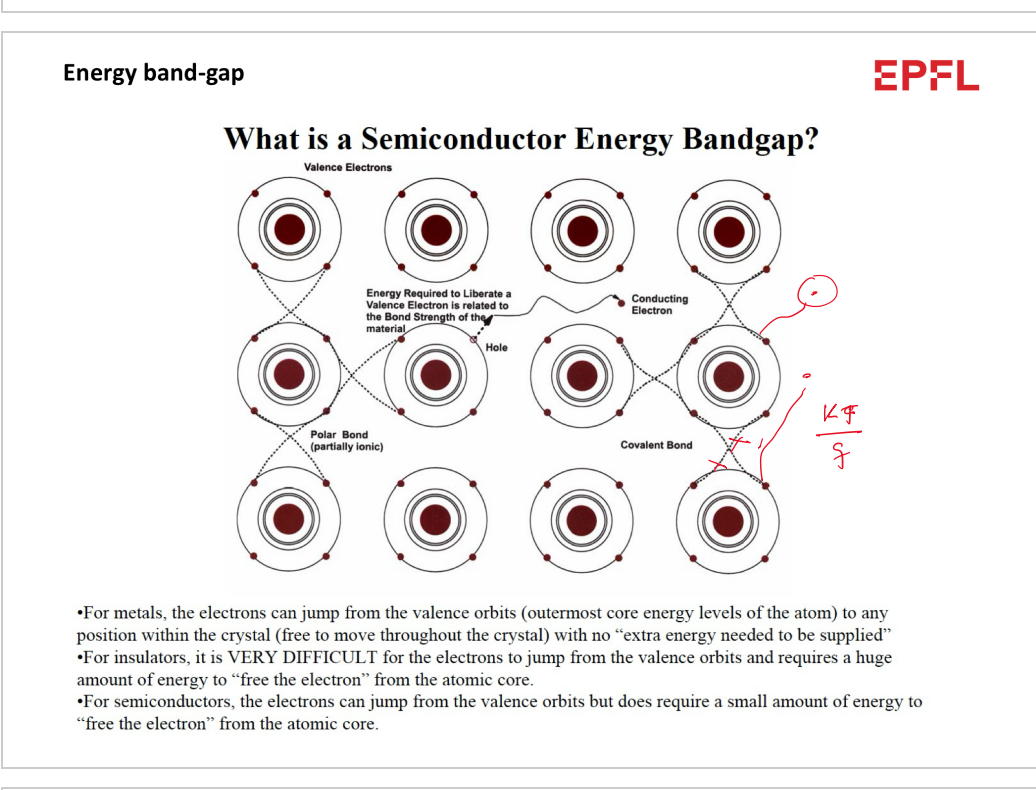
$\boxed{\#\ \text{atoms}/\text{cm}^3 = 5\times10^{22}\,\text{cm}^{-3}}$



Energy band-gap

What is an energy bang gap *Eg*?

metal
insulator
semiconductor
E0
Conduction band
Valence band
Eg=0
Eg
E
qV
+
−

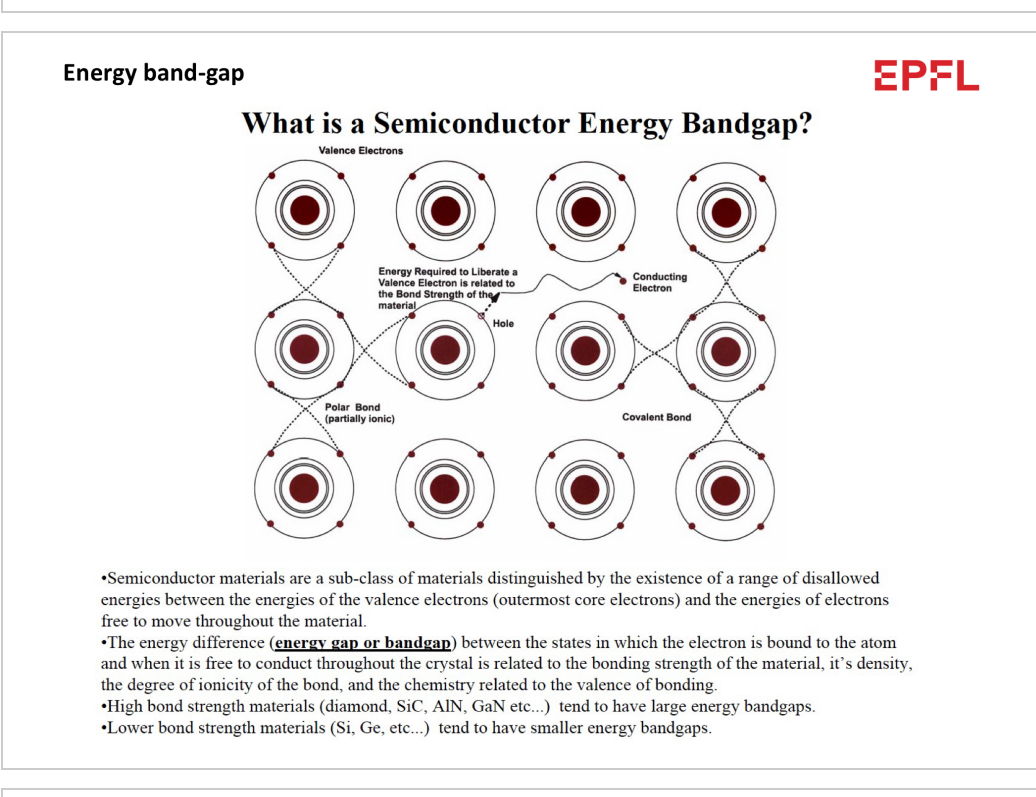


Energy band-gap

What is a Semiconductor Energy Bandgap?

Valence Electrons
Energy Required to Liberate a Valence Electron is related to the Bond Strength of the material
Conducting Electron
Hole
Polar Bond (partially ionic)
Covalent Bond
KT/q

•For metals, the electrons can jump from the valence orbits (outermost core energy levels of the atom) to any position within the crystal (free to move throughout the crystal) with no "extra energy needed to be supplied"
•For insulators, it is VERY DIFFICULT for the electrons to jump from the valence orbits and requires a huge amount of energy to "free the electron" from the atomic core.
•For semiconductors, the electrons can jump from the valence orbits but does require a small amount of energy to "free the electron" from the atomic core.



Energy band-gap

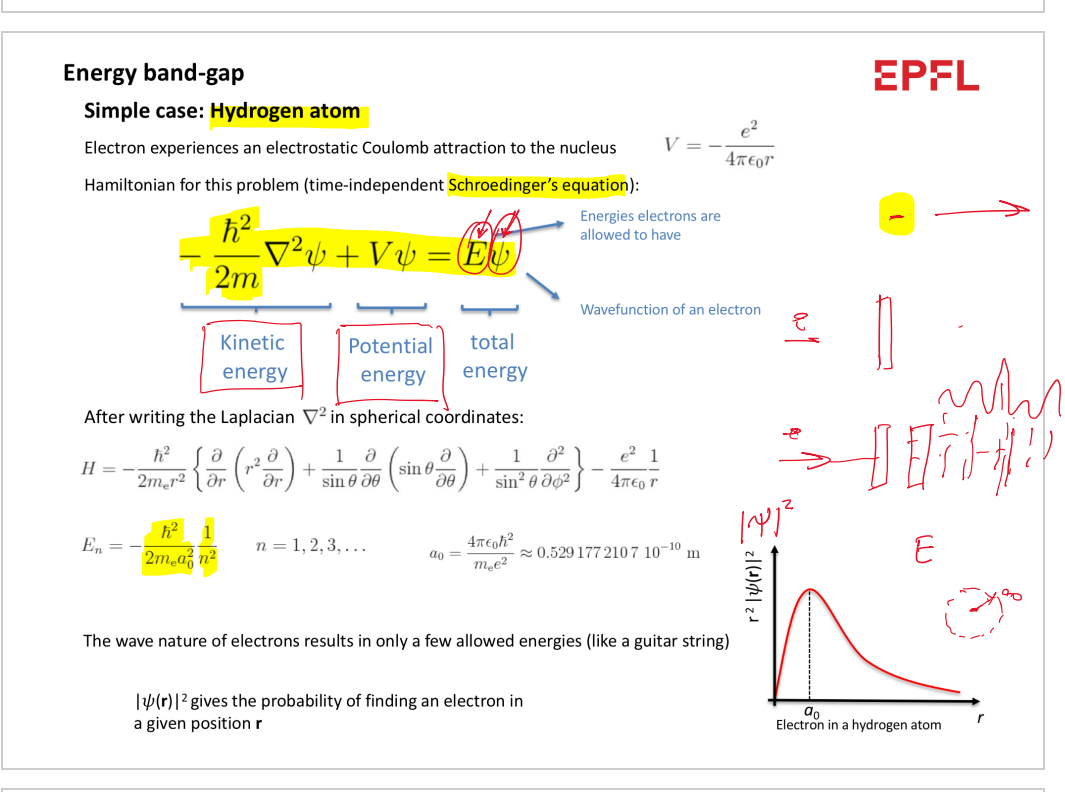
What is a Semiconductor Energy Bandgap?

Valence Electrons
Energy Required to Liberate a Valence Electron is related to the Bond Strength of the material
Conducting Electron
Hole
Polar Bond (partially ionic)
Covalent Bond

•Semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the valence electrons (outermost core electrons) and the energies of electrons free to move throughout the material.
•The energy difference (**energy gap or bandgap**) between the states in which the electron is bound to the atom and when it is free to conduct throughout the crystal is related to the bonding strength of the material, it's density, the degree of ionicity of the bond, and the chemistry related to the valence of bonding.
•High bond strength materials (diamond, SiC, AlN, GaN etc...) tend to have large energy bandgaps.
•Lower bond strength materials (Si, Ge, etc...) tend to have smaller energy bandgaps.

Energy band-gap

How do energy bands and band gaps form?



Energy band-gap

Simple case: Hydrogen atom

Electron experiences an electrostatic Coulomb attraction to the nucleus $V = -\frac{e^2}{4\pi\epsilon_0 r}$

Hamiltonian for this problem (time-independent Schroedinger's equation):

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi}_{\text{Kinetic energy}} + \underbrace{V\psi}_{\text{Potential energy}} = \underbrace{E\psi}_{\text{total energy}}$$

Energies electrons are allowed to have

Wavefunction of an electron

After writing the Laplacian ∇^2 in spherical coordinates:

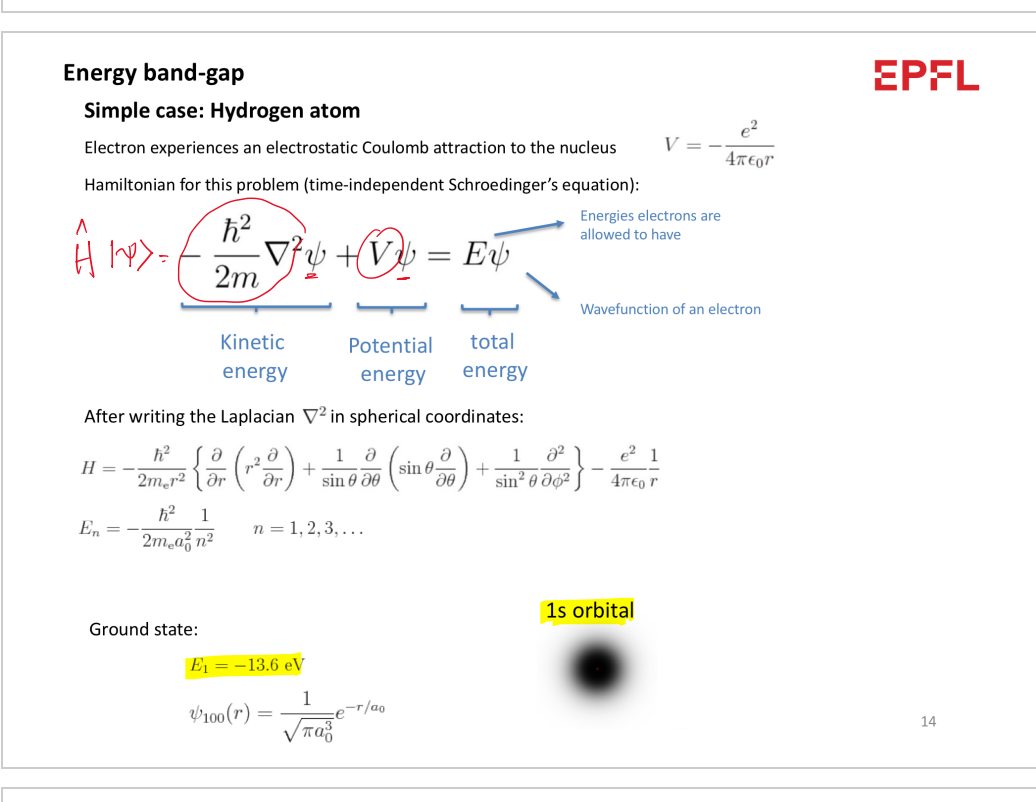
$$H = -\frac{\hbar^2}{2m_e r^2}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

$$E_n = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{n^2} \qquad n = 1,2,3,\ldots \qquad a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.529\,177\,210\,7\ 10^{-10}\ \text{m}$$

The wave nature of electrons results in only a few allowed energies (like a guitar string)

$|\psi(\mathbf{r})|^2$ gives the probability of finding an electron in a given position **r**

r² |ψ(r)|²
a0
r
Electron in a hydrogen atom
|ψ|²
E



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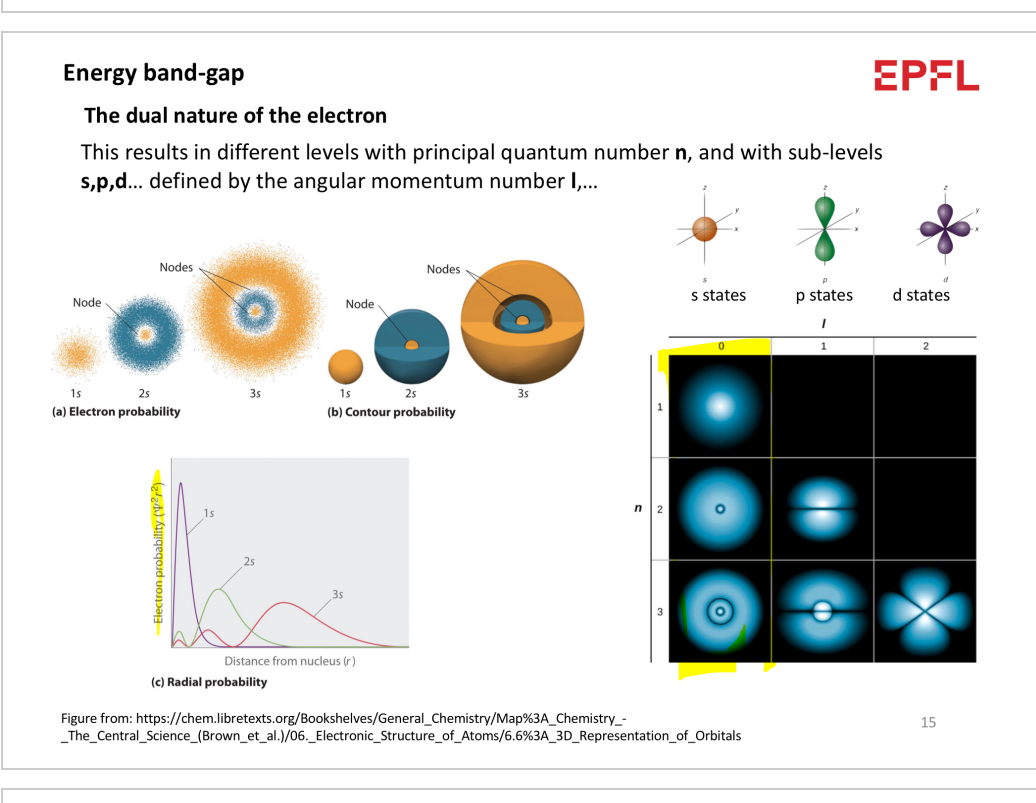
$$E_n = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{n^2} \qquad n = 1,2,3,\ldots$$

Ground state:

$E_1 = -13.6$ eV

$\psi_{100}(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$

1s orbital



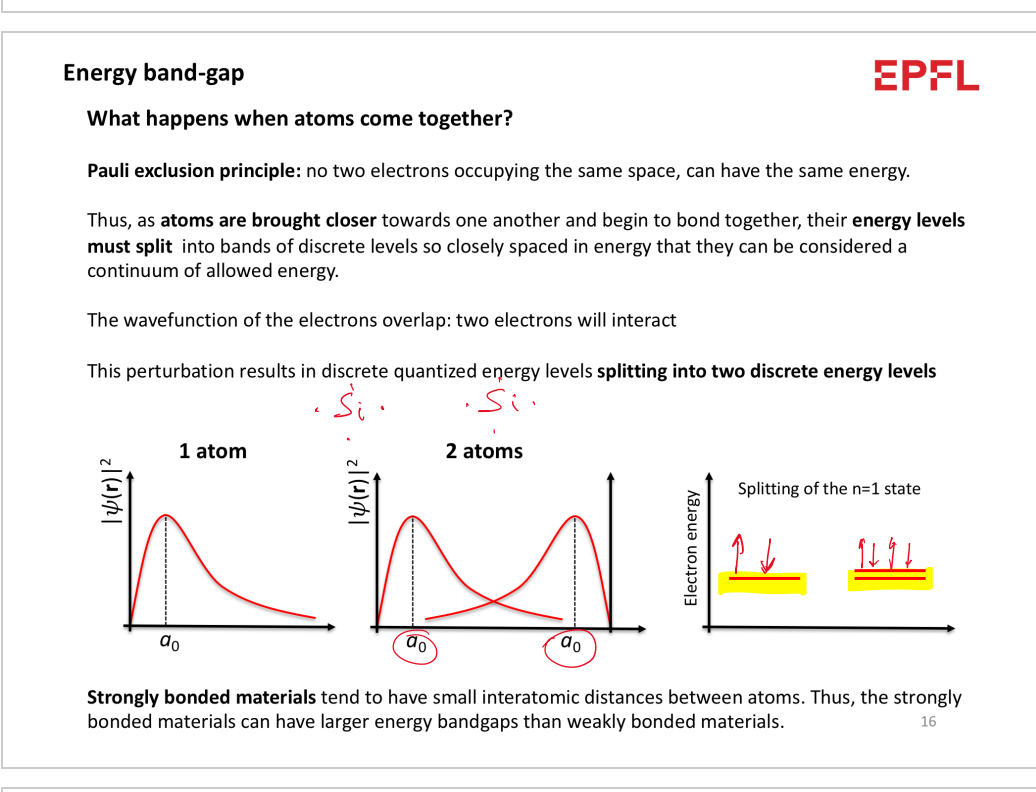
Energy band-gap

The dual nature of the electron

This results in different levels with principal quantum number **n**, and with sub-levels **s,p,d**… defined by the angular momentum number **l**,…

Nodes
Node
1s
2s
3s
(a) Electron probability
(b) Contour probability
Electron probability (4πr²ψ²)
Distance from nucleus (r)
(c) Radial probability
s states
p states
d states
l
n
0
1
2
1
2
3

Figure from: https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/06._Electronic_Structure_of_Atoms/6.6%3A_3D_Representation_of_Orbitals



Energy band-gap

What happens when atoms come together?

Pauli exclusion principle: no two electrons occupying the same space, can have the same energy.

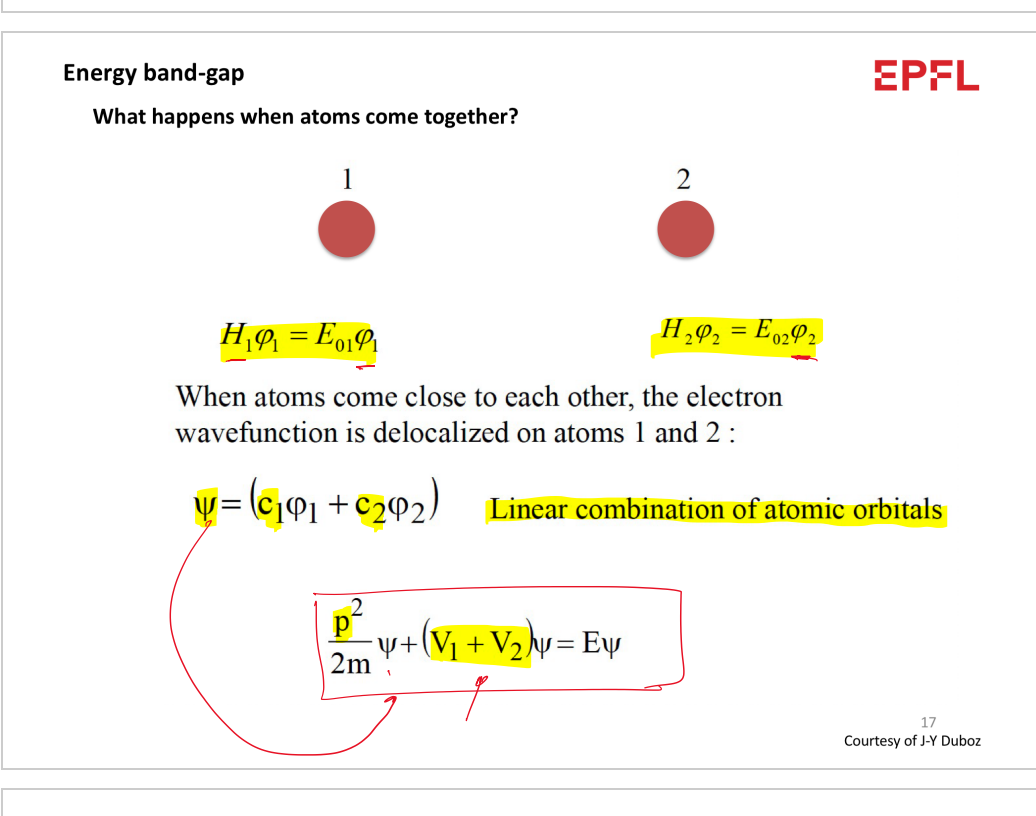
Thus, as **atoms are brought closer** towards one another and begin to bond together, their **energy levels must split** into bands of discrete levels so closely spaced in energy that they can be considered a continuum of allowed energy.

The wavefunction of the electrons overlap: two electrons will interact

This perturbation results in discrete quantized energy levels **splitting into two discrete energy levels**

Si
Si
1 atom
2 atoms
|ψ(r)|²
a0
Electron energy
Splitting of the n=1 state

Strongly bonded materials tend to have small interatomic distances between atoms. Thus, the strongly bonded materials can have larger energy bandgaps than weakly bonded materials.



Energy band-gap

What happens when atoms come together?

$H_1\varphi_1 = E_{01}\varphi_1$ $\qquad$ $H_2\varphi_2 = E_{02}\varphi_2$

When atoms come close to each other, the electron wavefunction is delocalized on atoms 1 and 2 :

$\psi = (c_1\varphi_1 + c_2\varphi_2)$ Linear combination of atomic orbitals

$$\boxed{\frac{p^2}{2m}\psi + (V_1 + V_2)\psi = E\psi}$$

Courtesy of J-Y Duboz

Energy band-gap

What happens when atoms come together?

$\psi = c_1\varphi_1 + c_2\varphi_2$

Develop and project on φ_1 and φ_2

$$c_1E_{01} + c_2E_{02}\langle\varphi_1|\varphi_2\rangle + c_2\langle\varphi_1|V_1|\varphi_2\rangle + c_1\langle\varphi_1|V_2|\varphi_1\rangle = Ec_1 + c_2E\langle\varphi_1|\varphi_2\rangle$$
$$c_1E_{01}\langle\varphi_2|\varphi_1\rangle + c_2E_{02} + c_2\langle\varphi_2|V_1|\varphi_2\rangle + c_1\langle\varphi_2|V_2|\varphi_1\rangle = Ec_2 + c_1E\langle\varphi_2|\varphi_1\rangle$$

$$\begin{vmatrix} (E_{01}-E)+\langle\varphi_1|V_2|\varphi_1\rangle & (E_{02}-E)\langle\varphi_1|\varphi_2\rangle+\langle\varphi_1|V_1|\varphi_2\rangle \\ (E_{01}-E)\langle\varphi_2|\varphi_1\rangle+\langle\varphi_2|V_2|\varphi_1\rangle & (E_{02}-E)+\langle\varphi_2|V_1|\varphi_2\rangle \end{vmatrix} = 0$$

- Can be solved as it is ☺
- But it can be simplified by introducing assumptions which are done in the real semiconductor band structure calculations based on this approach (Tight Binding) ☺ ☺

Courtesy of J-Y Duboz

Energy band-gap

What happens when atoms come together?

$$\begin{vmatrix} (E_{01}-E)+\langle\varphi_1|V_2|\varphi_1\rangle & (E_{02}-E)\langle\varphi_1|\varphi_2\rangle+\langle\varphi_1|V_1|\varphi_2\rangle \\ (E_{01}-E)\langle\varphi_2|\varphi_1\rangle+\langle\varphi_2|V_2|\varphi_1\rangle & (E_{02}-E)+\langle\varphi_2|V_1|\varphi_2\rangle \end{vmatrix} = 0$$

$\langle\varphi_1|\varphi_2\rangle = 0$ Not strictly true. In addition E_{02}-E is expected to be small

$\langle\varphi_1|V_2|\varphi_1\rangle = \langle\varphi_2|V_1|\varphi_2\rangle$ by symmetry

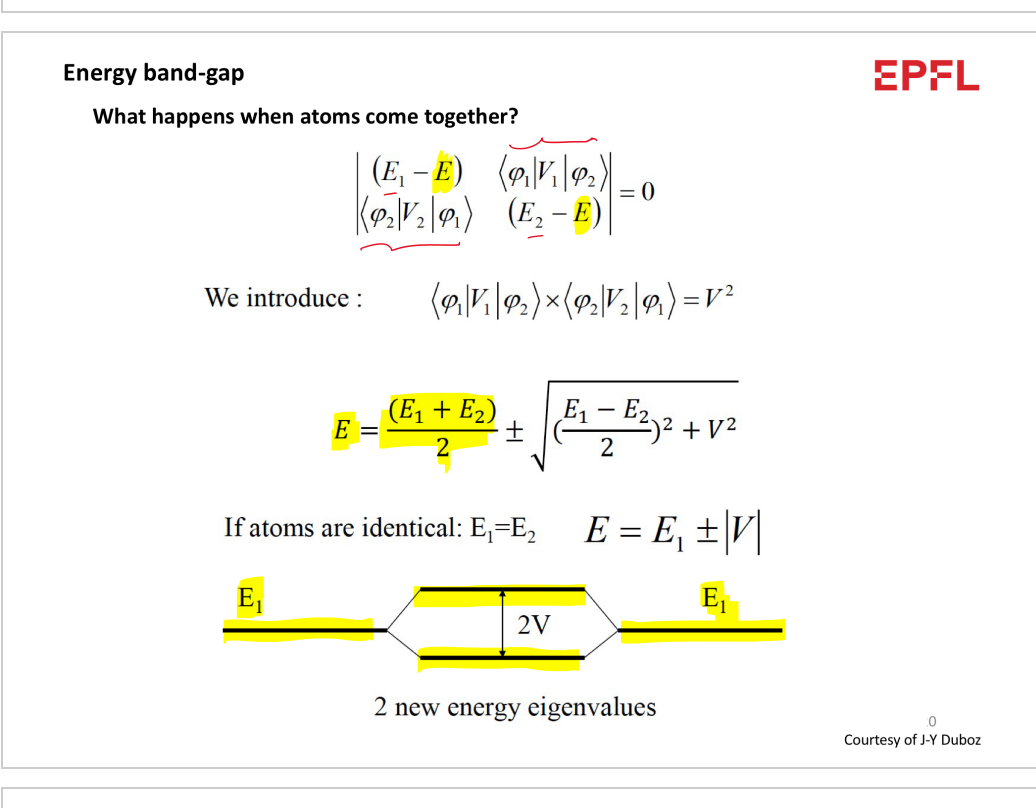
Describes the effect of the potential of atom 2 on the energy in atom 1, and vice versa. It is a shift of the energy, with no important effect.

(when atoms are different or with less trivial symmetries, it has an effect).

Let us renormalize the energies :

$$E_1 = E_{01} + \langle\varphi_1|V_2|\varphi_1\rangle$$
$$E_2 = E_{02} + \langle\varphi_2|V_1|\varphi_2\rangle$$

Courtesy of J-Y Duboz



Energy band-gap

What happens when atoms come together?

$$\begin{vmatrix} (E_1-E) & \langle\varphi_1|V_1|\varphi_2\rangle \\ \langle\varphi_2|V_2|\varphi_1\rangle & (E_2-E) \end{vmatrix} = 0$$

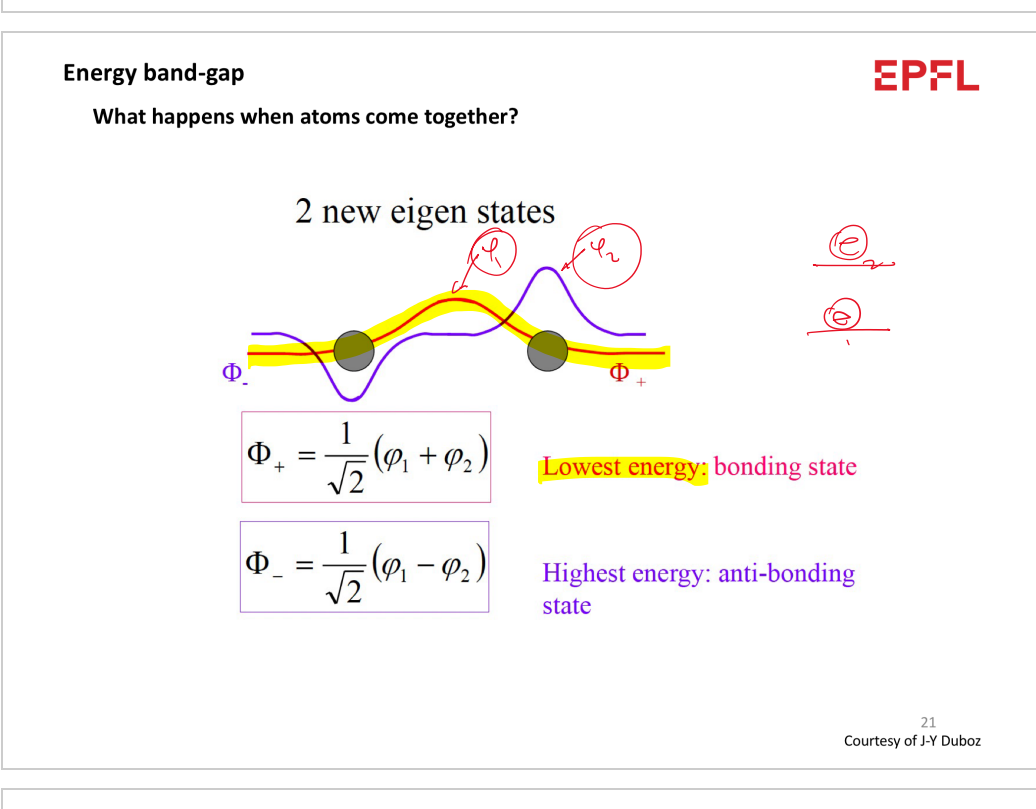
We introduce : $\langle\varphi_1|V_1|\varphi_2\rangle\times\langle\varphi_2|V_2|\varphi_1\rangle = V^2$

$$E = \frac{(E_1+E_2)}{2} \pm \sqrt{\left(\frac{E_1-E_2}{2}\right)^2 + V^2}$$

If atoms are identical: $E_1=E_2$ $\quad E = E_1 \pm |V|$

2 new energy eigenvalues

Courtesy of J-Y Duboz



Energy band-gap

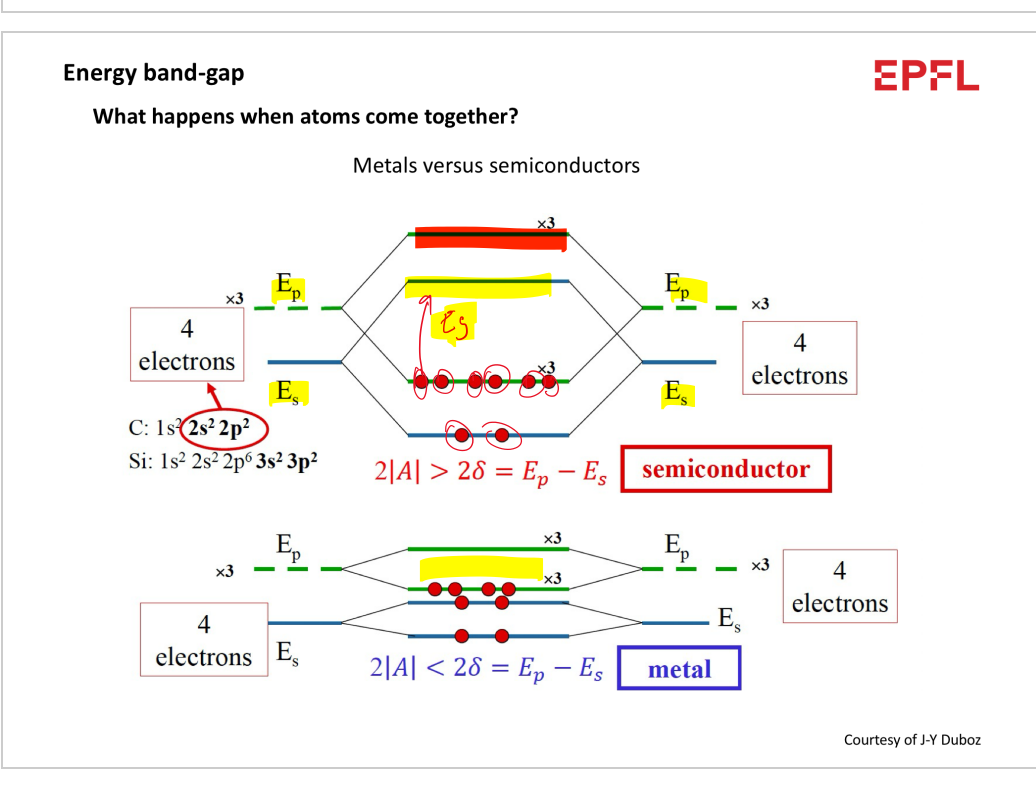
What happens when atoms come together?

2 new eigen states

$\Phi_+ = \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2)$ Lowest energy: bonding state

$\Phi_- = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2)$ Highest energy: anti-bonding state

Courtesy of J-Y Duboz



Energy band-gap

What happens when atoms come together?

Metals versus semiconductors

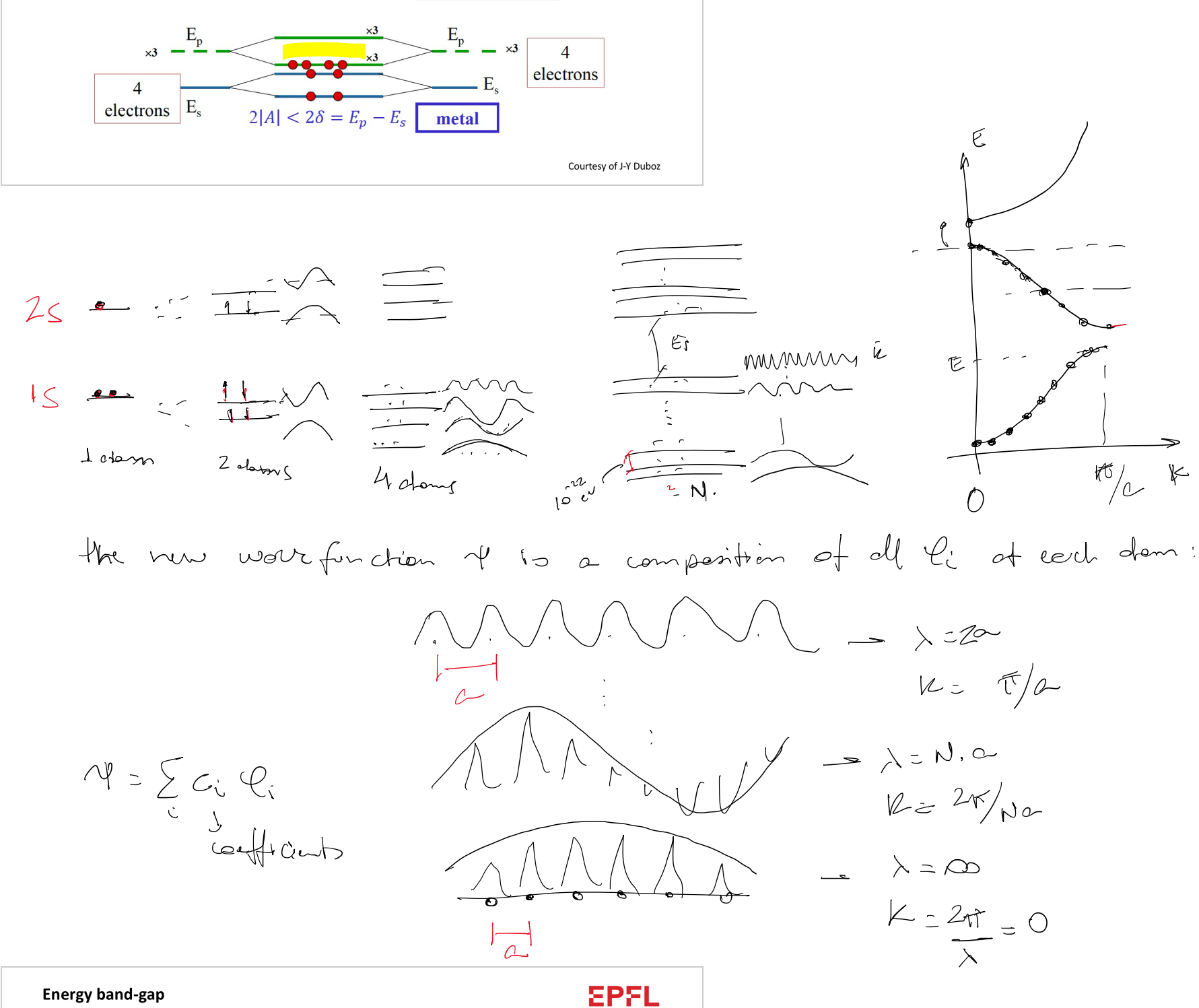
×3
Ep
Es
4 electrons
Eg

C: 1s² 2s² 2p²
Si: 1s² 2s² 2p⁶ 3s² 3p²

$2|A| > 2\delta = E_p - E_s$ **semiconductor**

$2|A| < 2\delta = E_p - E_s$ **metal**

Courtesy of J-Y Duboz


2s
1s
1 atom
2 atoms
4 atoms
10⁻²² eV
N.
E
0
π/a
k

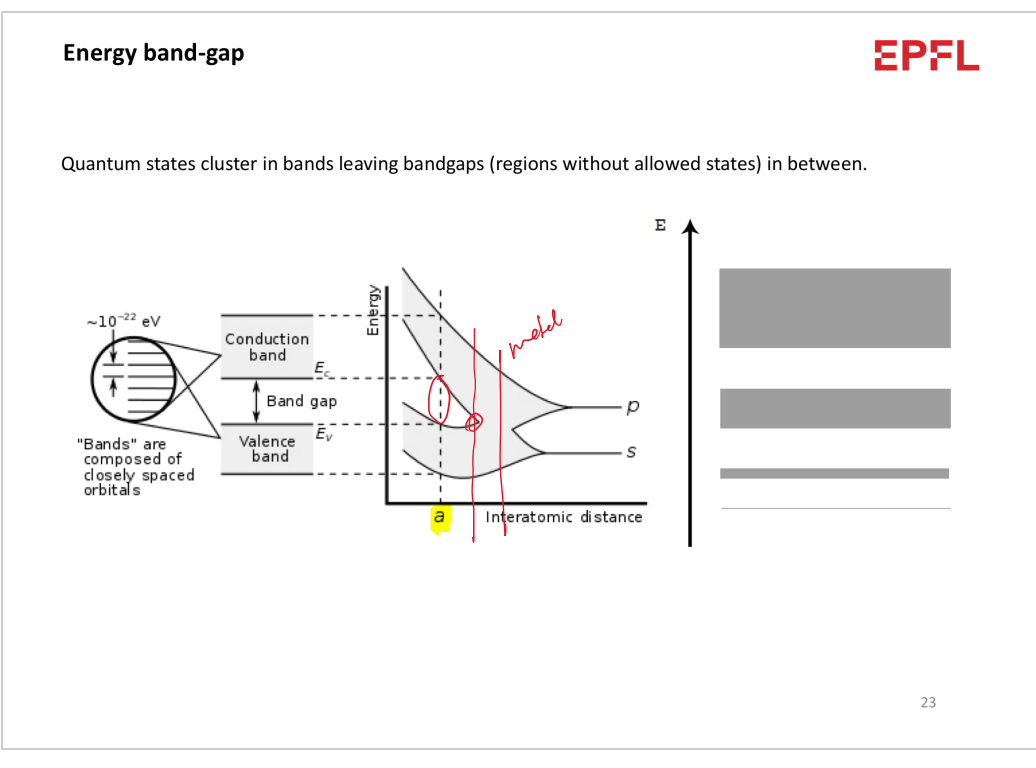
the new wave function ψ is a composition of all φi of each atom:

$\psi = \sum_i c_i\varphi_i$ (coefficients)

$\rightarrow \lambda = 2a$, $k = \pi/a$

$\rightarrow \lambda = N.a$, $k = 2\pi/Na$

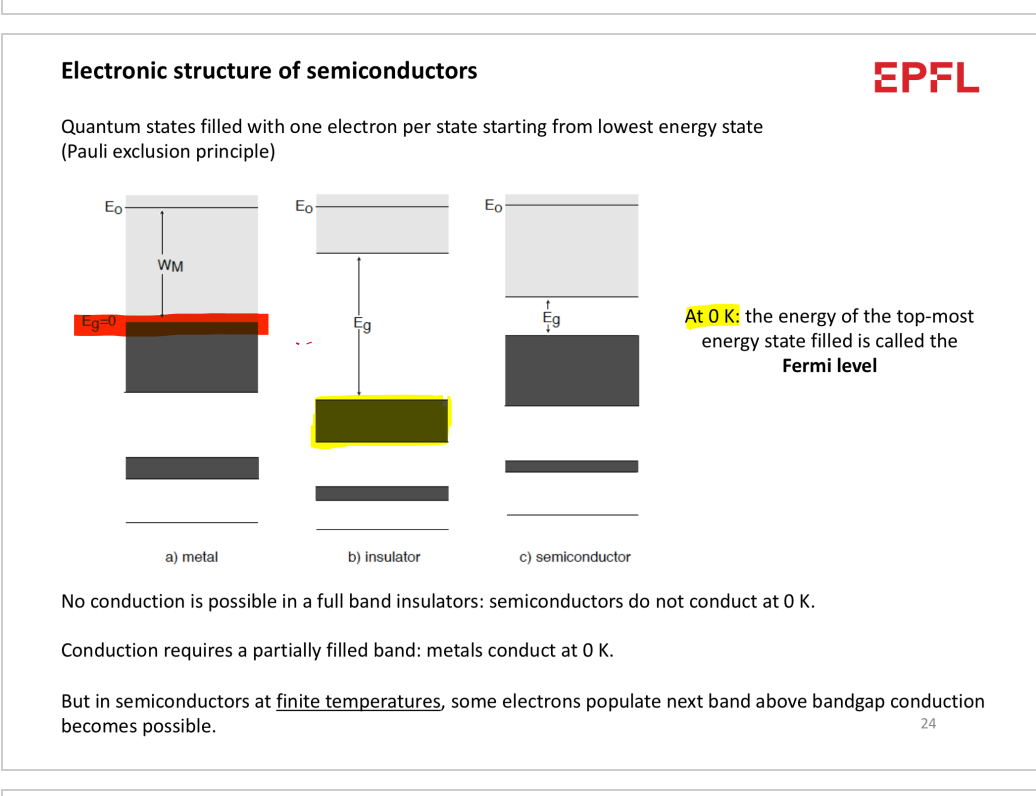
$\rightarrow \lambda = \infty$, $k = \frac{2\pi}{\lambda} = 0$



Energy band-gap

Quantum states cluster in bands leaving bandgaps (regions without allowed states) in between.

~10⁻²² eV
"Bands" are composed of closely spaced orbitals
Conduction band
Ec
Band gap
Valence band
Ev
Energy
metal
p
s
a
Interatomic distance
E



Electronic structure of semiconductors

Quantum states filled with one electron per state starting from lowest energy state (Pauli exclusion principle)

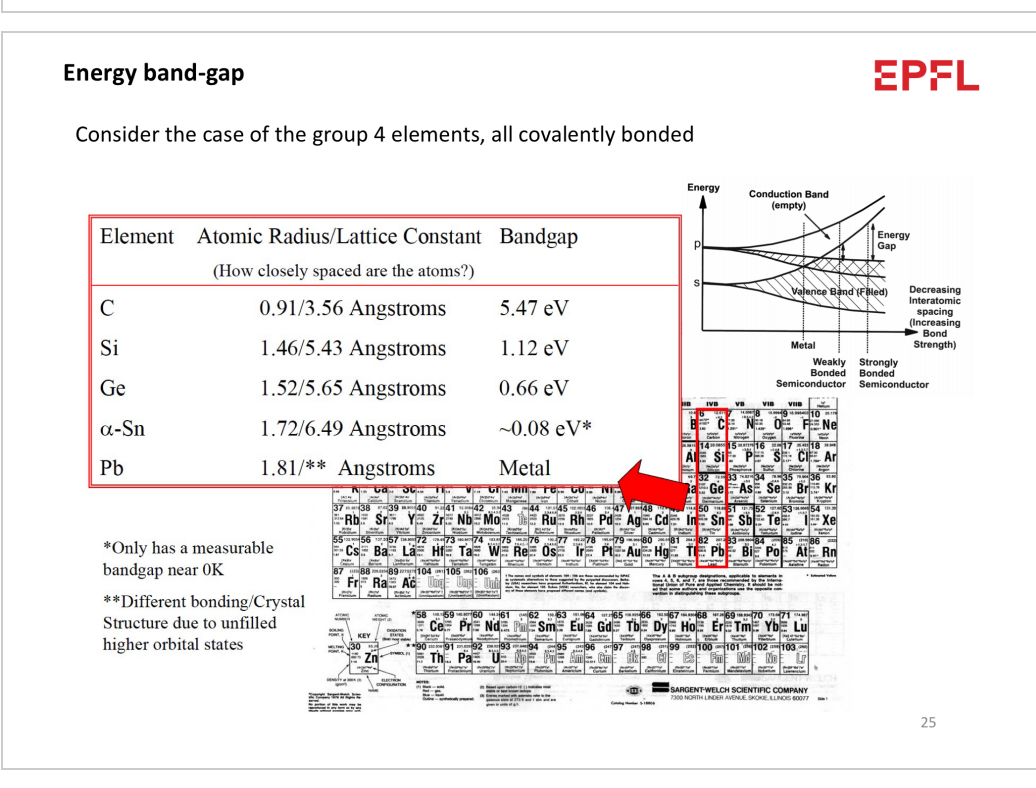
E0
WM
Eg=0
Eg
a) metal
b) insulator
c) semiconductor

At 0 K: the energy of the top-most energy state filled is called the **Fermi level**

No conduction is possible in a full band insulators: semiconductors do not conduct at 0 K.

Conduction requires a partially filled band: metals conduct at 0 K.

But in semiconductors at finite temperatures, some electrons populate next band above bandgap conduction becomes possible.



Energy band-gap

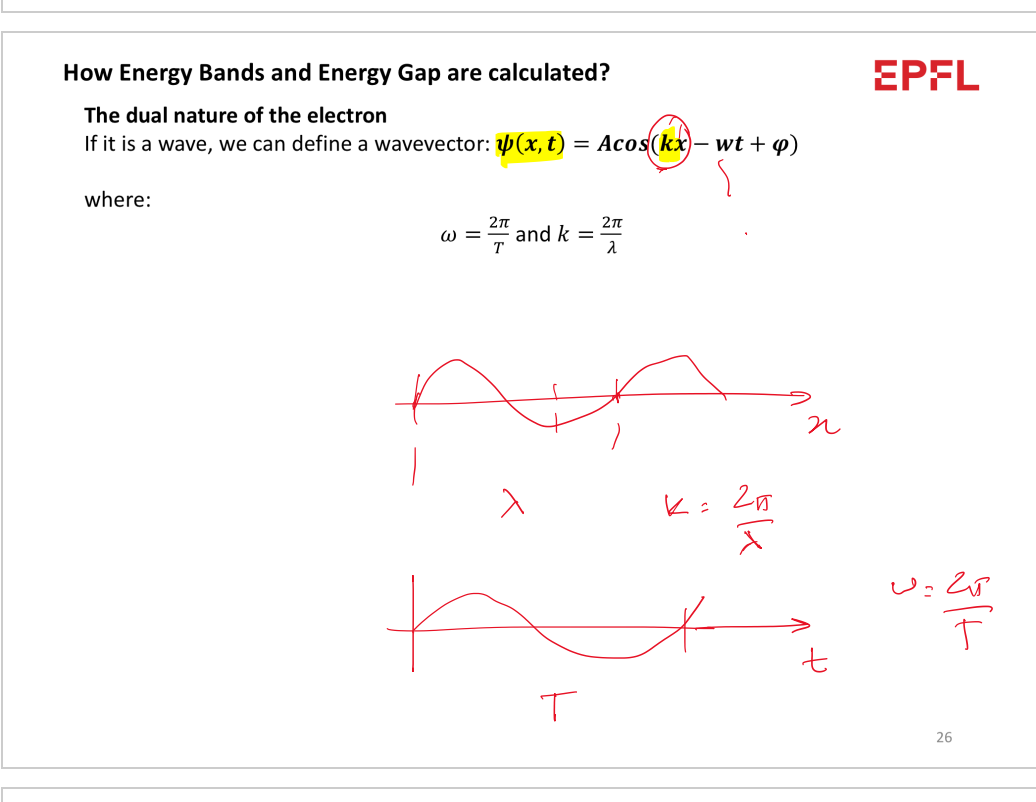
Consider the case of the group 4 elements, all covalently bonded

Element	Atomic Radius/Lattice Constant (How closely spaced are the atoms?)	Bandgap
C	0.91/3.56 Angstroms	5.47 eV
Si	1.46/5.43 Angstroms	1.12 eV
Ge	1.52/5.65 Angstroms	0.66 eV
α-Sn	1.72/6.49 Angstroms	~0.08 eV*
Pb	1.81/** Angstroms	Metal

*Only has a measurable bandgap near 0K

**Different bonding/Crystal Structure due to unfilled higher orbital states

Energy
Conduction Band (empty)
Energy Gap
p
s
Valence Band (filled)
Decreasing Interatomic spacing (Increasing Bond Strength)
Metal
Weakly Bonded Semiconductor
Strongly Bonded Semiconductor
SARGENT-WELCH SCIENTIFIC COMPANY



How Energy Bands and Energy Gap are calculated?

The dual nature of the electron

If it is a wave, we can define a wavevector: $\psi(x,t) = A\cos(kx - wt + \varphi)$

where:

$\omega = \frac{2\pi}{T}$ and $k = \frac{2\pi}{\lambda}$

x
λ
k = 2π/λ
t
T
ω = 2π/T

How Energy Bands and Energy Gap are calculated?

Energy-momentum relationship: characterizes the band structure

- Important for the interactions with photons and phonons

Schrödinger's equation: $\left[-\frac{\hbar^2}{2m^*}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r},\mathbf{k}) = E(\mathbf{k})\psi(\mathbf{r},\mathbf{k})$

Bloch function $\psi(\mathbf{r},\mathbf{k}) = \exp(j\mathbf{k}\cdot\mathbf{r})U_b(\mathbf{r},\mathbf{k})$

$\psi(\mathbf{r},\mathbf{k})$ and $U_b(\mathbf{r},\mathbf{k})$ are periodic in R in real space

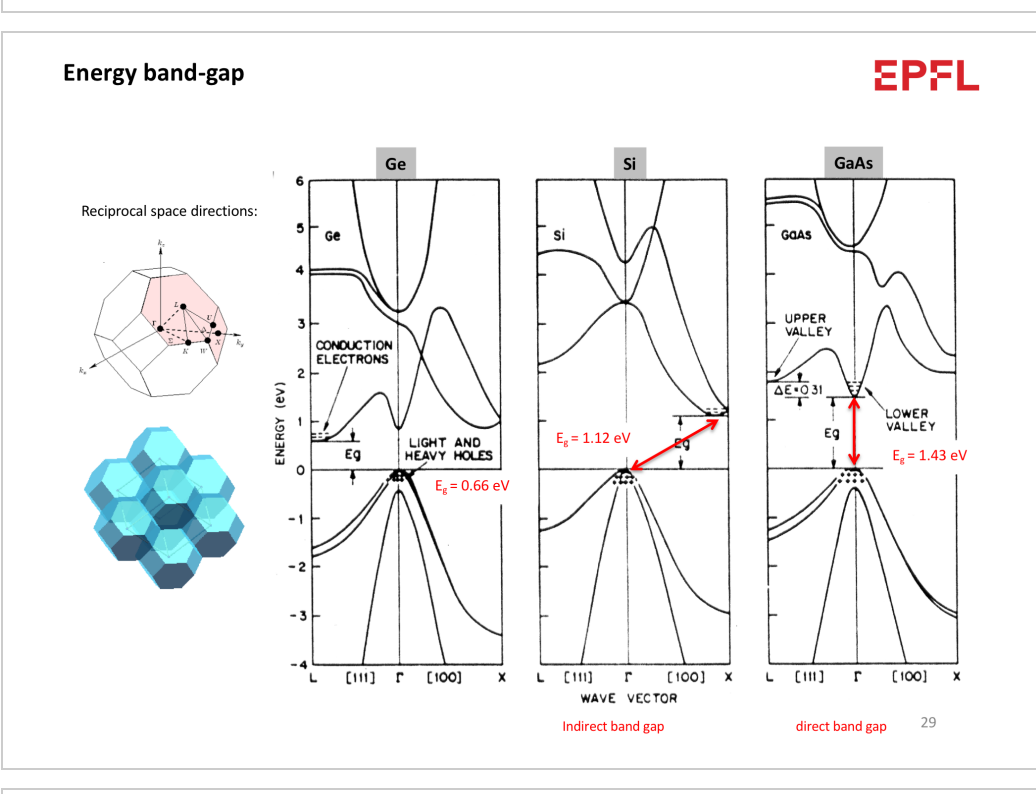
Thus:

$$\psi(\mathbf{r}+\mathbf{R},\mathbf{k}) = \exp[j\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})]U_b(\mathbf{r}+\mathbf{R},\mathbf{k})$$
$$= \exp(j\mathbf{k}\cdot\mathbf{r})\exp(j\mathbf{k}\cdot\mathbf{R})U_b(\mathbf{r},\mathbf{k})$$

$\mathbf{k}\cdot\mathbf{R}$ is a multiple of 2π.

Consequences:

- In 1D: only *k* = 2**π**/*a* are allowed (where *a* is the real space period)
- E(*k*) is periodic in k-space: E(*k*) = E(*k*+G)
- It is sufficient to define *k* in a primitive cell, which is defined by the Brillouin zone
- Entire band structures need only to be calculated within the brillouin zone.

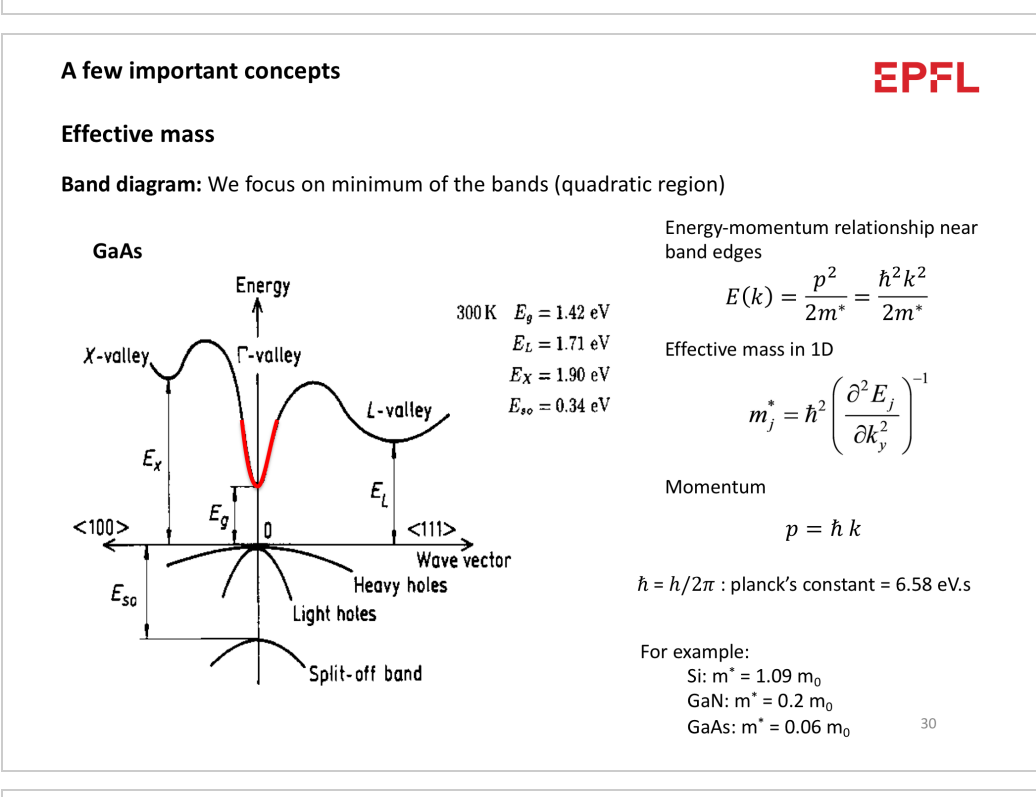


Energy band-gap

Reciprocal space directions:

Indirect band gap

direct band gap



A few important concepts

Effective mass

Band diagram: We focus on minimum of the bands (quadratic region)

GaAs
Energy
X-valley
Γ-valley
L-valley
Ex
Eg
EL
Eso
<100>
<111>
0
Wave vector
Heavy holes
Light holes
Split-off band

300 K $E_g = 1.42$ eV
$E_L = 1.71$ eV
$E_X = 1.90$ eV
$E_{so} = 0.34$ eV

Energy-momentum relationship near band edges

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

Effective mass in 1D

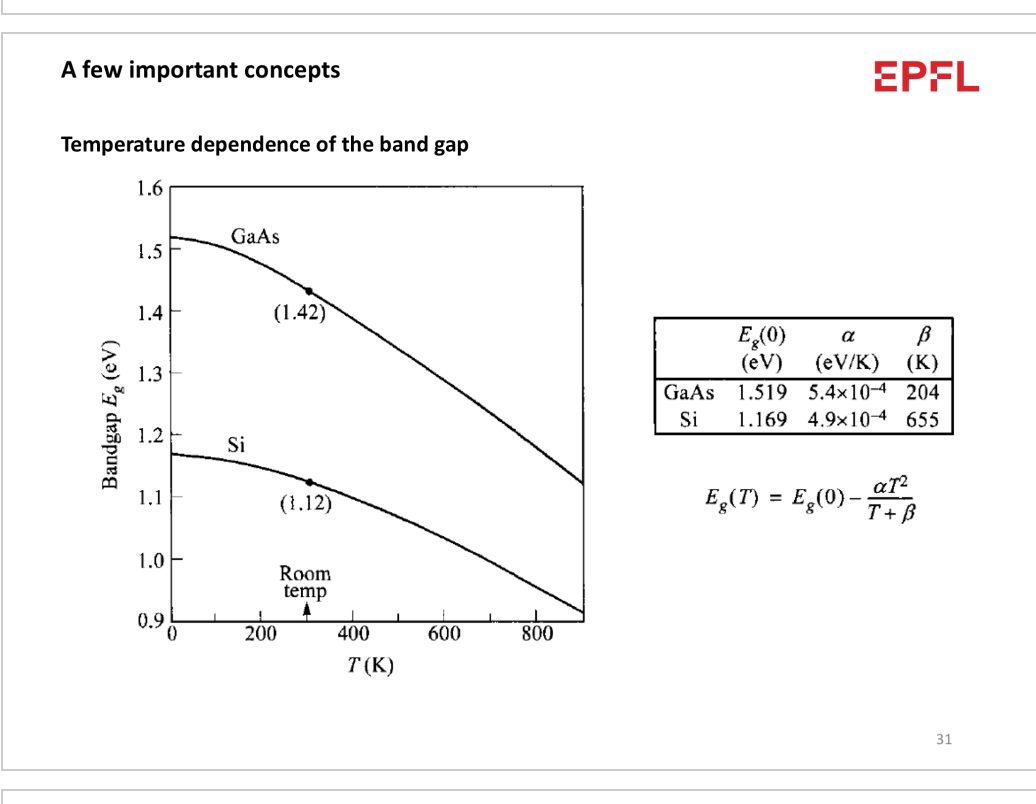
$$m_j^* = \hbar^2\left(\frac{\partial^2 E_j}{\partial k_y^2}\right)^{-1}$$

Momentum

$$p = \hbar k$$

ħ = h/2π : planck's constant = 6.58 eV.s

For example:
Si: m* = 1.09 m_0
GaN: m* = 0.2 m_0
GaAs: m* = 0.06 m_0



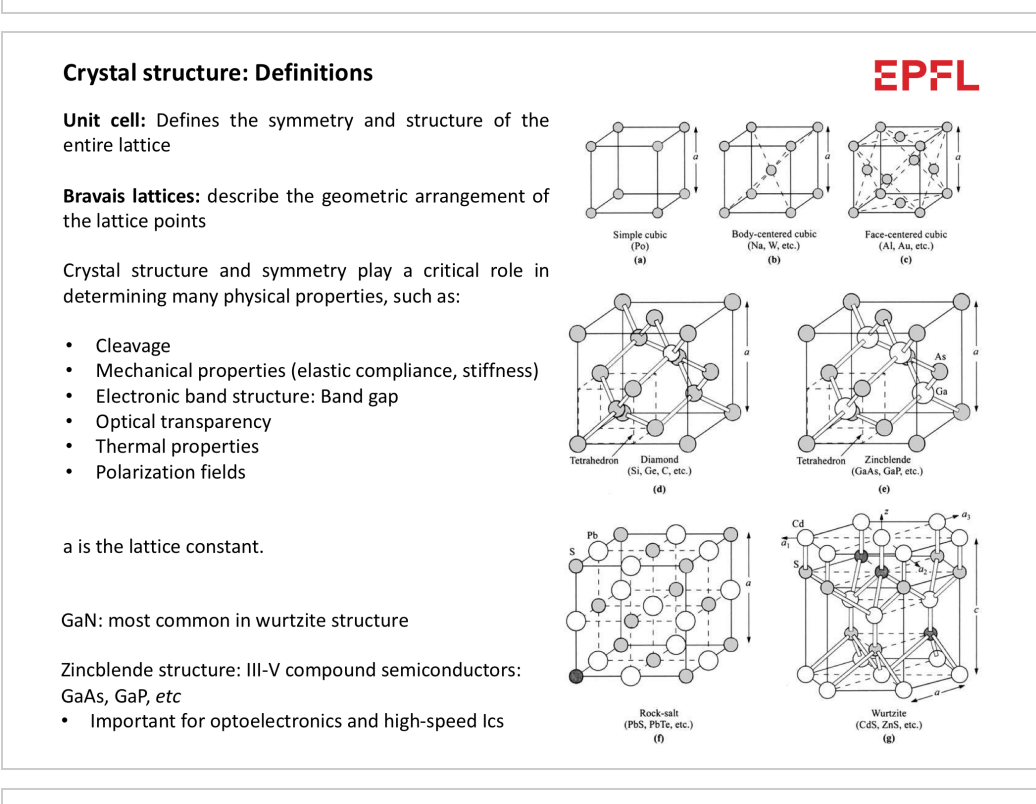
A few important concepts

Temperature dependence of the band gap

	$E_g(0)$ (eV)	α (eV/K)	β (K)
GaAs	1.519	5.4×10^{-4}	204
Si	1.169	4.9×10^{-4}	655

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta}$$

Appendix – Supplementary Material



Crystal structure: Definitions

Unit cell: Defines the symmetry and structure of the entire lattice

Bravais lattices: describe the geometric arrangement of the lattice points

Crystal structure and symmetry play a critical role in determining many physical properties, such as:

- Cleavage
- Mechanical properties (elastic compliance, stiffness)
- Electronic band structure: Band gap
- Optical transparency
- Thermal properties
- Polarization fields

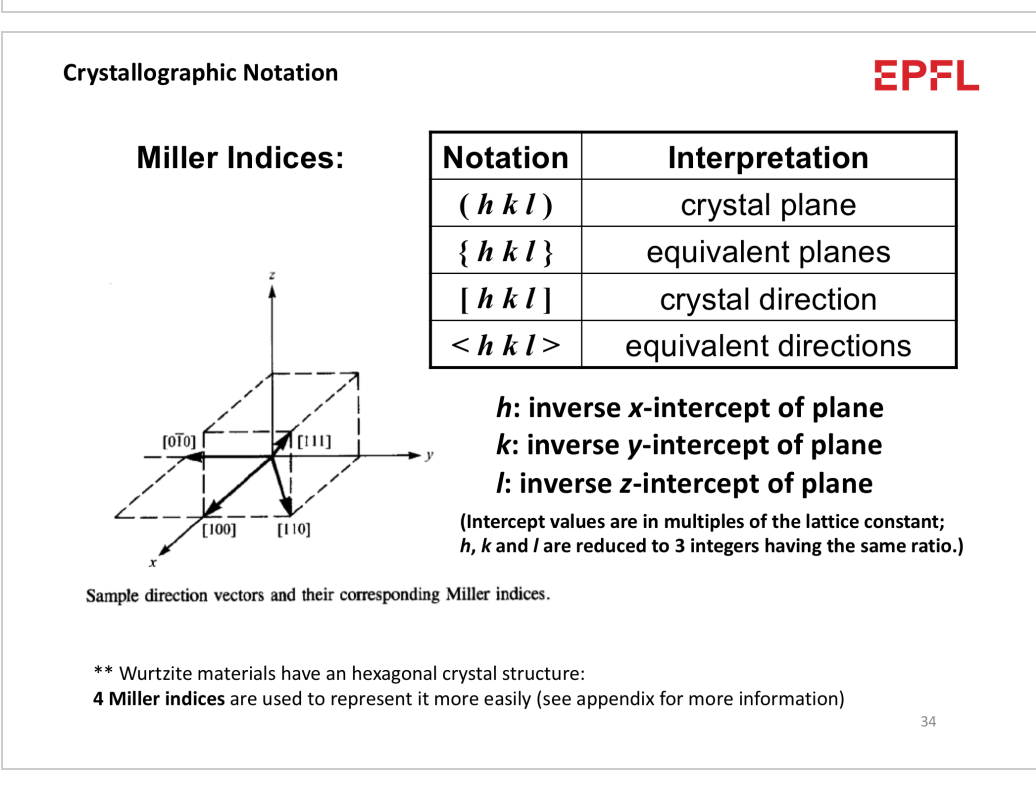
a is the lattice constant.

GaN: most common in wurtzite structure

Zincblende structure: III-V compound semiconductors: GaAs, GaP, *etc*

- Important for optoelectronics and high-speed Ics

Simple cubic (Po) (a)
Body-centered cubic (Na, W, etc.) (b)
Face-centered cubic (Al, Au, etc.) (c)
Tetrahedron
Diamond (Si, Ge, C, etc.) (d)
Zincblende (GaAs, GaP, etc.) (e)
Rock-salt (PbS, PbTe, etc.) (f)
Wurtzite (CdS, ZnS, etc.) (g)



Crystallographic Notation

Miller Indices:

Notation	Interpretation
(*h k l*)	crystal plane
{ *h k l* }	equivalent planes
[*h k l*]	crystal direction
< *h k l* >	equivalent directions

***h*: inverse *x*-intercept of plane**
***k*: inverse *y*-intercept of plane**
***l*: inverse *z*-intercept of plane**

(Intercept values are in multiples of the lattice constant; *h*, *k* and *l* are reduced to 3 integers having the same ratio.)

z
y
x
[0$\bar{1}$0]
[111]
[100]
[110]

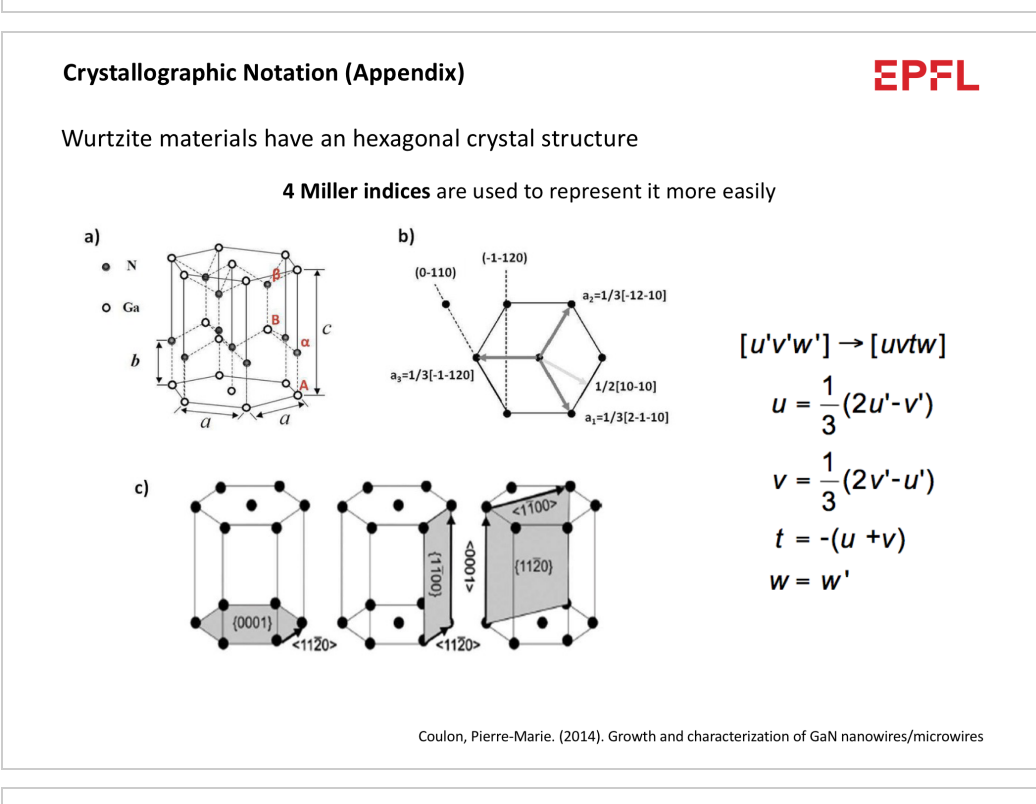
Sample direction vectors and their corresponding Miller indices.

** Wurtzite materials have an hexagonal crystal structure:
4 Miller indices are used to represent it more easily (see appendix for more information)

Crystal structure

How Many Silicon Atoms per cm³?

- **Number of atoms in a unit cell:**
  - 4 atoms completely inside cell
  - Each of the 8 atoms on corners are shared among cells → count as 1 atom inside cell
  - Each of the 6 atoms on the faces are shared among 2 cells → count as 3 atoms inside cell
  - ⇒ Total number inside the cell = 4 + 1 + 3 = **8**
- **Cell volume:**
  (.543 nm)³ = 1.6 x 10⁻²² cm³
- **Density of silicon atoms**
  = (8 atoms) / (cell volume) = **5 x 10²² atoms/cm³**



Crystallographic Notation (Appendix)

Wurtzite materials have an hexagonal crystal structure

4 Miller indices are used to represent it more easily

a)
N
Ga
b
a
c
B
α
A
β
b)
(0-110)
(-1-120)
a2=1/3[-12-10]
a3=1/3[-1-120]
1/2[10-10]
a1=1/3[2-1-10]
c)
{0001}
<11$\bar{2}$0>
{1$\bar{1}$00}
<0001>
{11$\bar{2}$0}
<1$\bar{1}$00>

$[u'v'w'] \rightarrow [uvtw]$

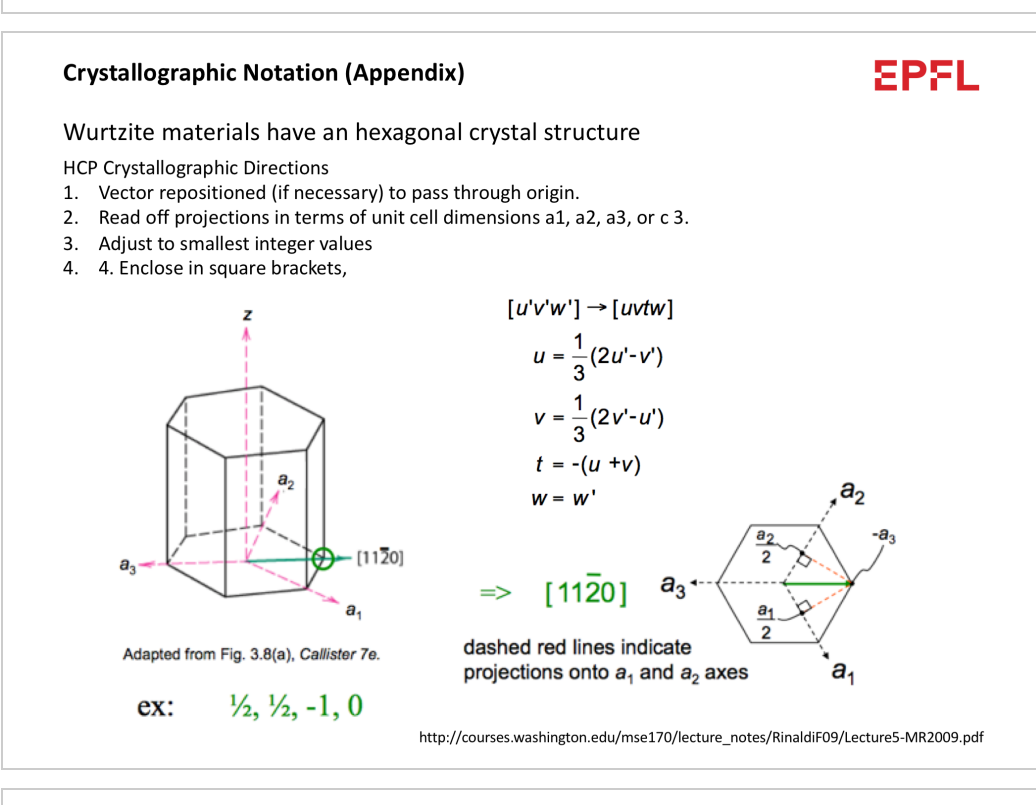
$u = \frac{1}{3}(2u' - v')$

$v = \frac{1}{3}(2v' - u')$

$t = -(u + v)$

$w = w'$

Coulon, Pierre-Marie. (2014). Growth and characterization of GaN nanowires/microwires



Crystallographic Notation (Appendix)

Wurtzite materials have an hexagonal crystal structure

HCP Crystallographic Directions

1. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions a1, a2, a3, or c 3.
3. Adjust to smallest integer values
4. 4. Enclose in square brackets,

$[u'v'w'] \rightarrow [uvtw]$

$u = \frac{1}{3}(2u' - v')$

$v = \frac{1}{3}(2v' - u')$

$t = -(u + v)$

$w = w'$

z
a2
a3
a1
[11$\bar{2}$0]
-a3
a2/2
a1/2

=> $[11\bar{2}0]$

dashed red lines indicate projections onto a_1 and a_2 axes

Adapted from Fig. 3.8(a), *Callister 7e.*

ex: ½, ½, -1, 0

http://courses.washington.edu/mse170/lecture_notes/RinaldiF09/Lecture5-MR2009.pdf

Interesting links and videos

Crystallography and reciprocal space
https://www.youtube.com/watch?v=DFFU39A3fPY

Quantum mechanics through walkers
https://www.youtube.com/watch?v=WIyTZDHuarQ

Slides on semiconductor physics
https://slideplayer.com/slide/6940114/