ICTP – Trieste 2024

Modelling Optical Properties using WIEN2k

Xavier Rocquefelte
Institut des Sciences Chimiques de Rennes (UMR 6226) Université de Rennes 1, FRANCE

Modelling the Optical Properties of Inorganic Materials

1 – MULTIPLE FACETS OF COLOURED MATTER

2 – ELECTRONIC STRUCTURE OF A SOLID

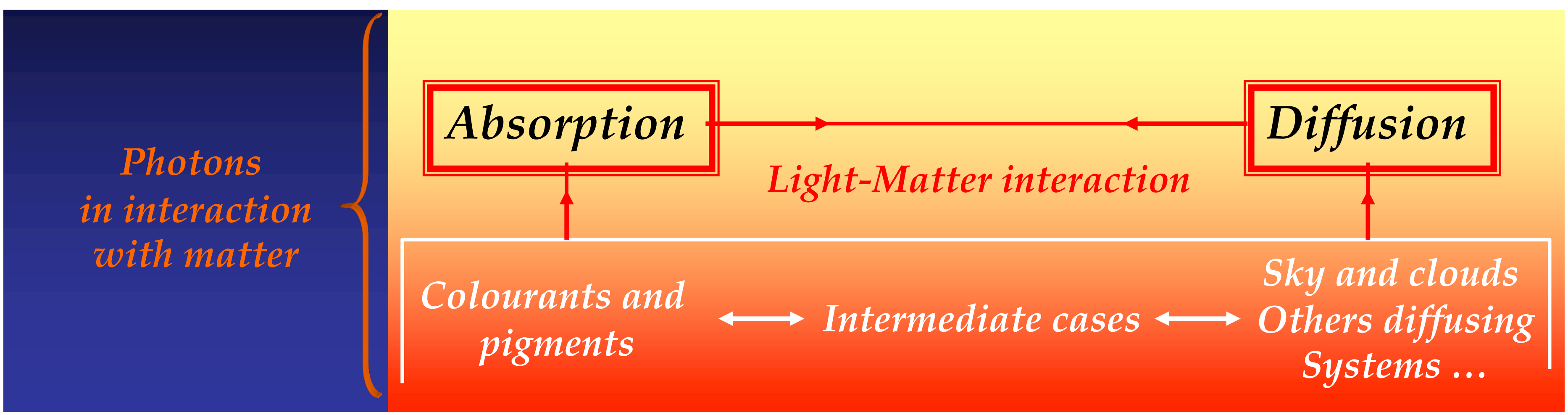
3 – UNDERSTANDING OF COLORS FROM BANDS

4 – LIGHT-MATTER INTERACTION

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

6 – ILLUSTRATIONS

1 – MULTIPLE FACETS OF COLOURED MATTER



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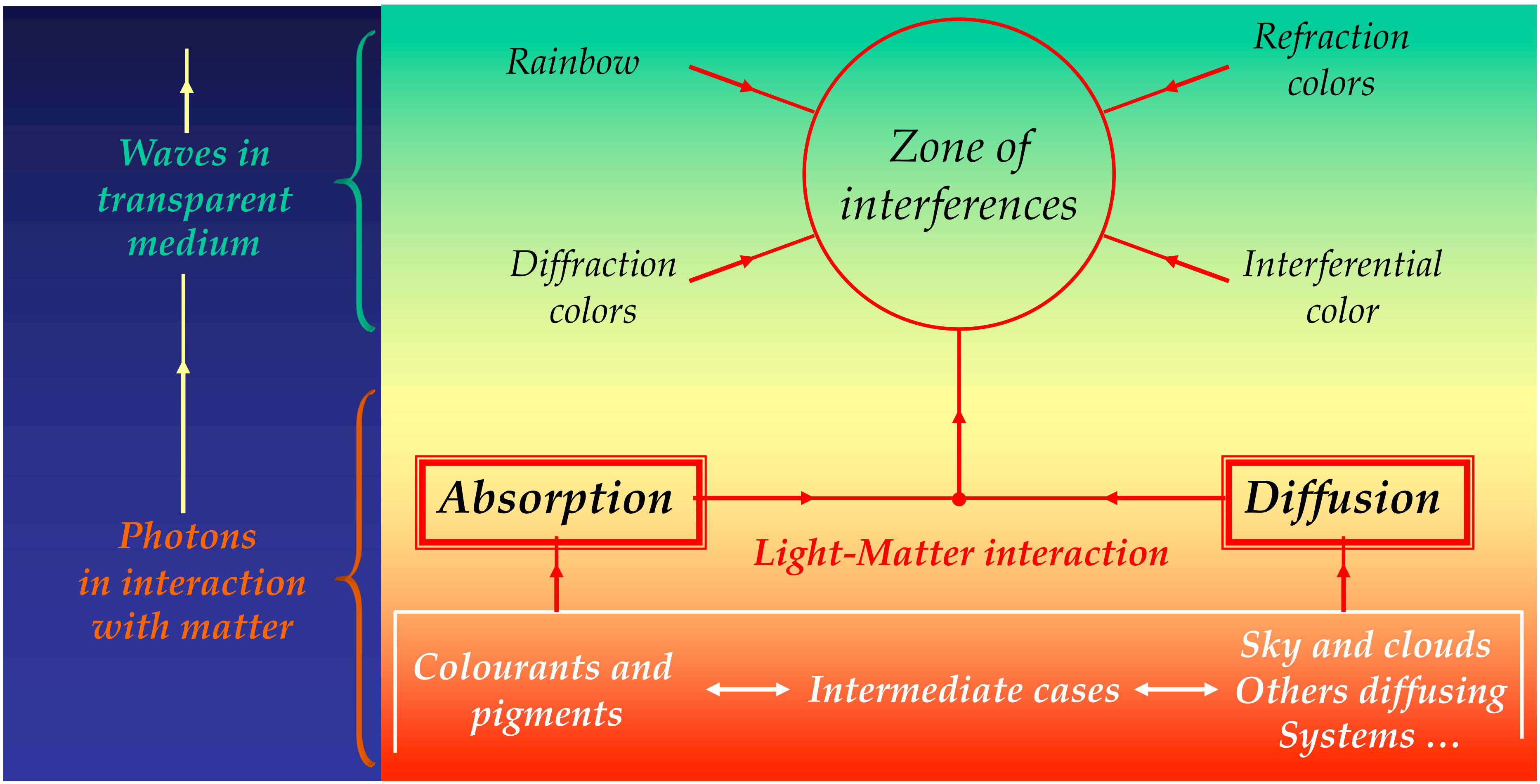

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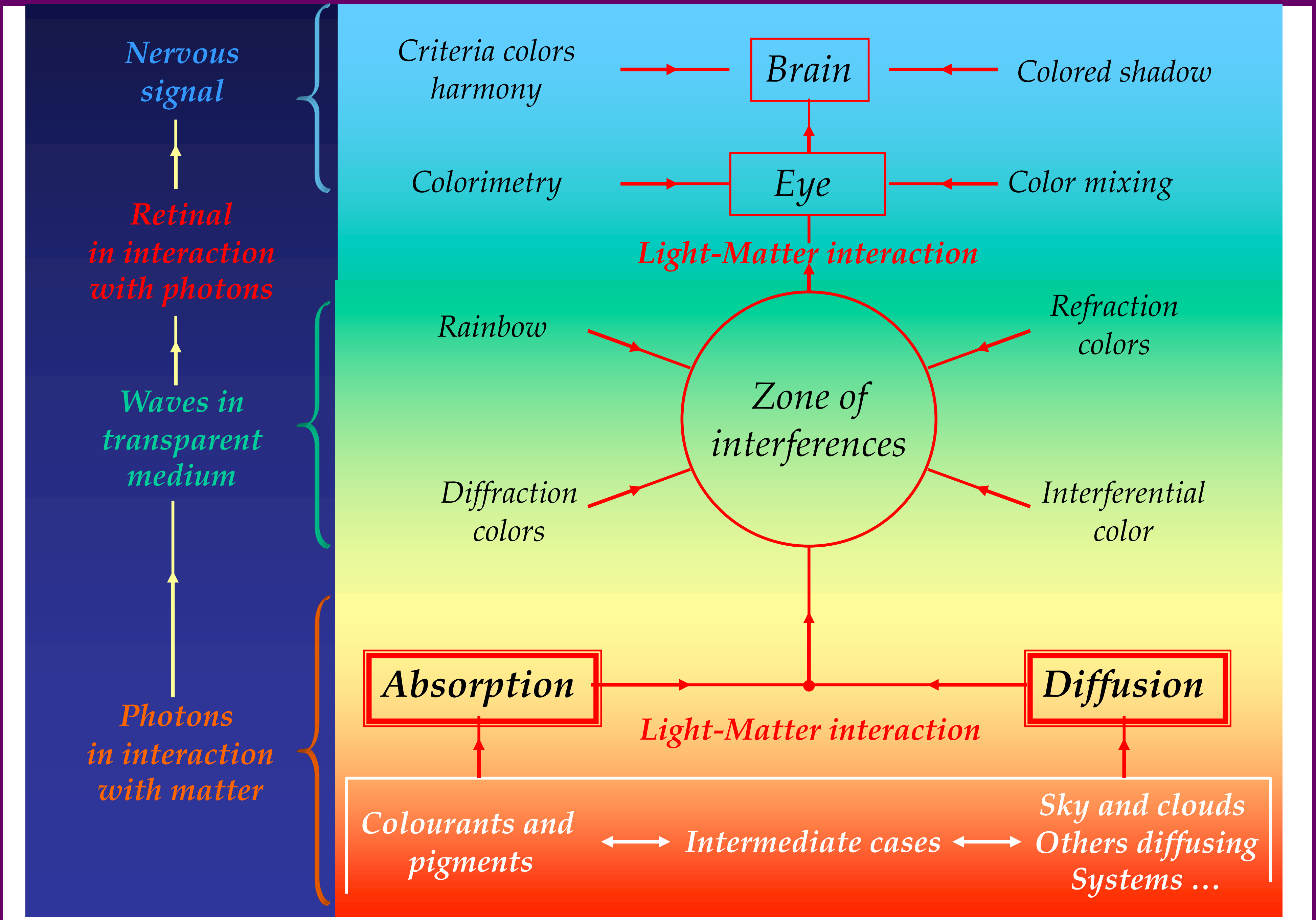

1 – MULTIPLE FACETS OF COLOURED MATTER

Interaction between the electromagnetic field and matter

Physical color

Diffusion et interferences
Dispersion / Reflection et Refraction / Scattering

Transparent matter

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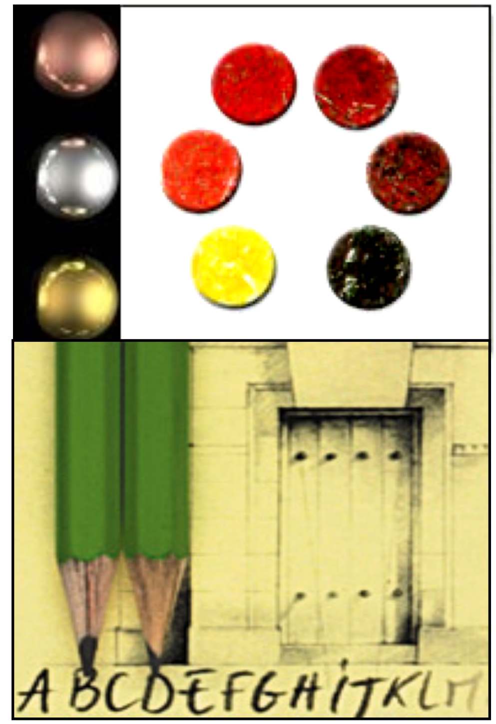
Chemical color



Absorption
Energy dissipation

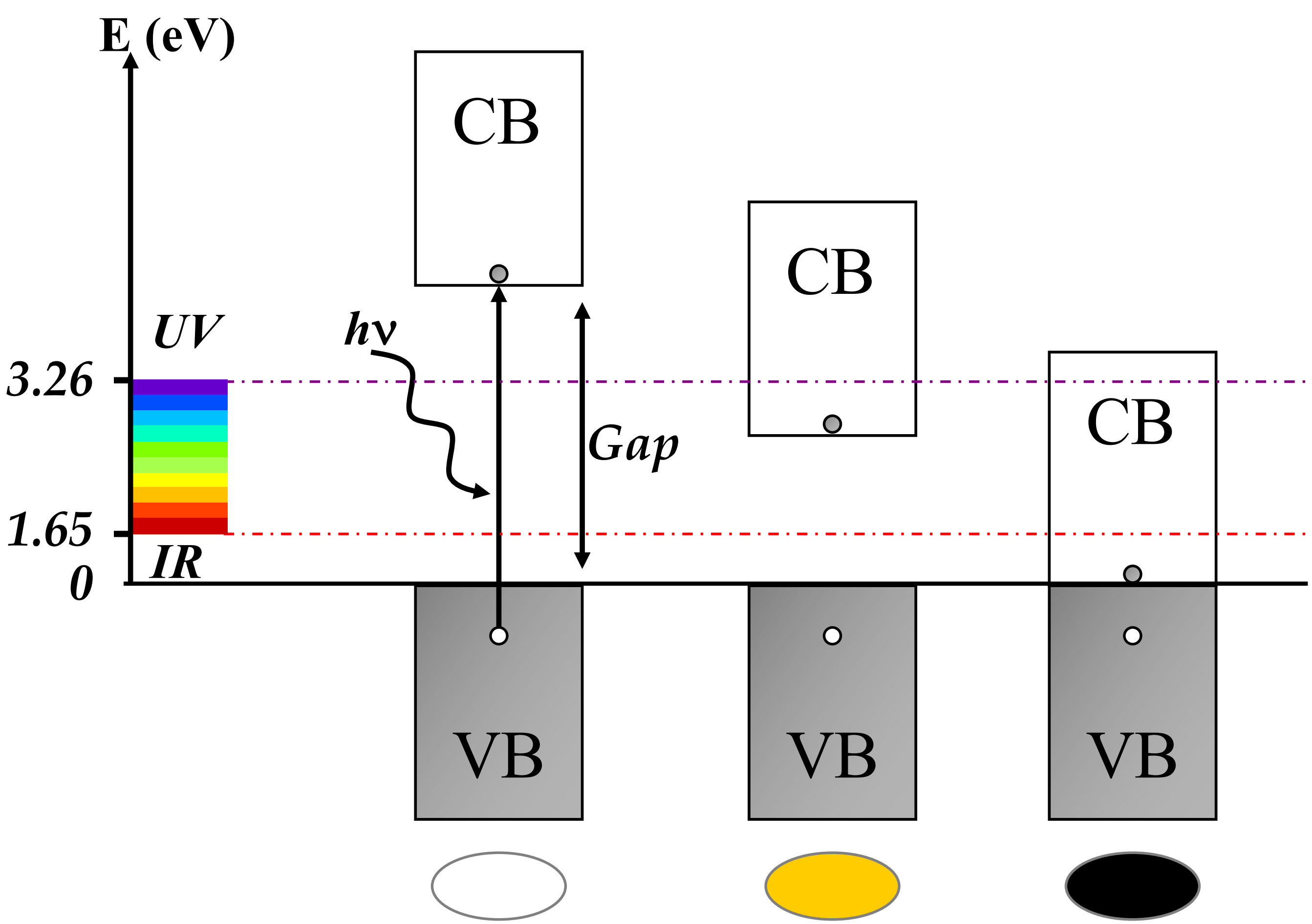
Opaque matter

1 – MULTIPLE FACETS OF COLOURED MATTER

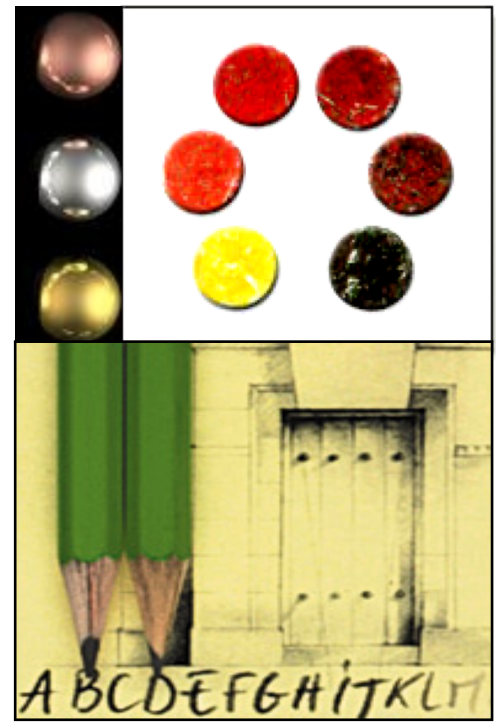
Chemical color → « Inelastic diffusion »

Acceptor electron levels ⇒ Dissipative absorption

From insulator to semiconductor to metal systems



Chemical colors



Absorption
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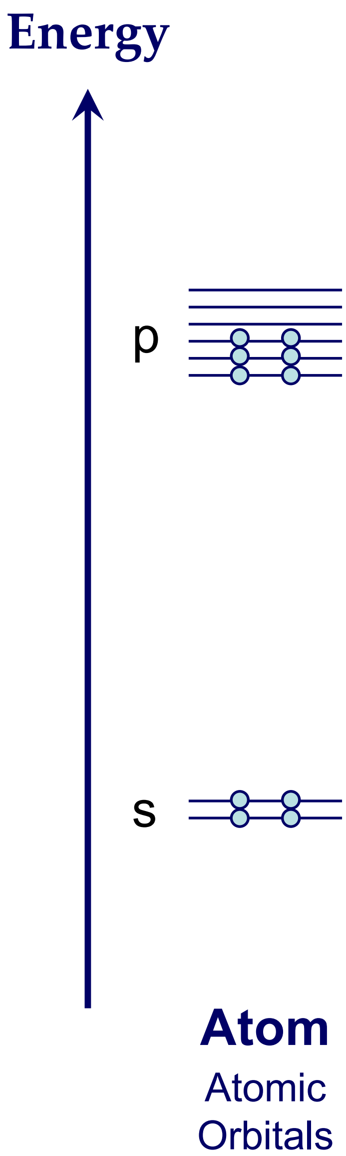
Opaque Matter

2 – ELECTRONIC STRUCTURE OF A SOLID

From the atom to the molecule and to the solid



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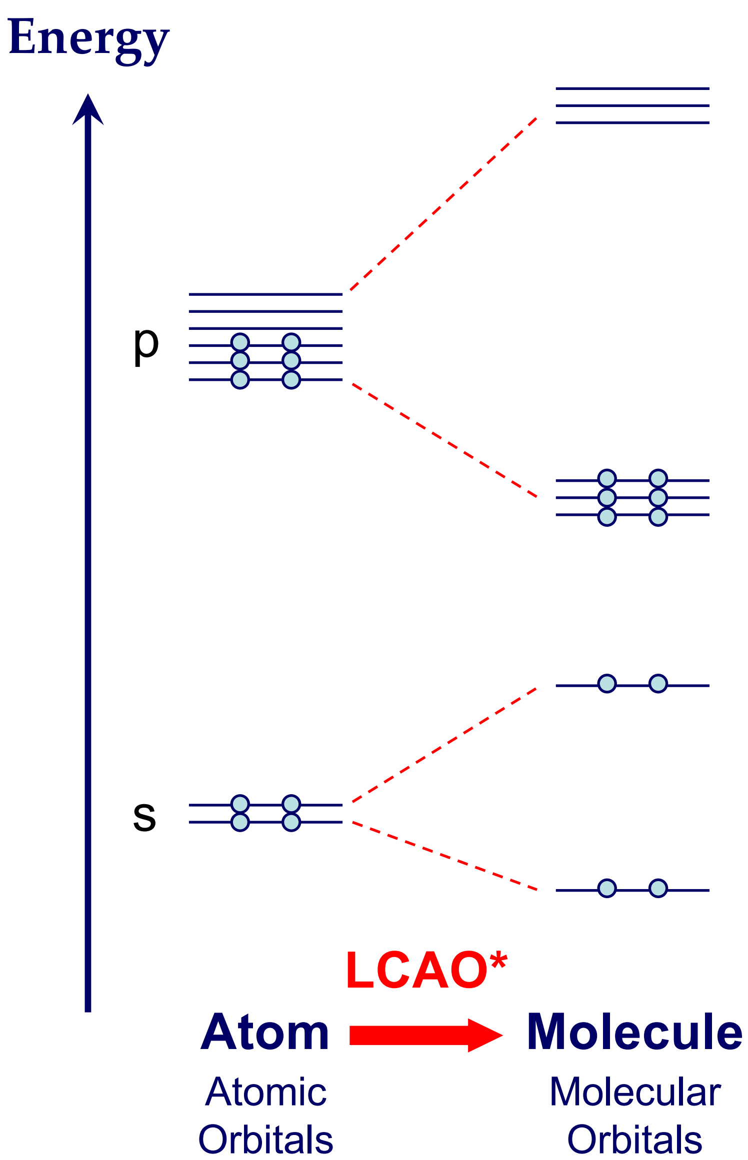

*LCAO : Linear Combination of Atomic Orbitals

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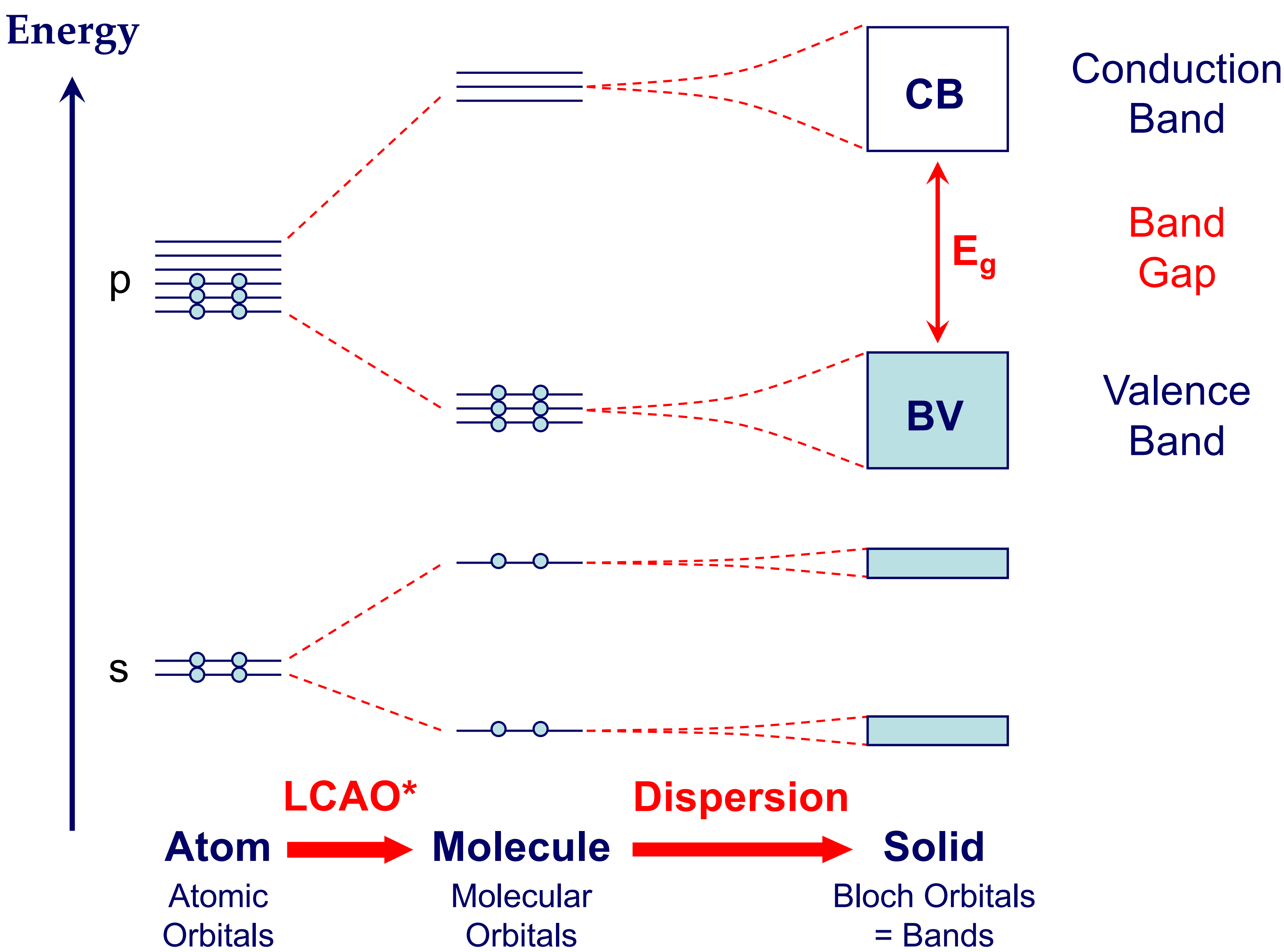
From the atom to the molecule and to the solid



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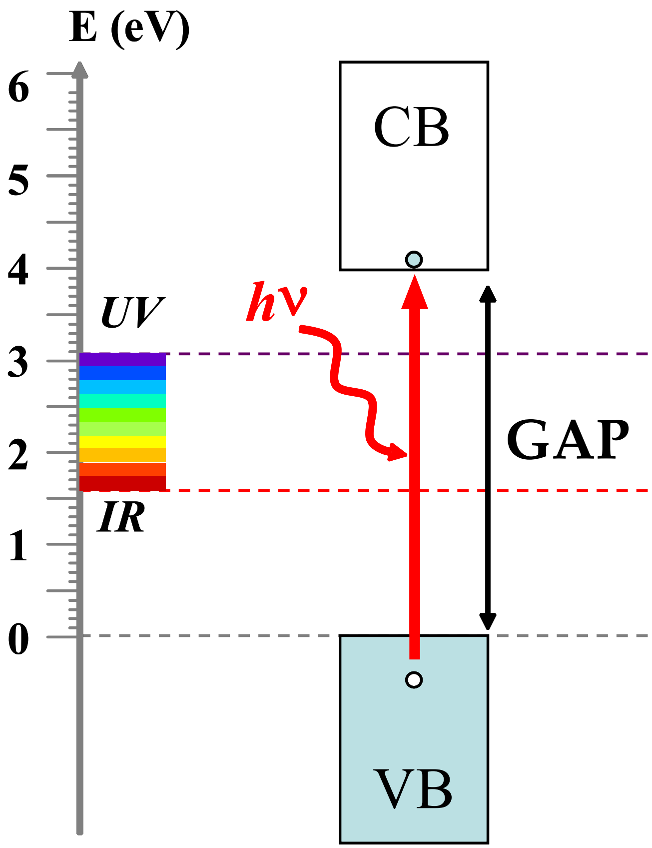
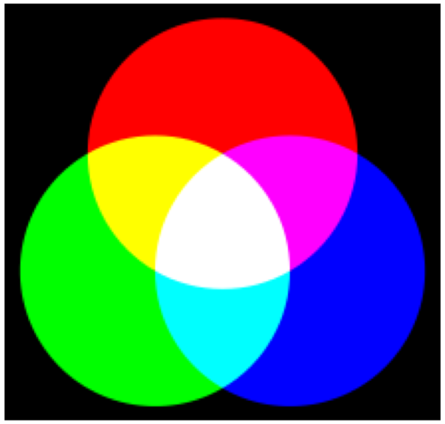
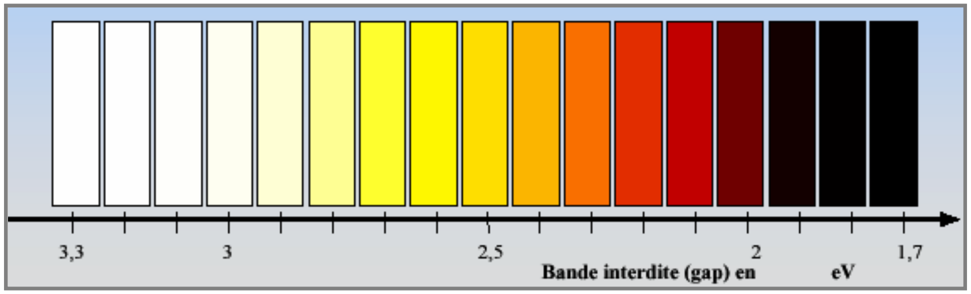
3 – UNDERSTANDING OF COLORS FROM BANDS





Color of a SC* with 1 gap



*SC : Semiconductor

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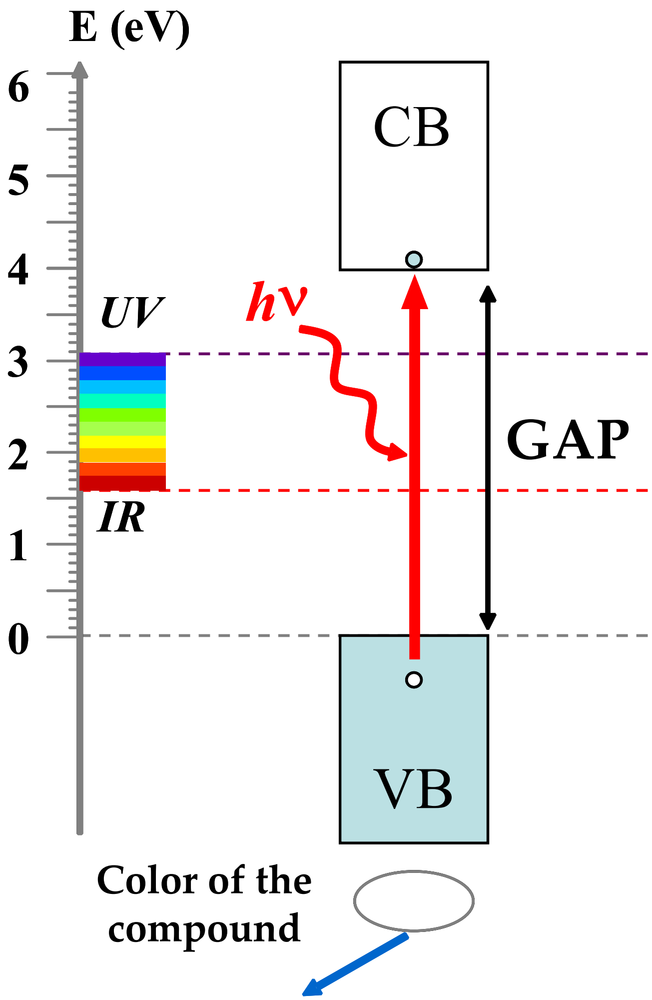

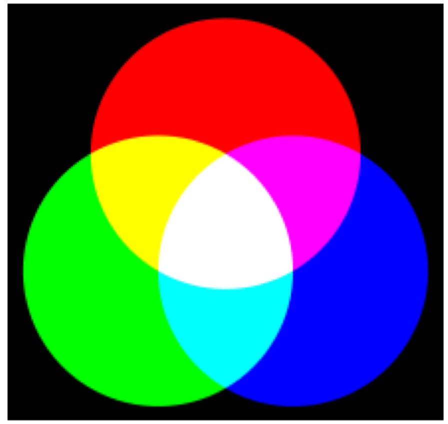

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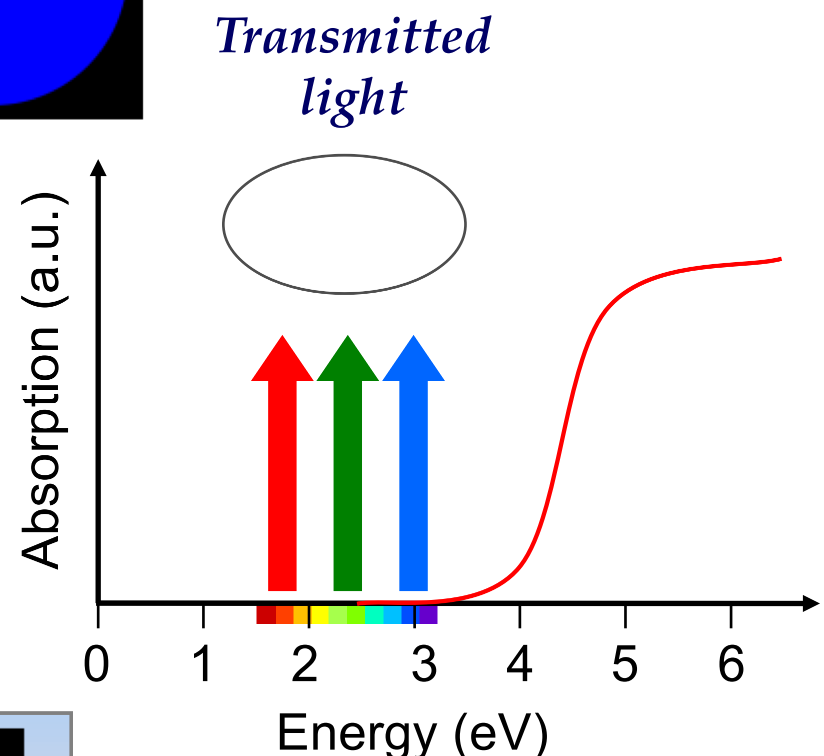

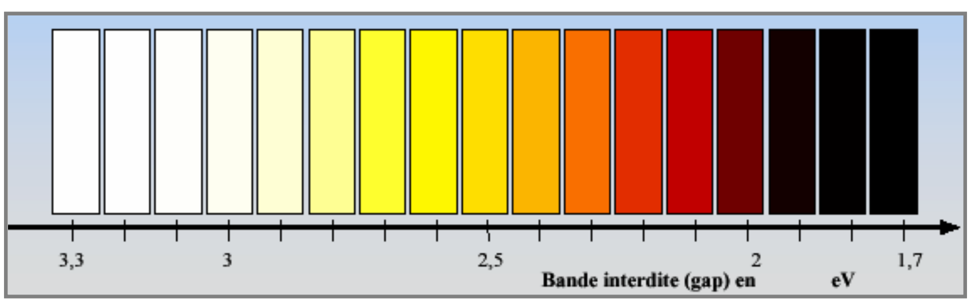

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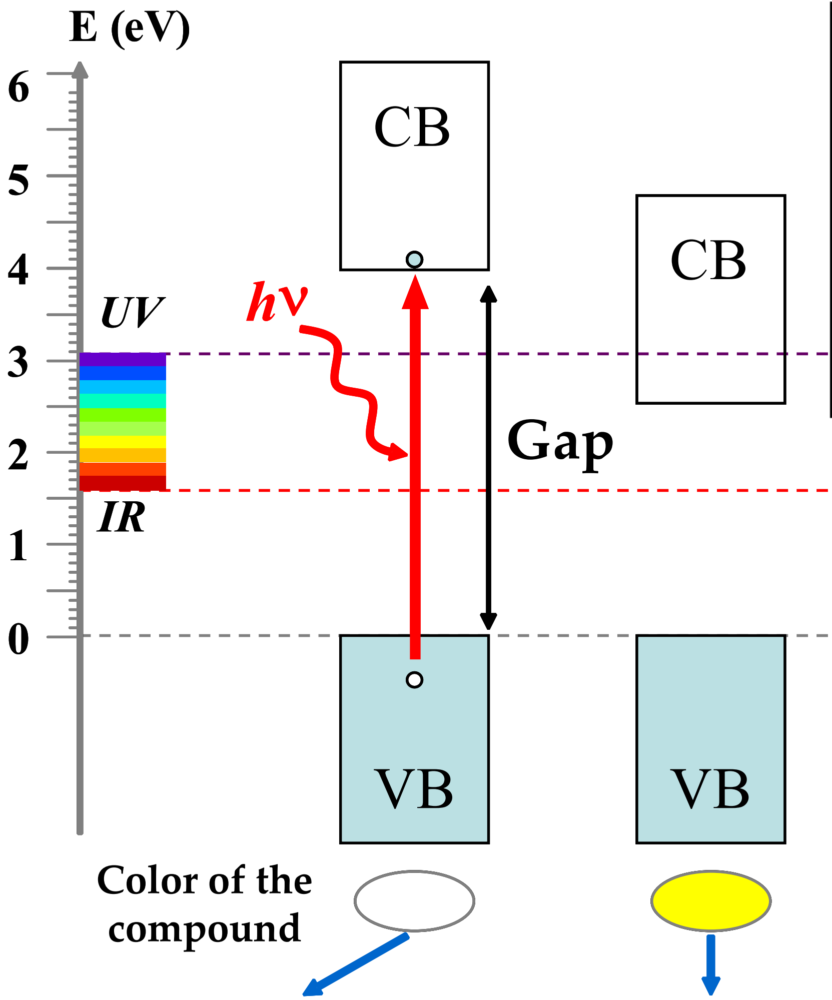

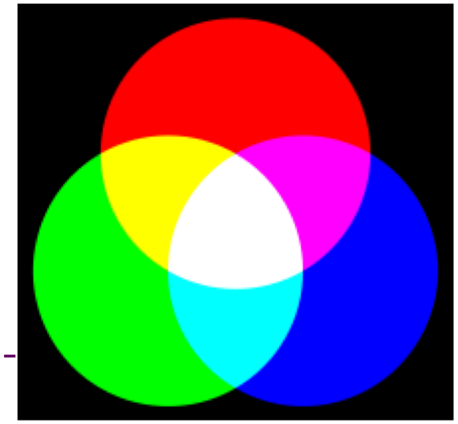

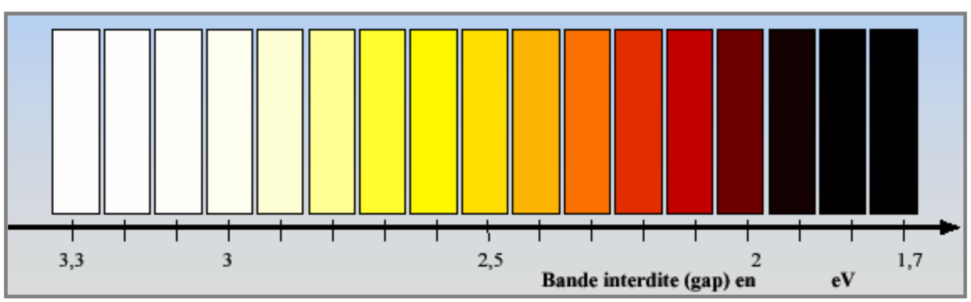

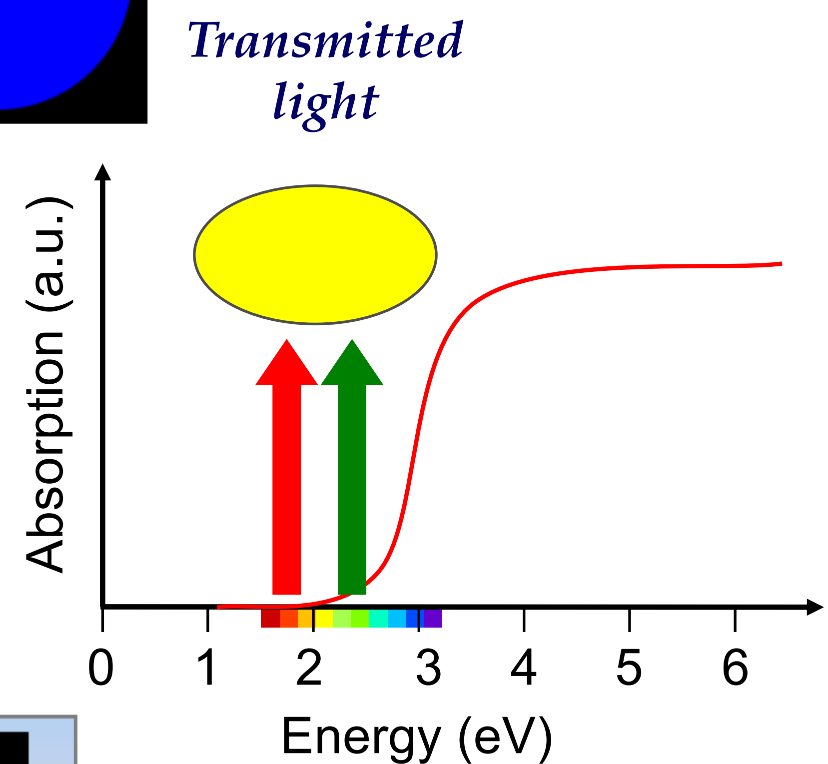

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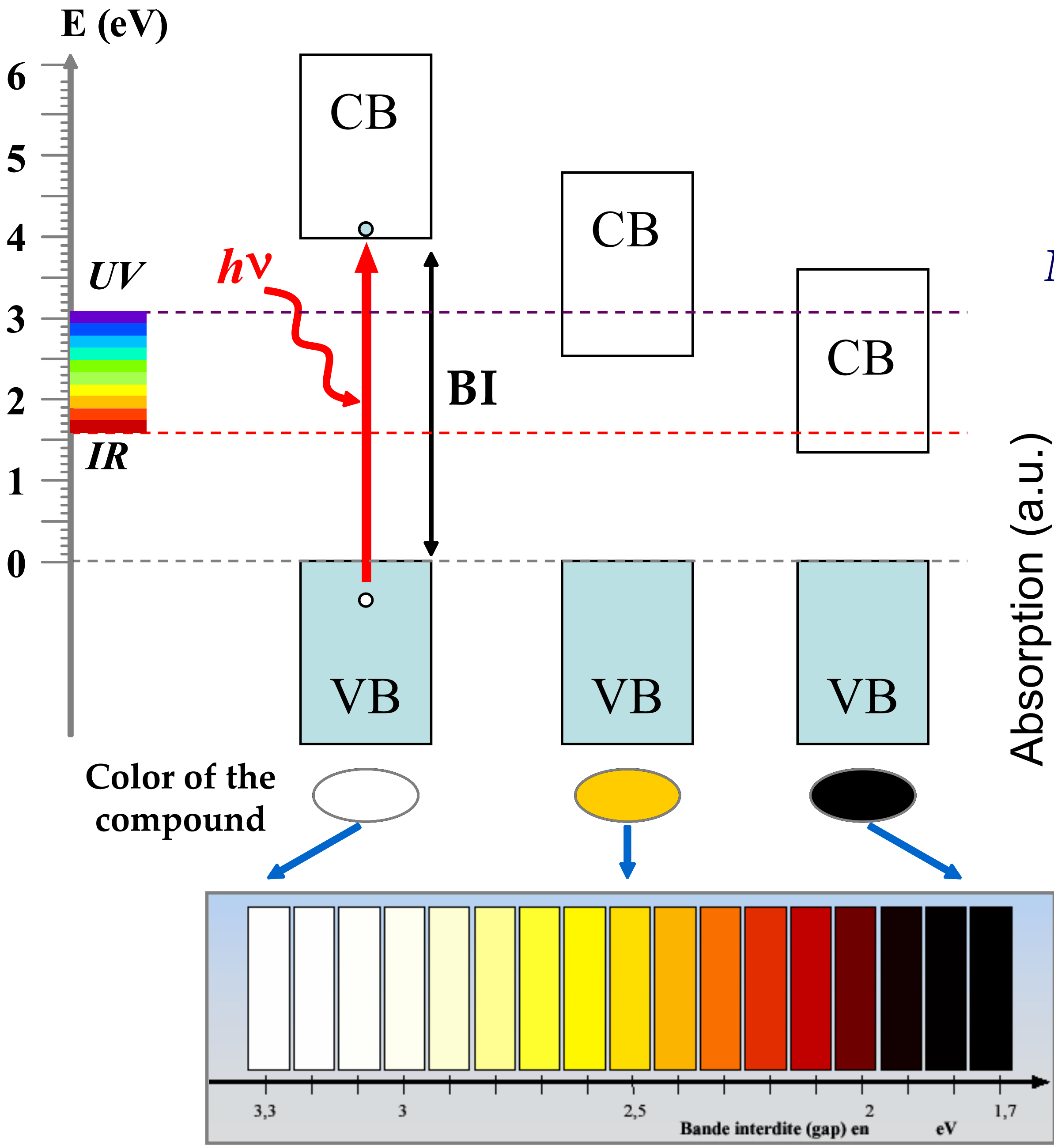

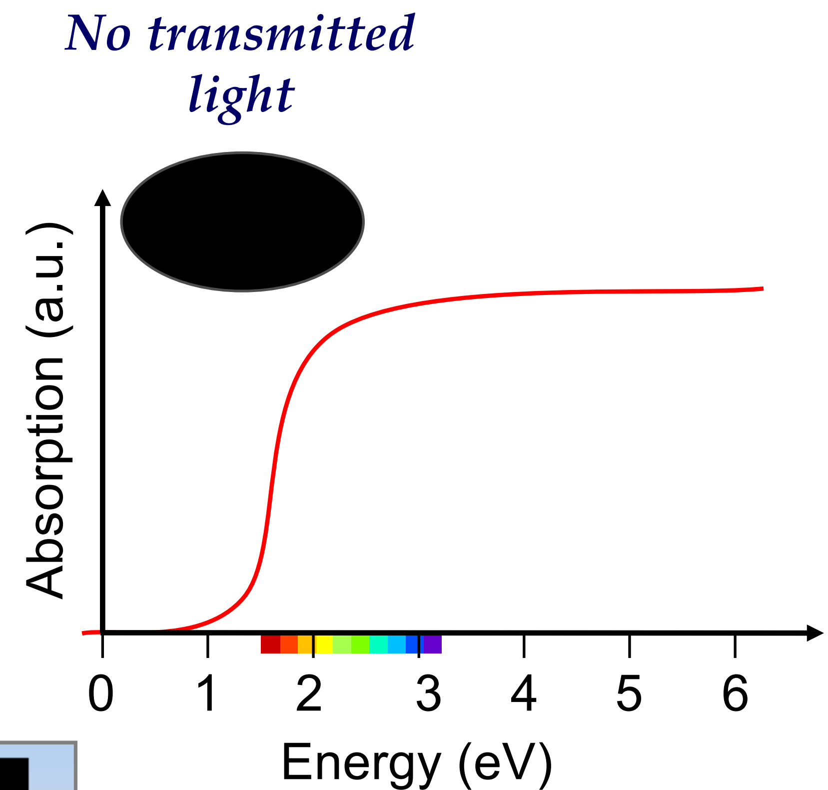

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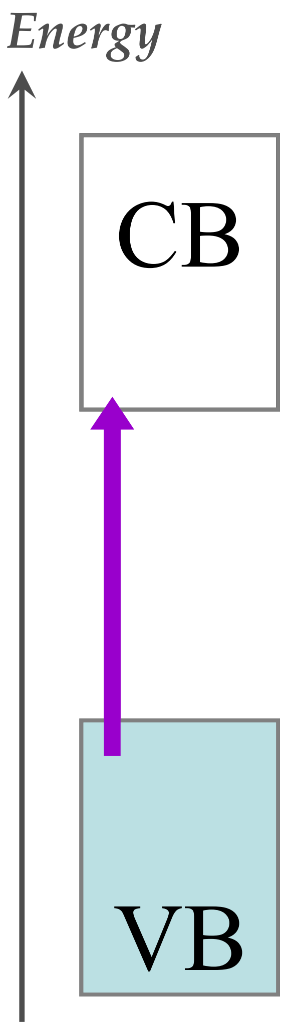
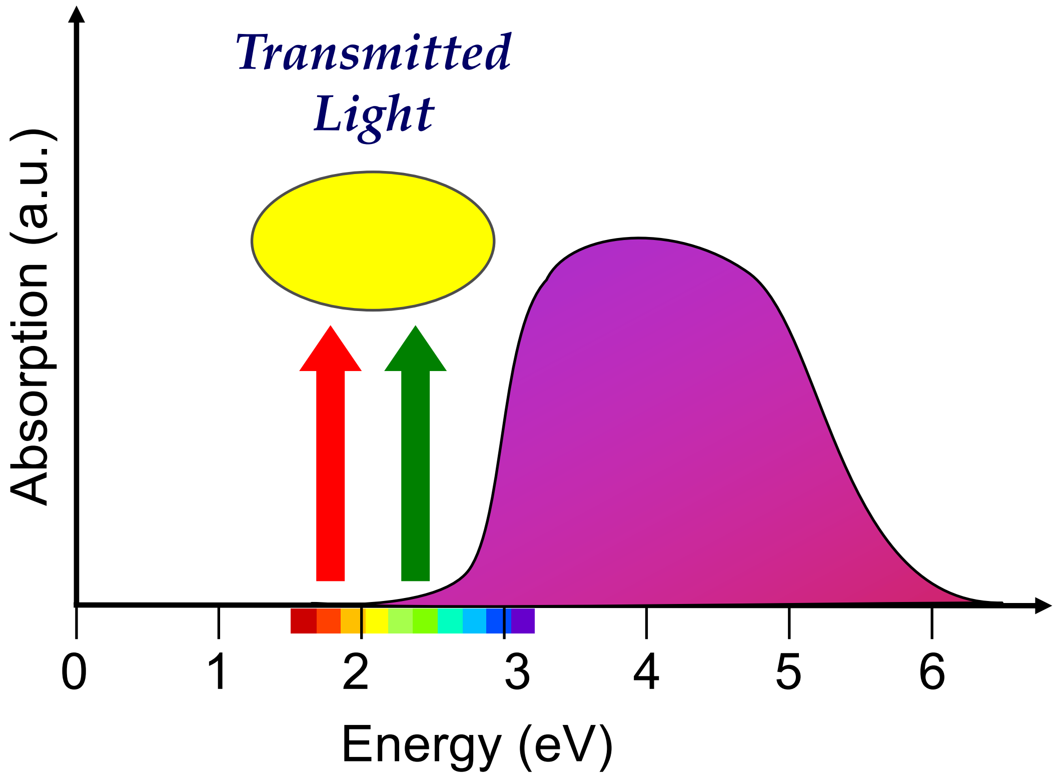
3 – UNDERSTANDING OF COLORS FROM BANDS

Color of a SC* with several gaps





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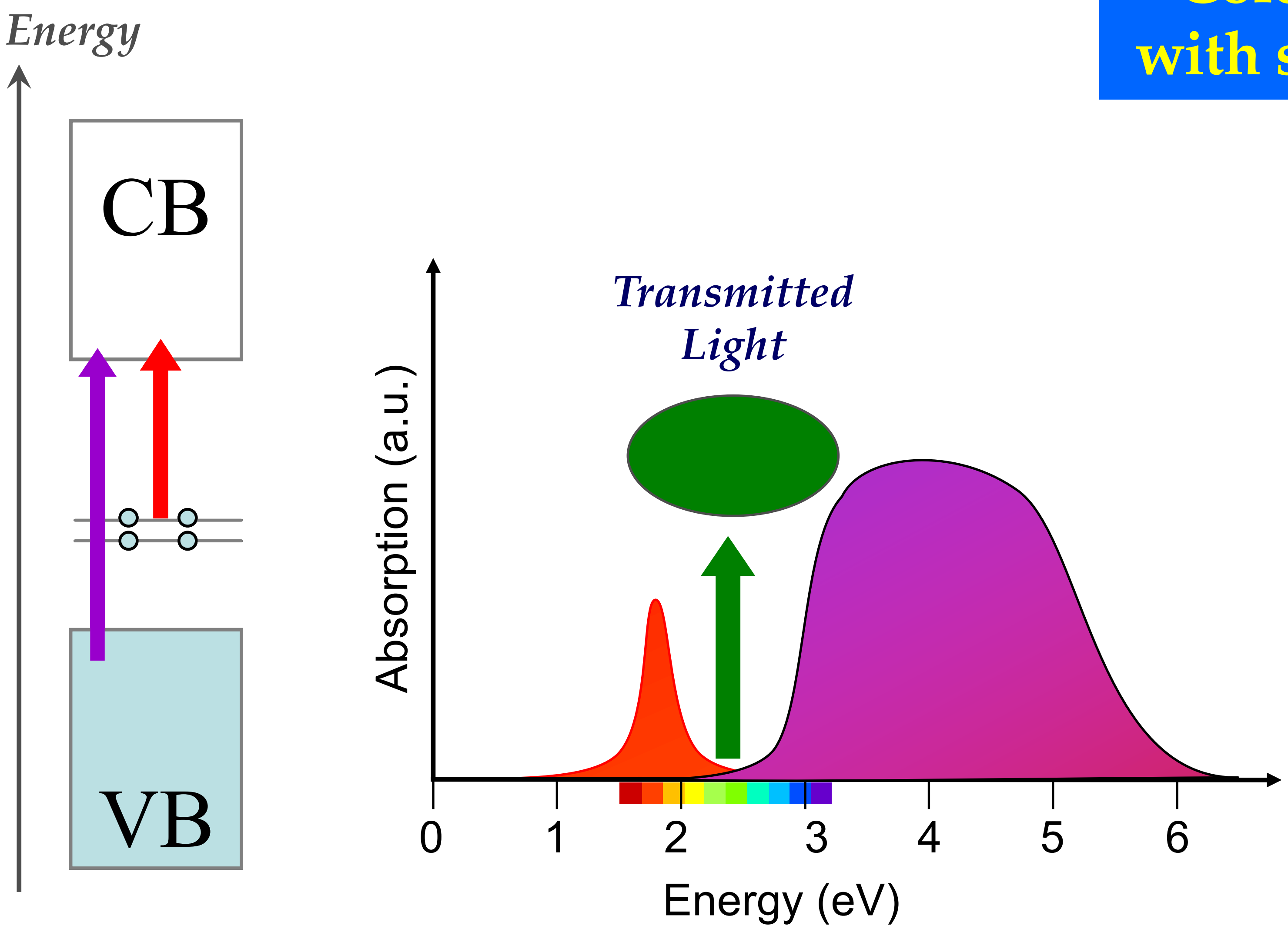
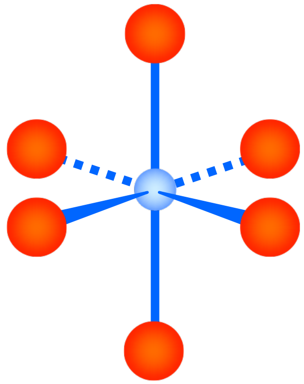


*SC : Semi-conducteur – BI : Bande interdite

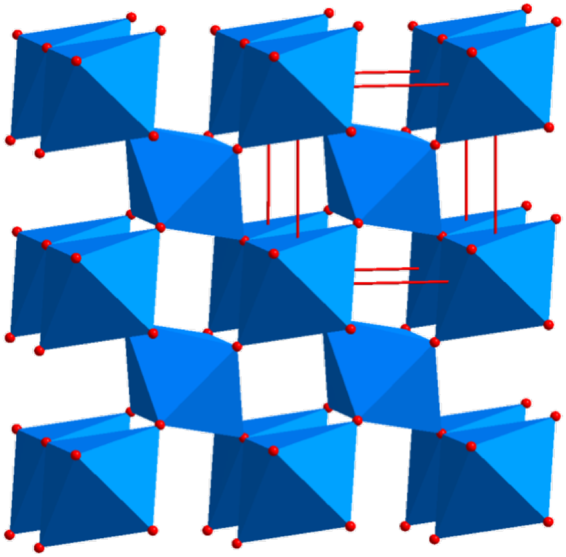
3 – UNDERSTANDING OF COLORS FROM BANDS

Charge transfer→ color

Powder sample of TiO_2 (rutile)



TiO_2



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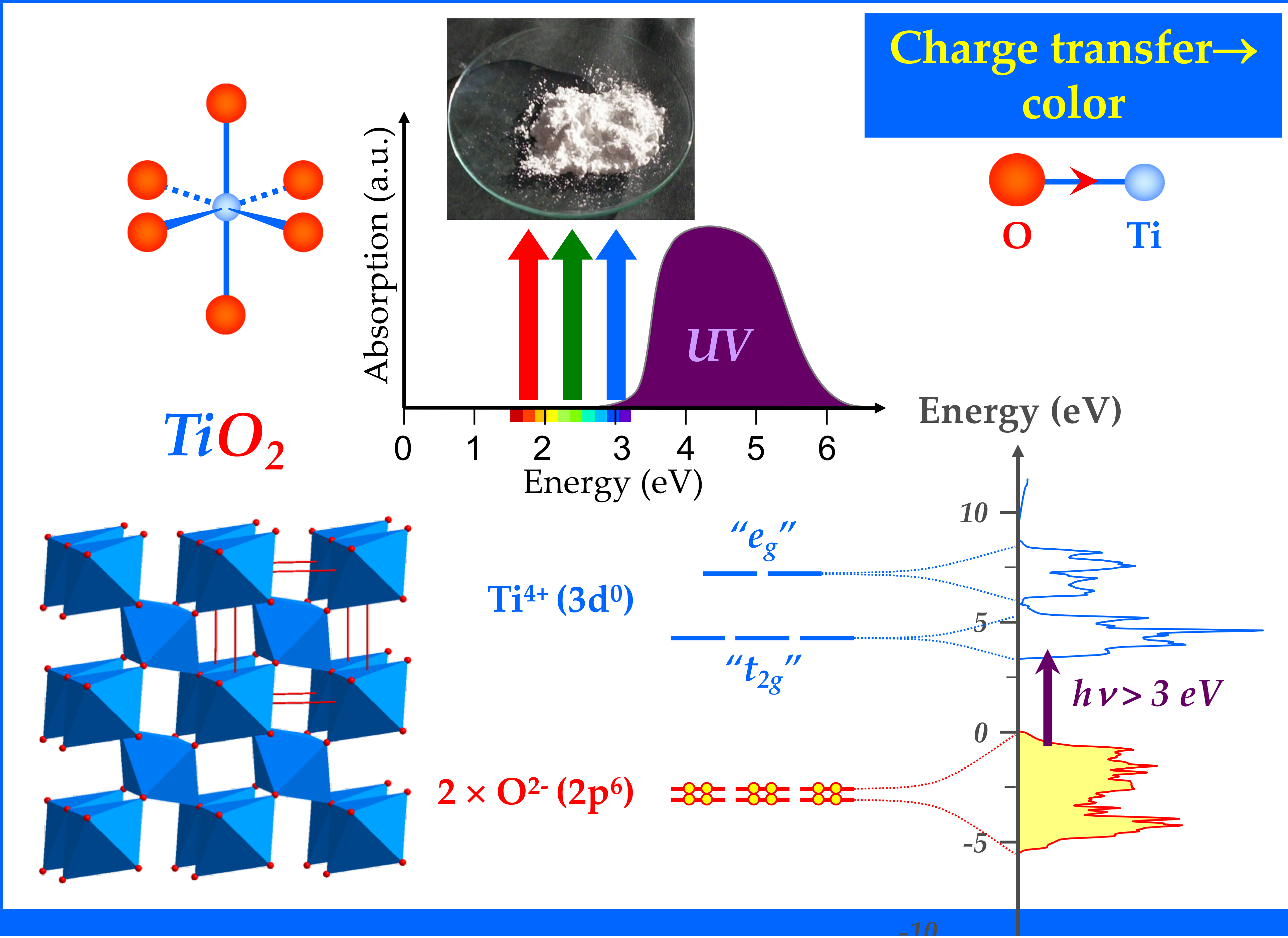
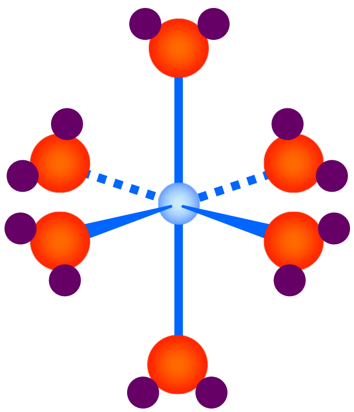


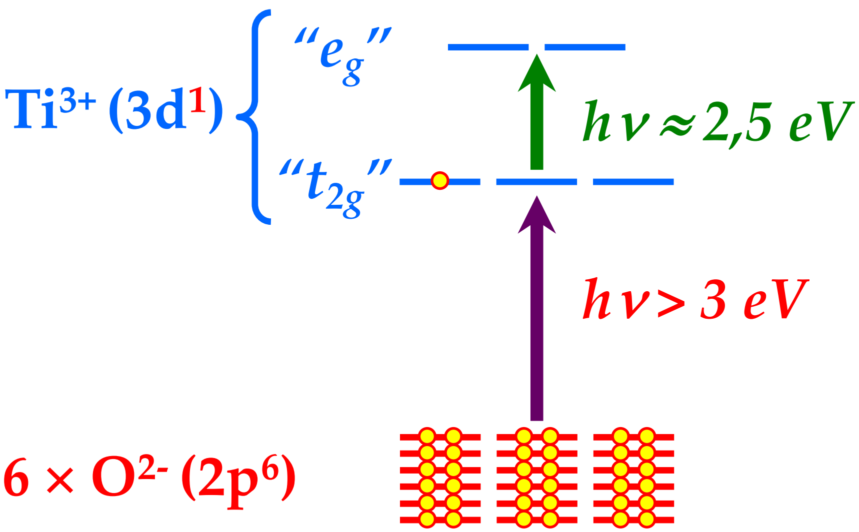
3 – UNDERSTANDING OF COLORS FROM BANDS

d-d transition
→ color

$TiCl_3$
in solution



$Ti[H_2O]^{3+}$



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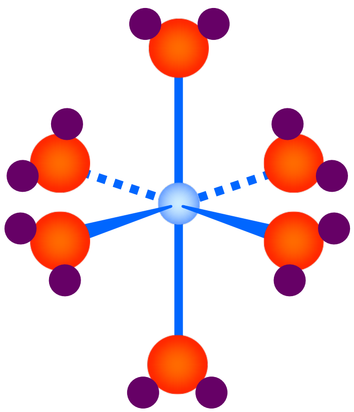

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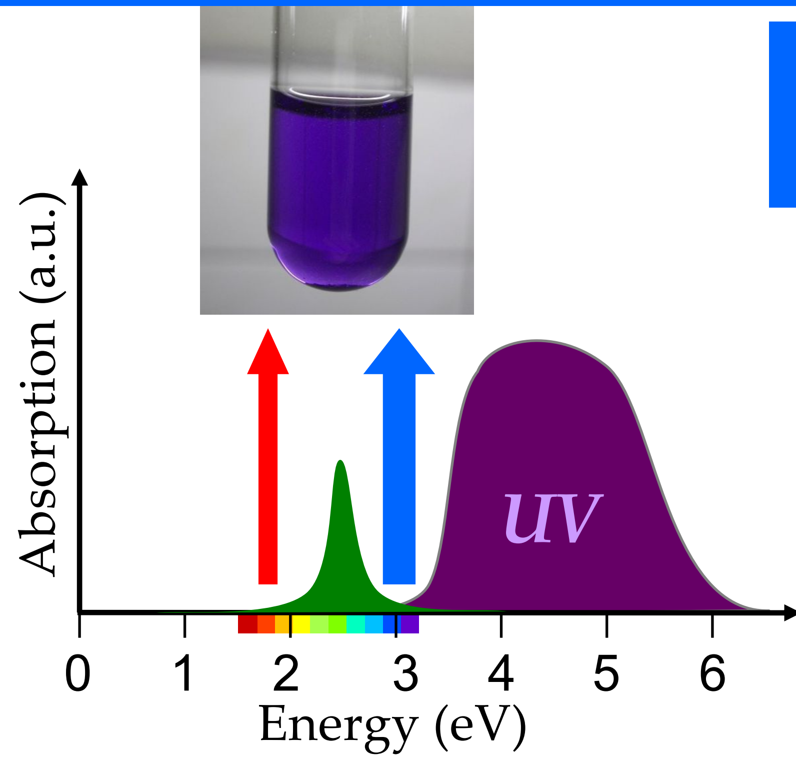

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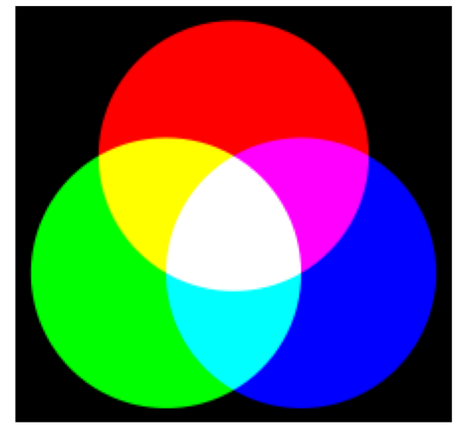
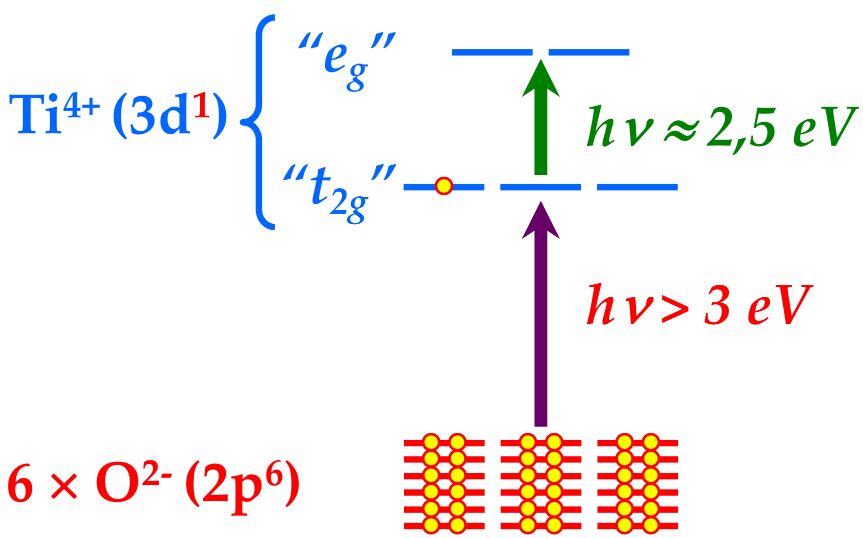




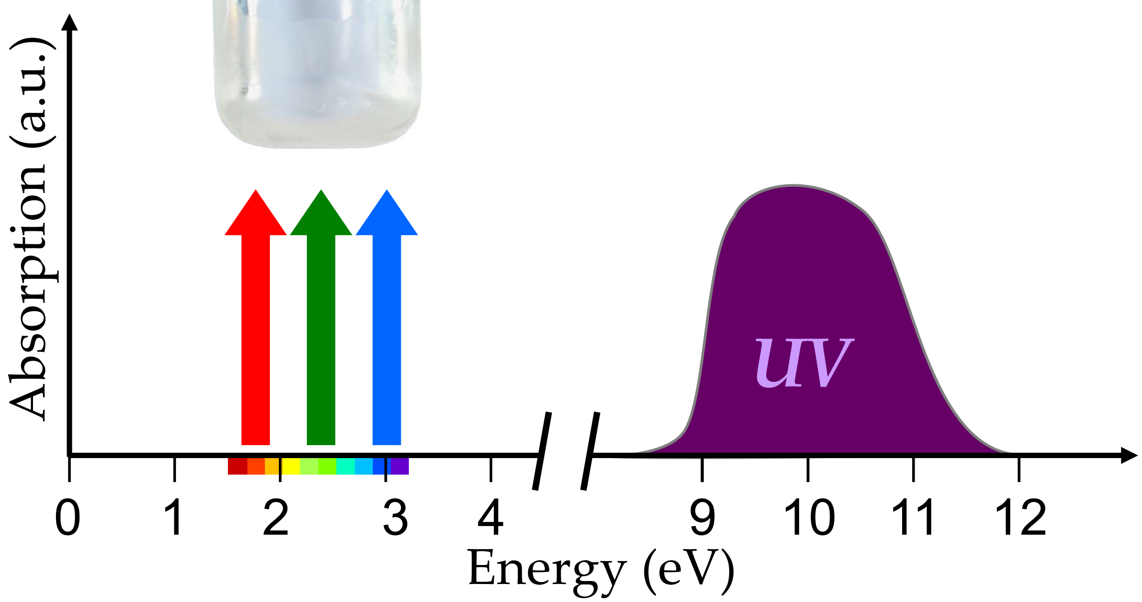
Rq. : For d^n with $n > 1$

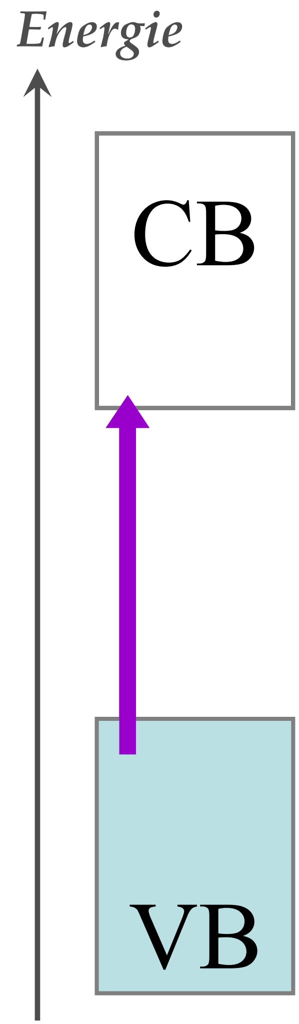
→ Interelectronic correlations must be taken into account

→Tanabe-Sugano diagrams (spectroscopic terms)

3 – UNDERSTANDING OF COLORS FROM BANDS

Alumine corindon (Al_2O_3)





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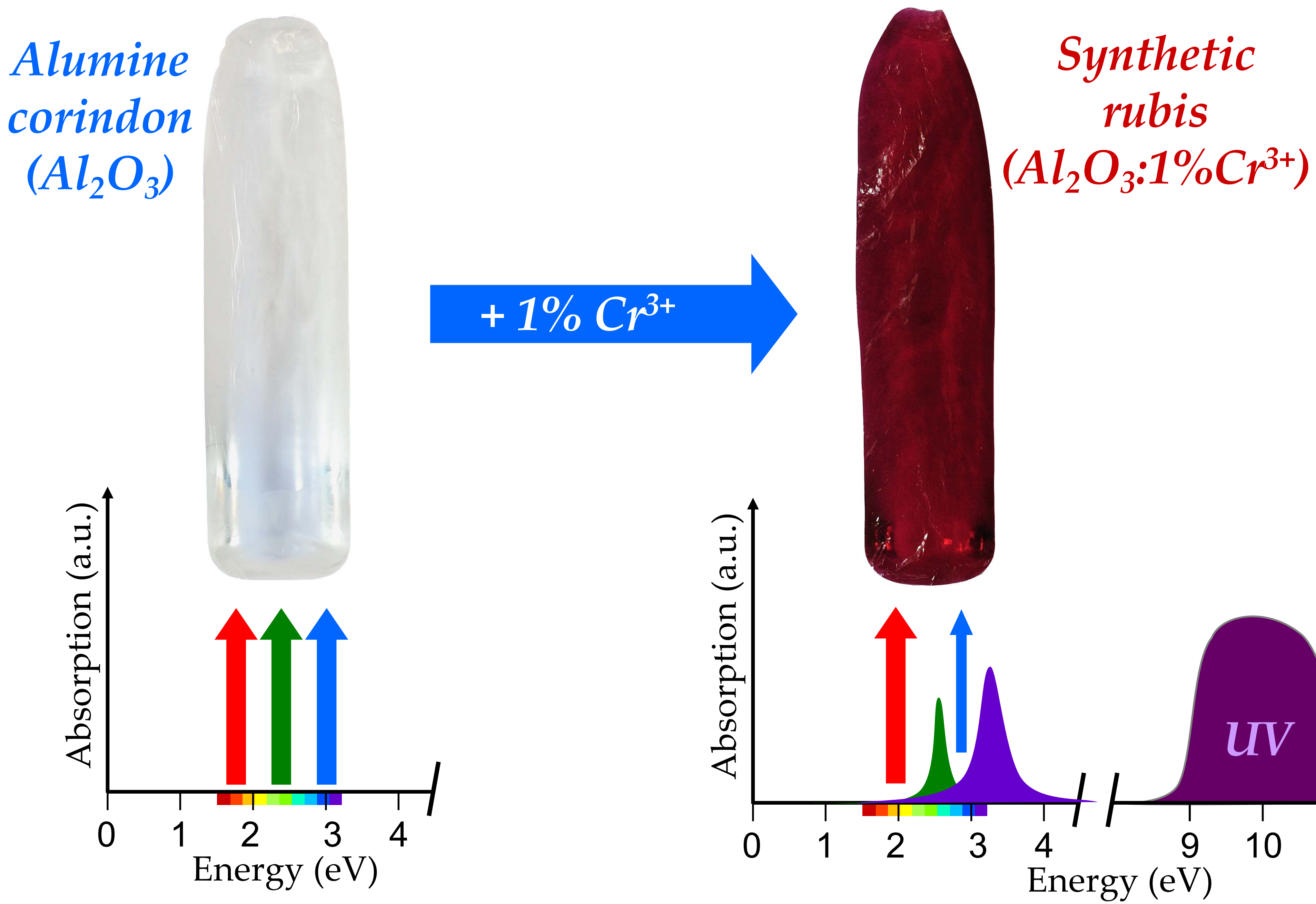

3 – UNDERSTANDING OF COLORS FROM BANDS

Rubis
(Al_2O_3:1%Cr^{3+})

Impurity (d-d)
→ color

Cr^{3+} : electronic conf. d^3

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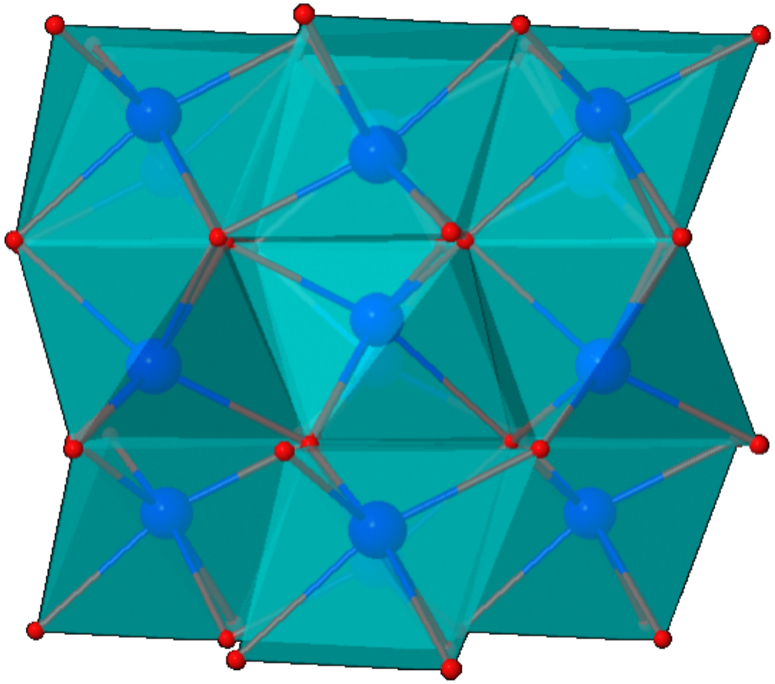

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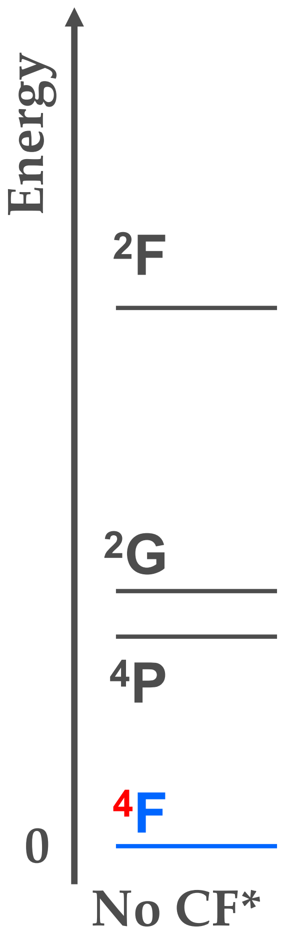
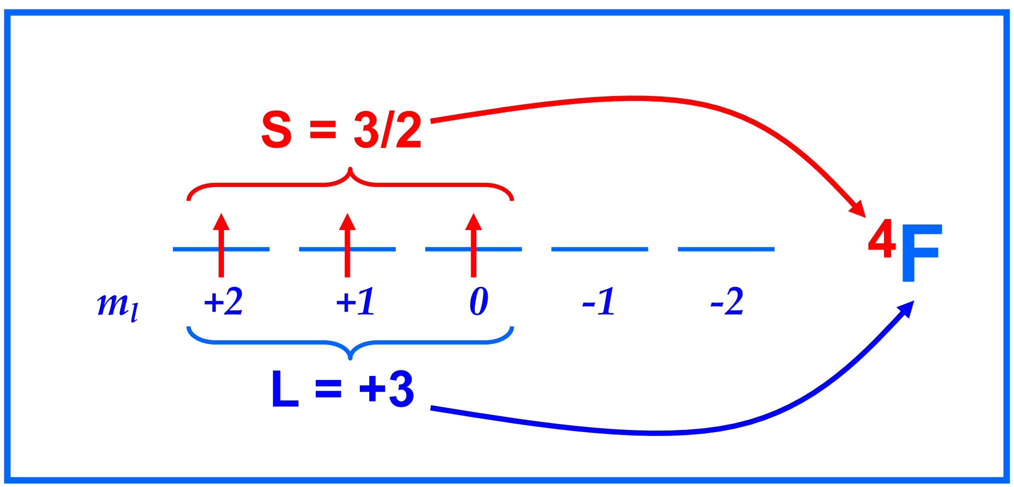


Free ion: we define the spectroscopic terms :

Spin multiplicity → ^{2S+1}X



*CF : Cristal Field

3 – UNDERSTANDING OF COLORS FROM BANDS

Impurity (d-d)
→ color

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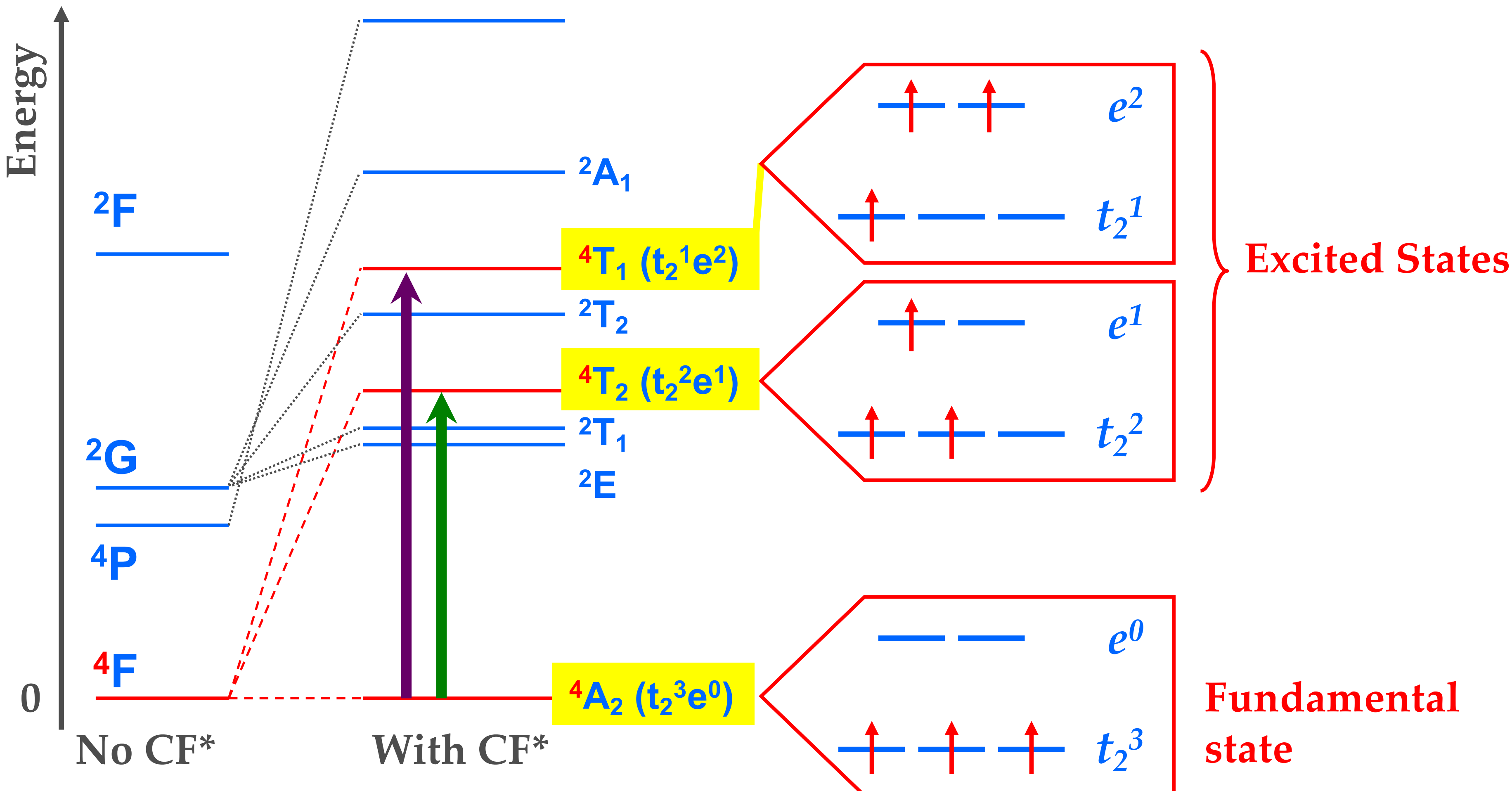
Cr^{3+} : conf. e^q d^3

→ Degeneracy lifting due to the octahedral crystal field effect created by the ligands



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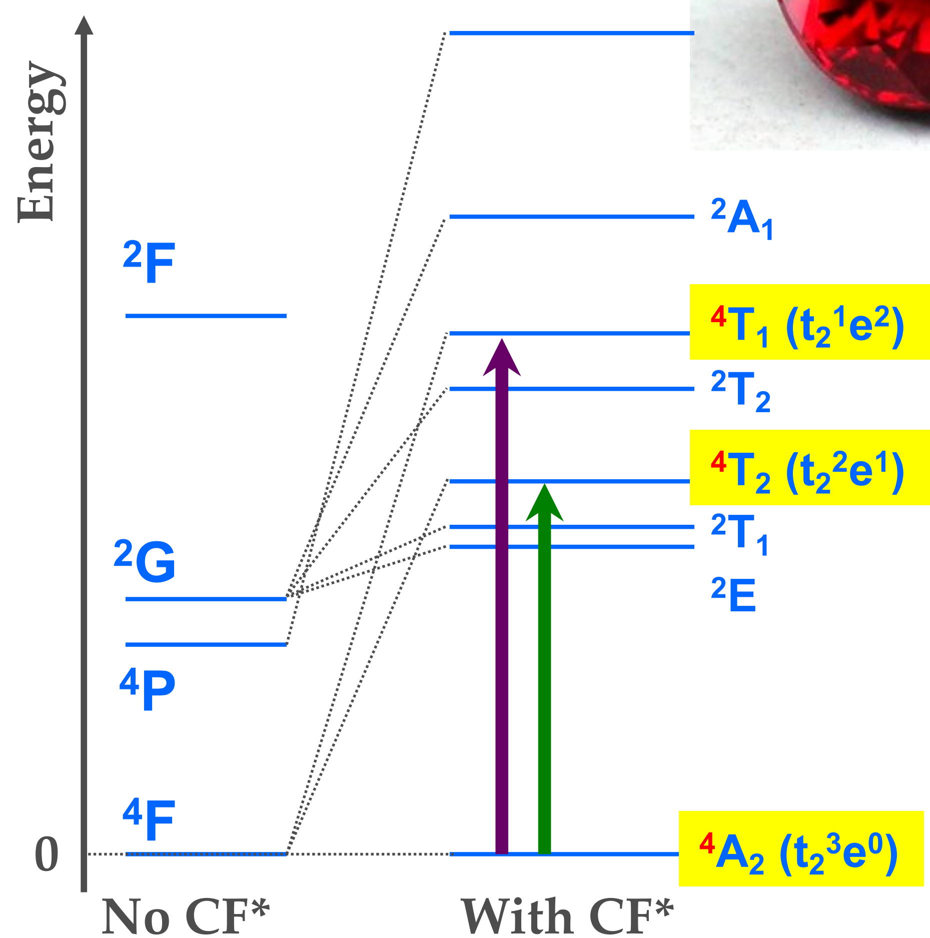
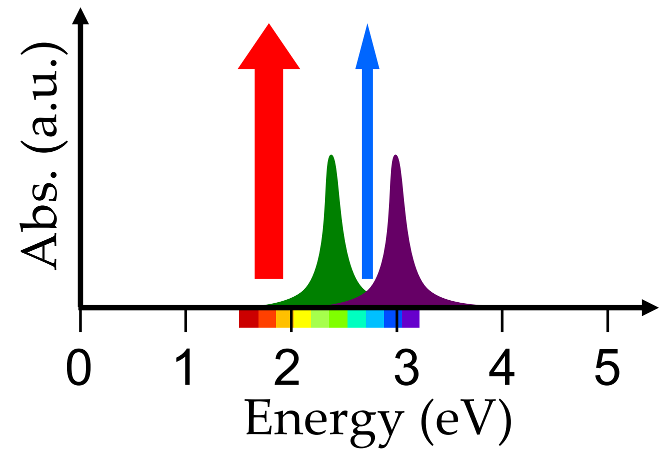


Impurity (d-d)
→ color

Red color
+
Slightly blue



Cr^{3+} : electronic conf. d^3

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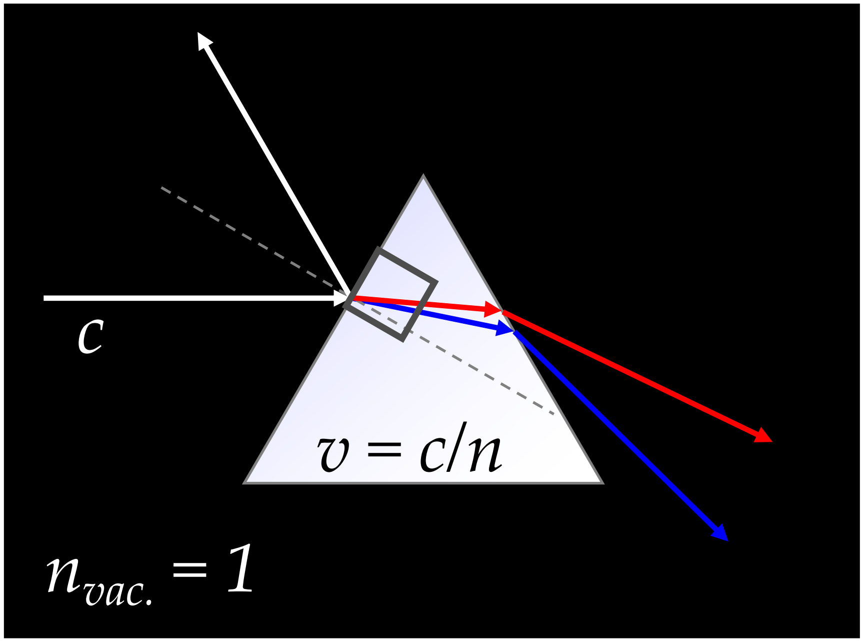
*CF : Cristal Field

4 – LIGHT-MATTER INTERACTION

Physical color → « Elastic diffusion »

Example of a prism



n : index of refraction

Propagation speed is changed

4 – LIGHT-MATTER INTERACTION

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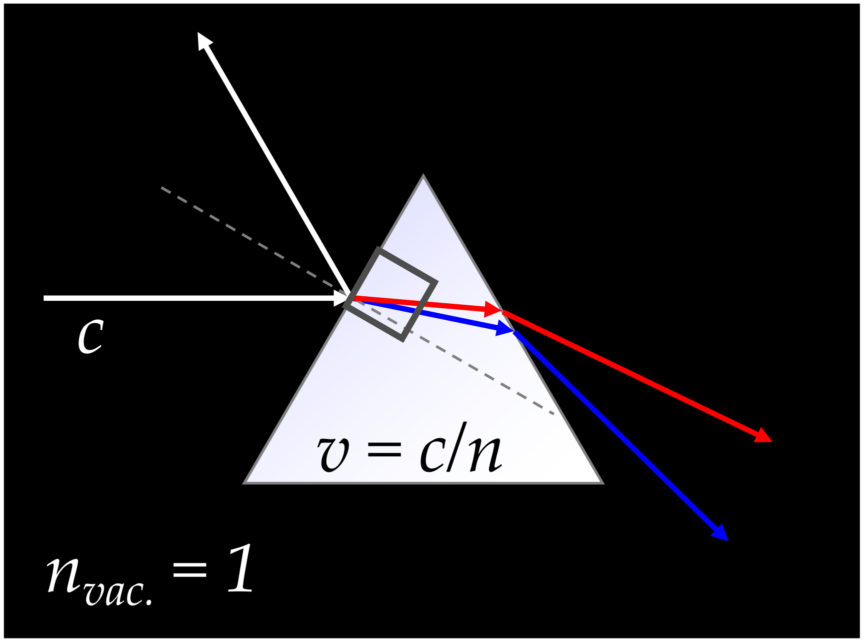
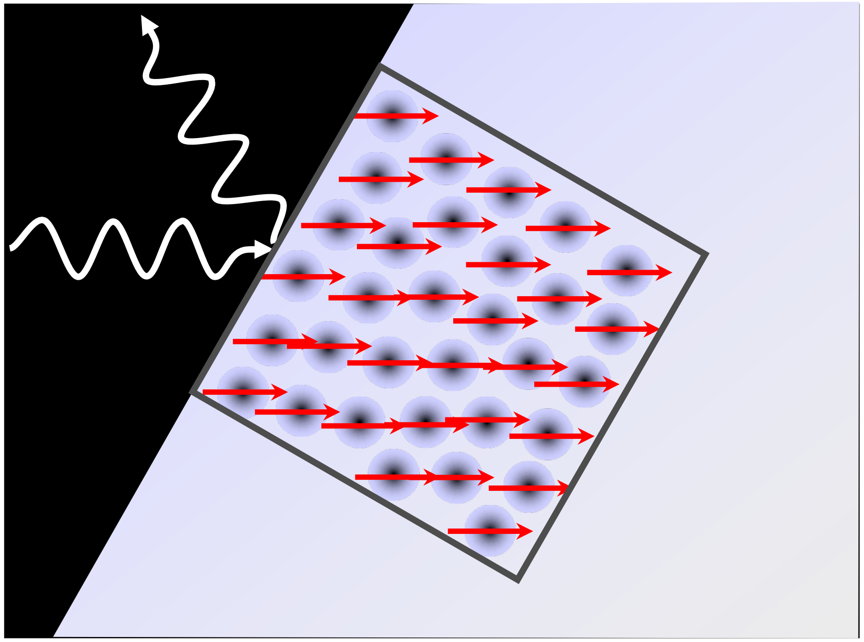


n : index of refraction

Propagation speed is changed

Elastic diffusion mechanism at the atomic level



→ *: Inductive dipole moment ⇔ Receiver-transmitter **antenna***

Succession of absorption and emission

4 – LIGHT-MATTER INTERACTION

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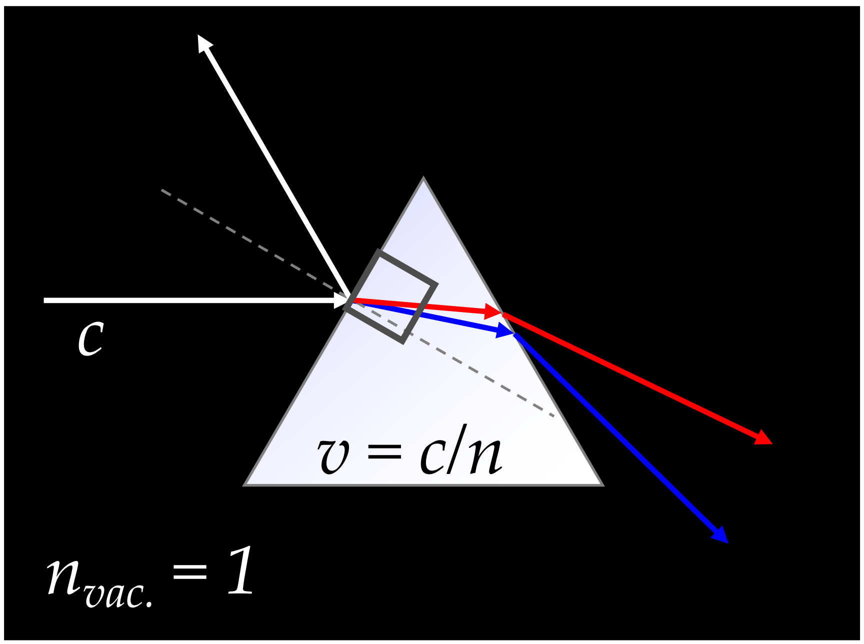
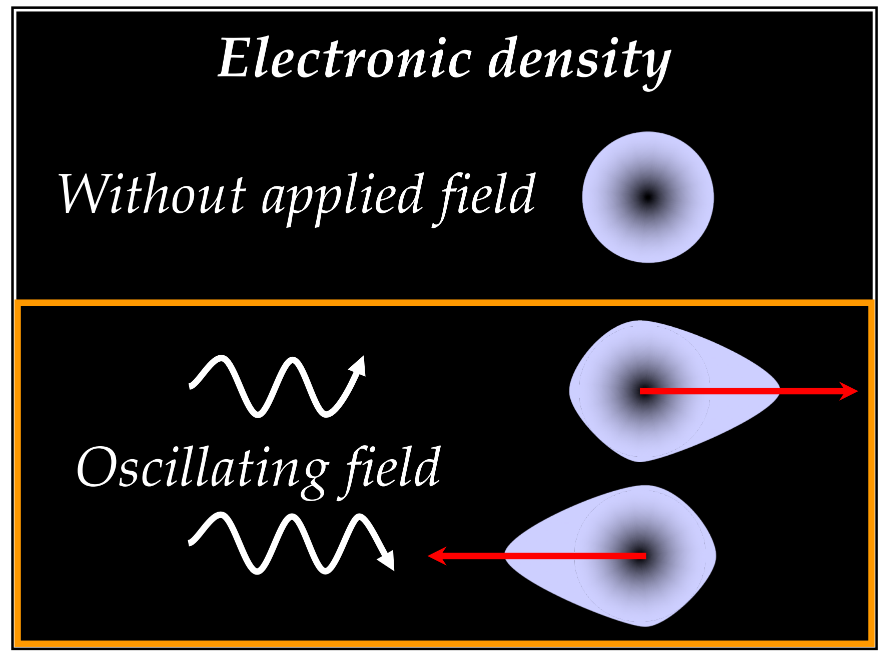
Example of a prism



Dipole moment

$$\vec{\mu} = -e.\vec{r}$$

Elastic diffusion mechanism
at the electronic level



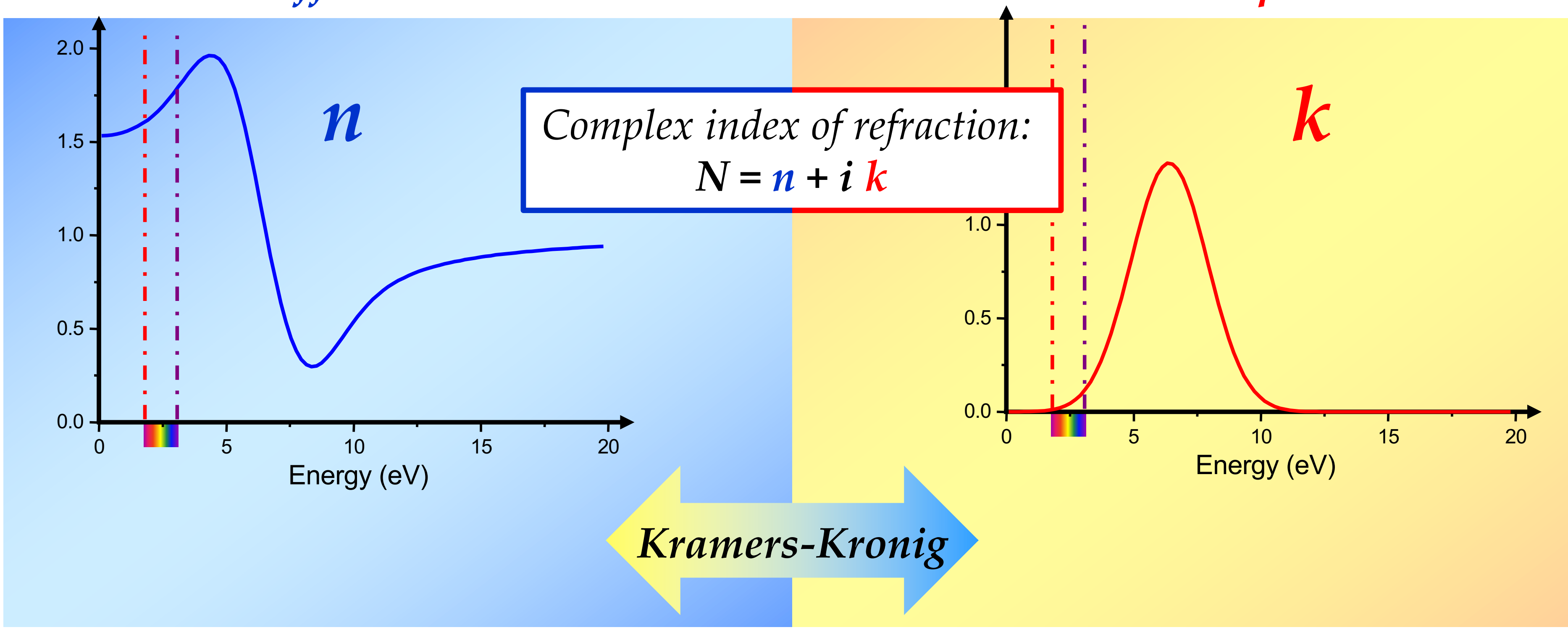
Oscillating **Electric Field** polarize ρ

→ : *Inductive dipole moment* ⇔ *Receiver-transmitter* ***antenna***

Succession of absorption and emission

4 – LIGHT-MATTER INTERACTION

Diffusion ***Absorption***



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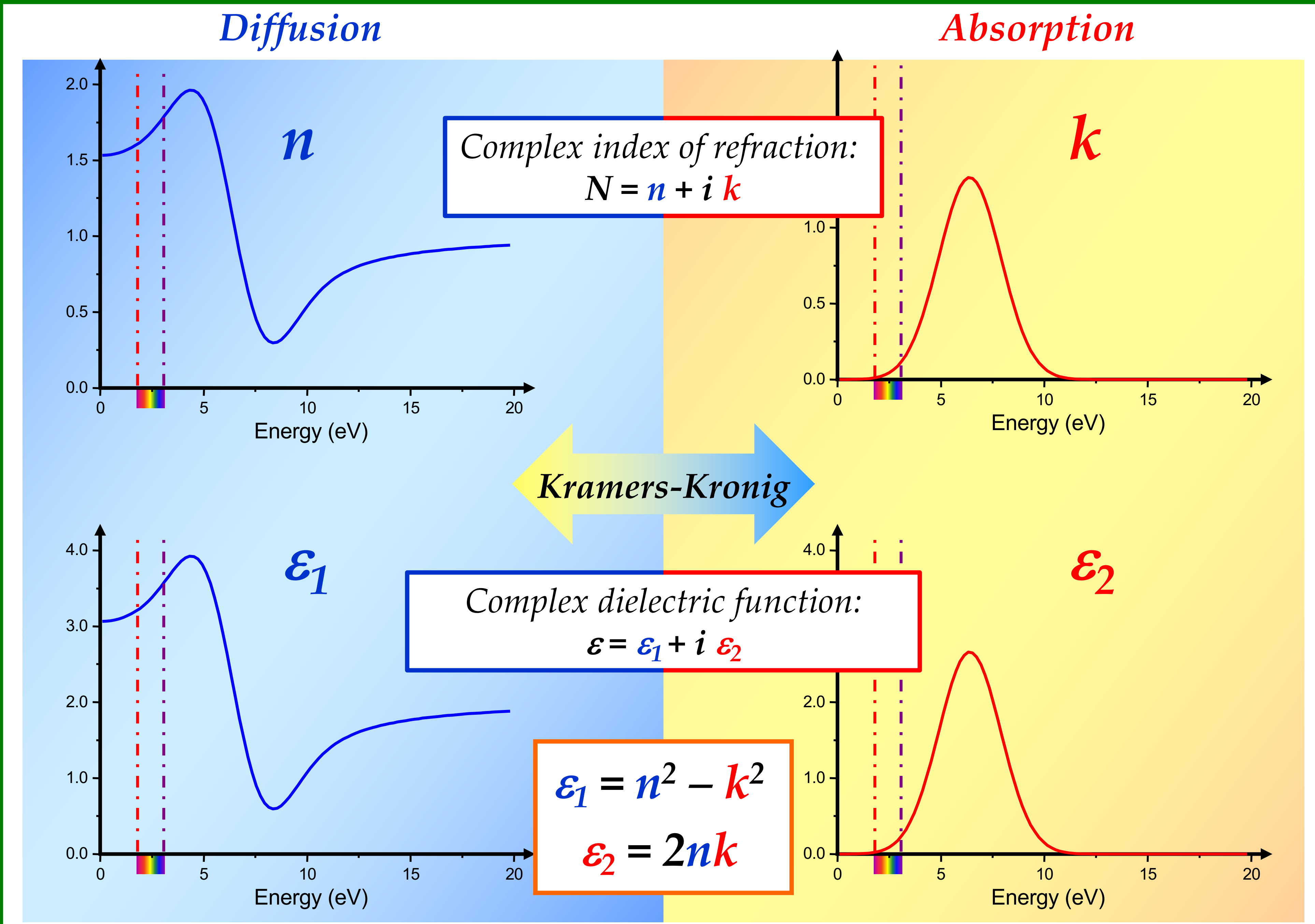
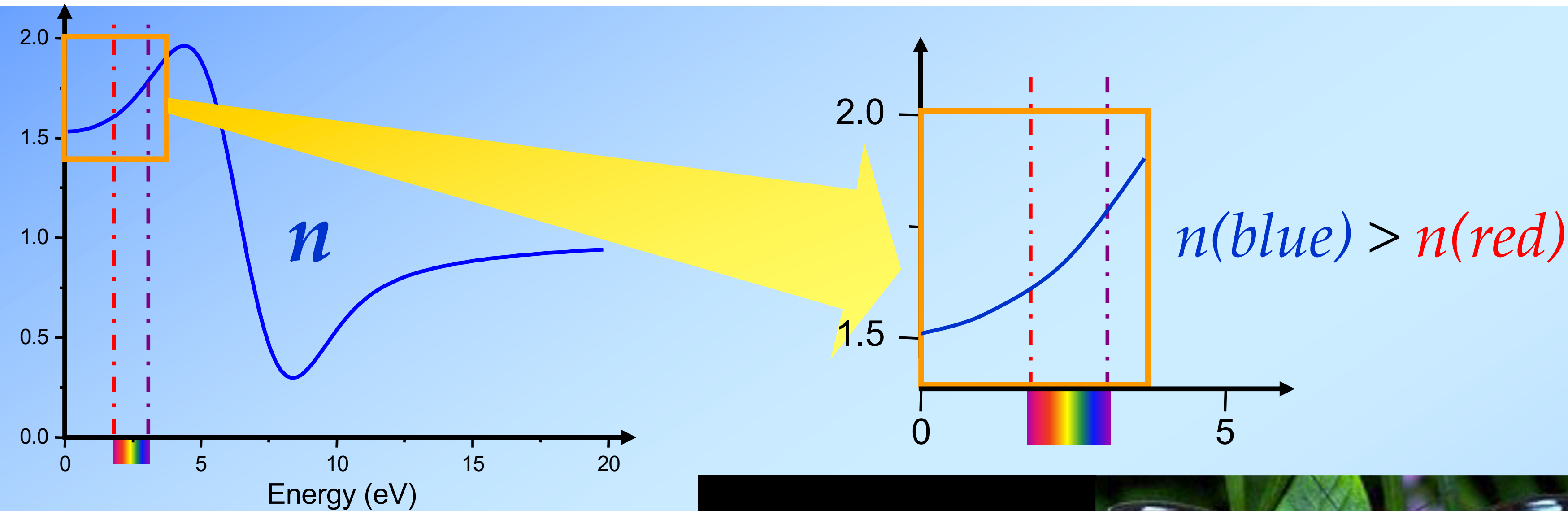
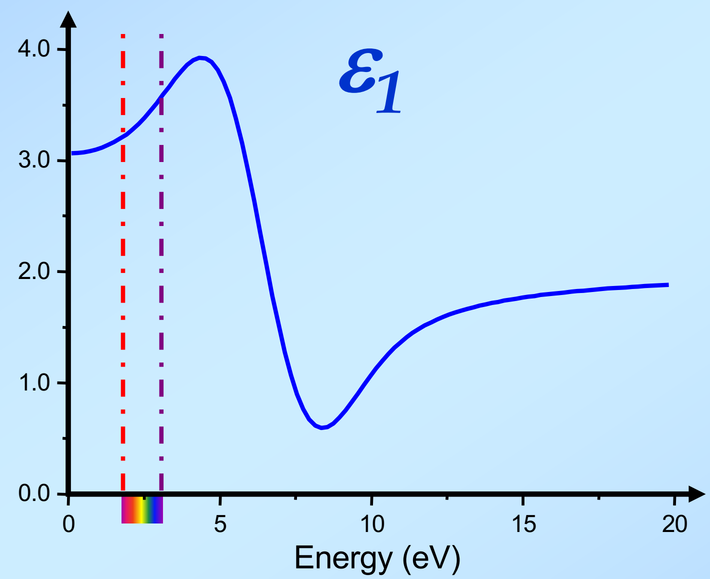


4 – LIGHT-MATTER INTERACTION

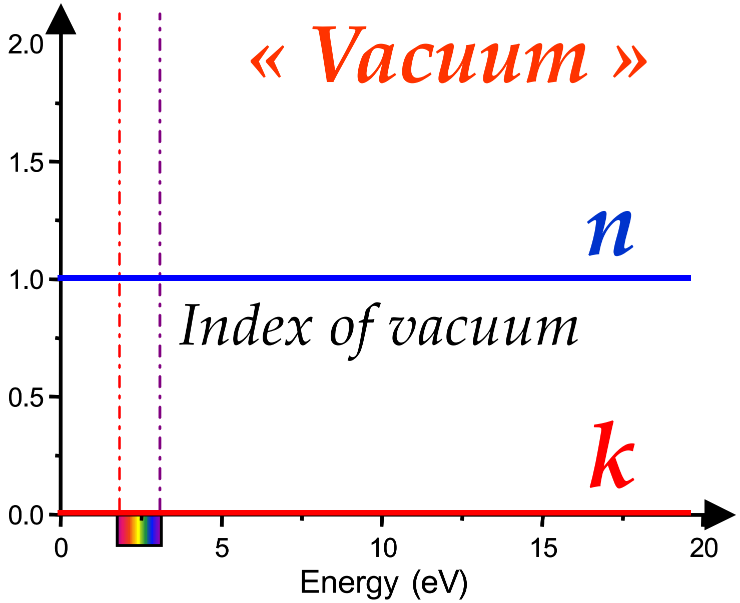
Diffusion in the case of a prism





4 – LIGHT-MATTER INTERACTION

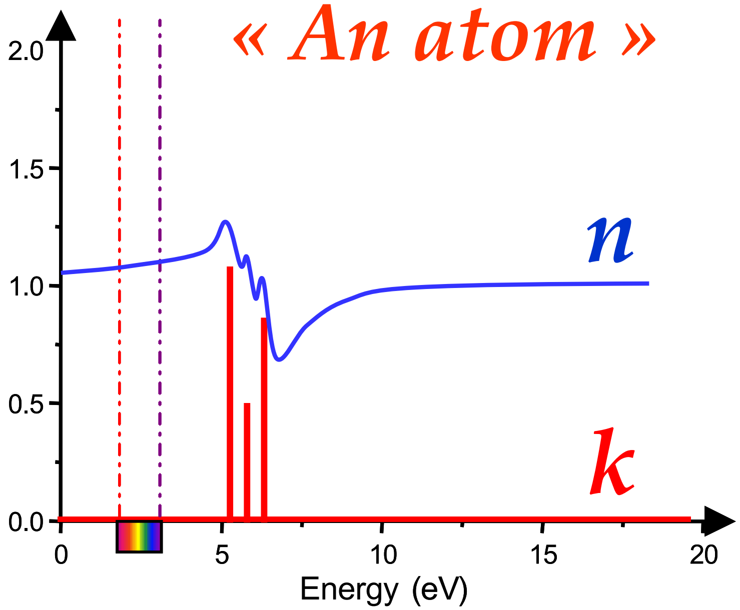
« Vacuum »



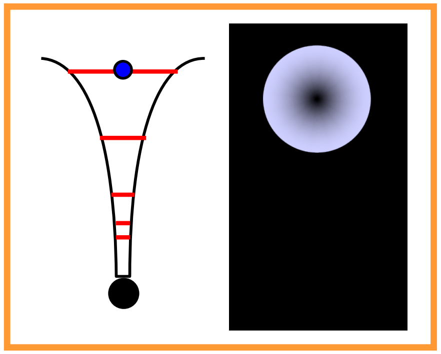
Index of refraction :
$n = 1$

No Absorption

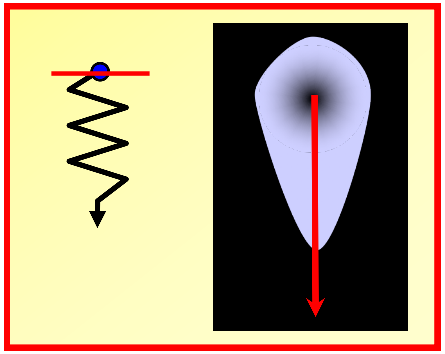
« An atom »



Without applied electric field

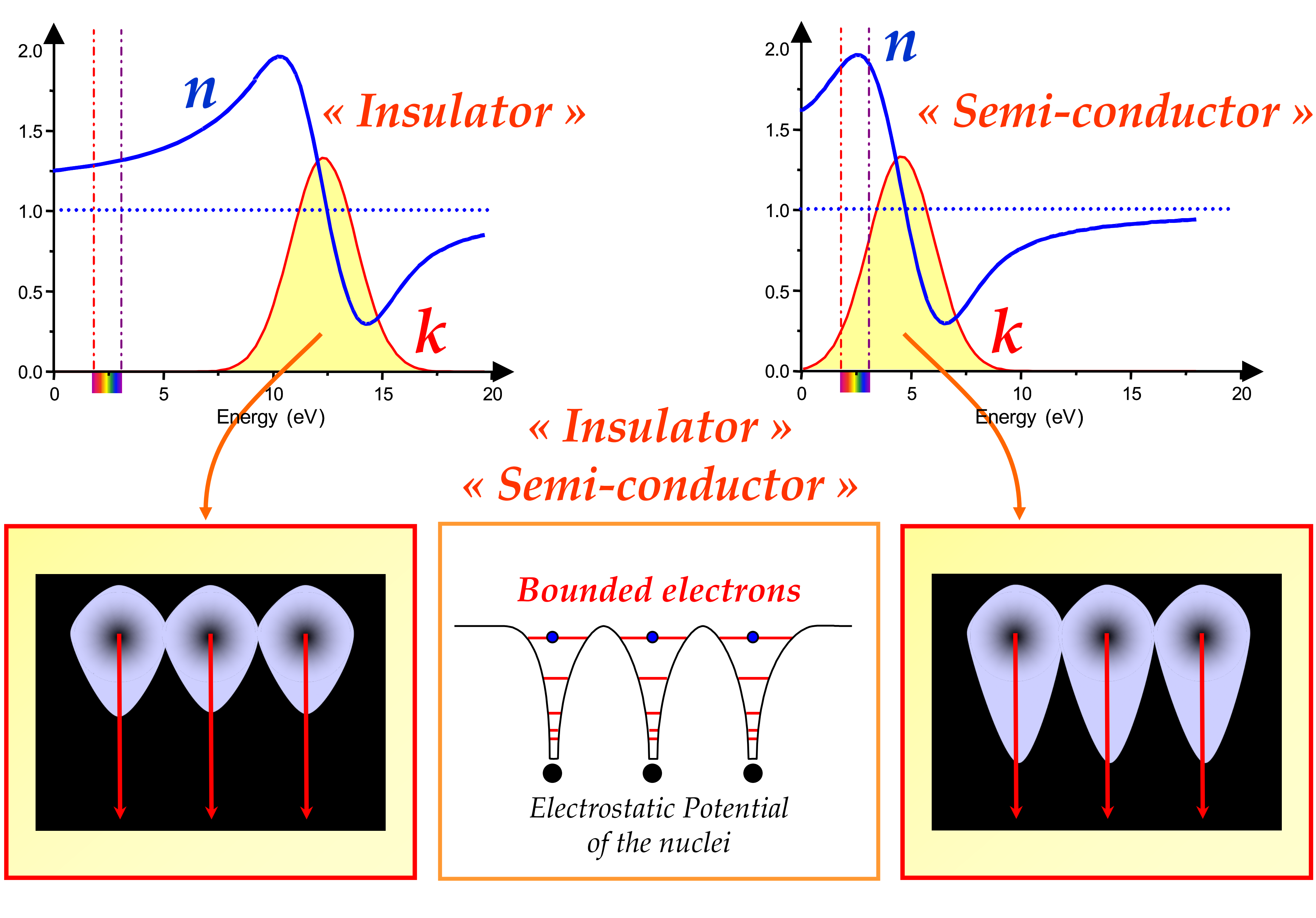


Answer to an applied electric fied

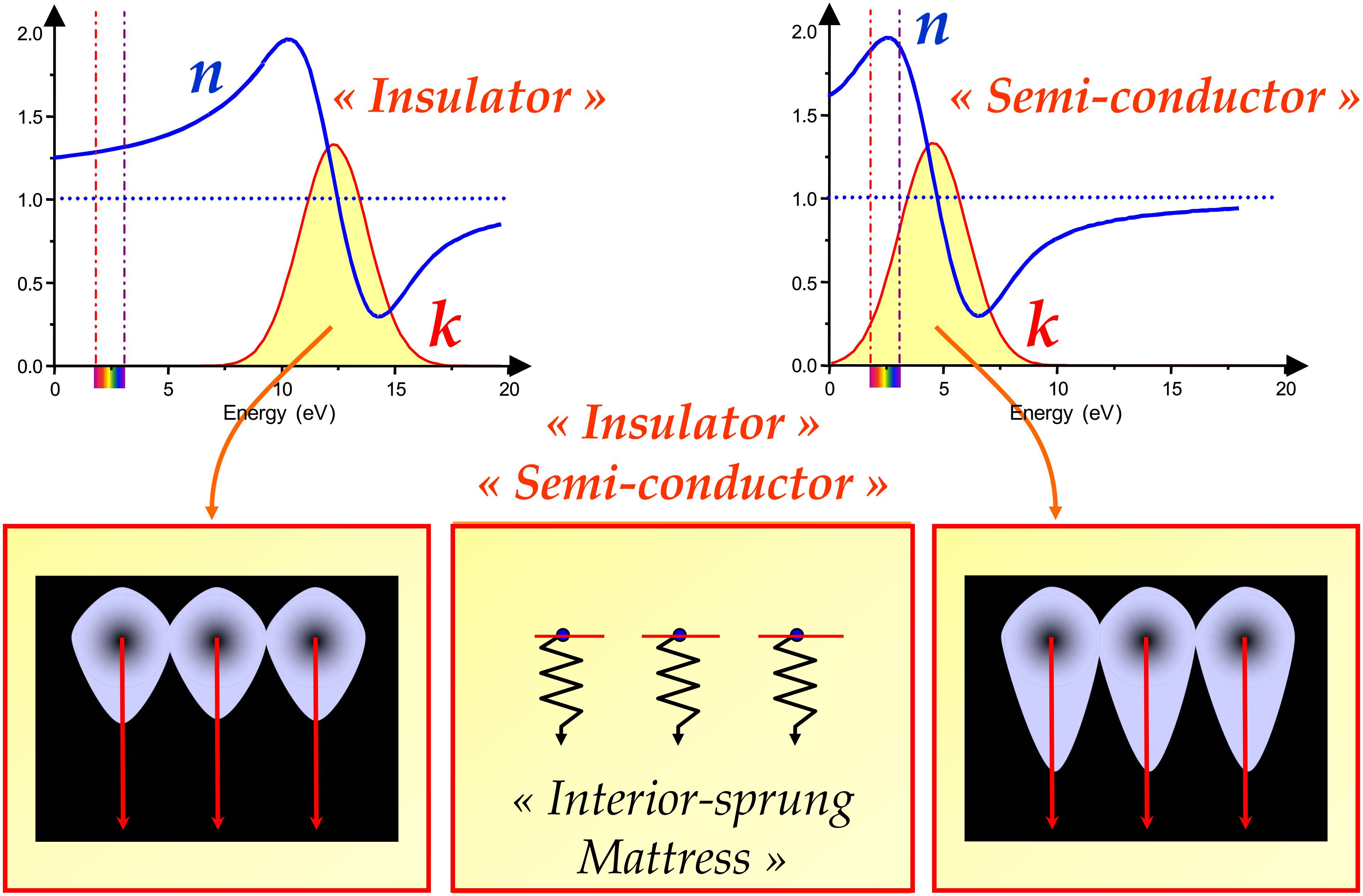


« Spring »

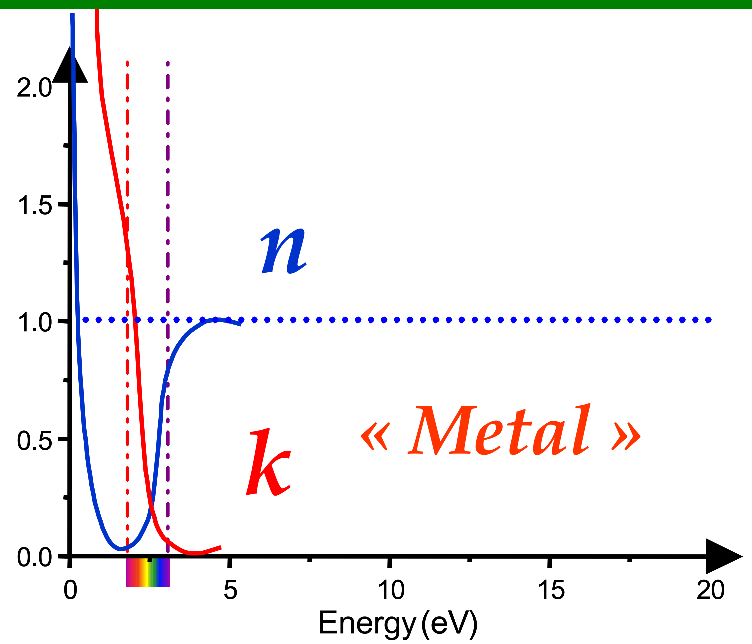
4 – LIGHT-MATTER INTERACTION

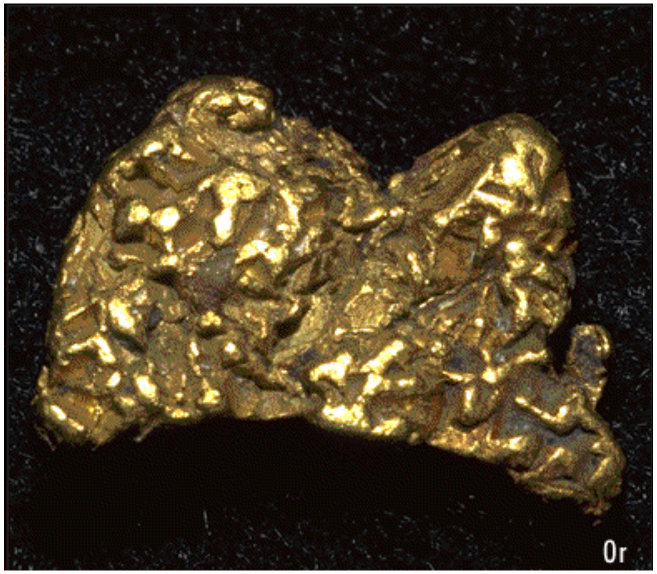


4 – LIGHT-MATTER INTERACTION

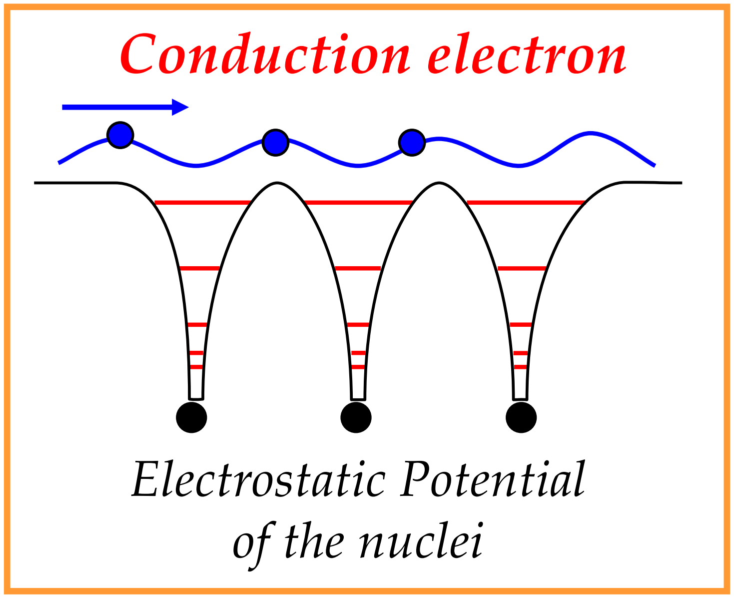


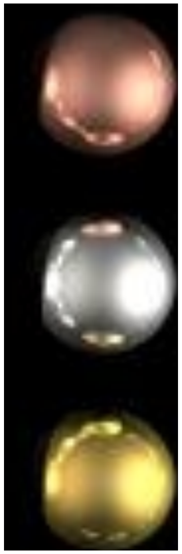
4 – LIGHT-MATTER INTERACTION

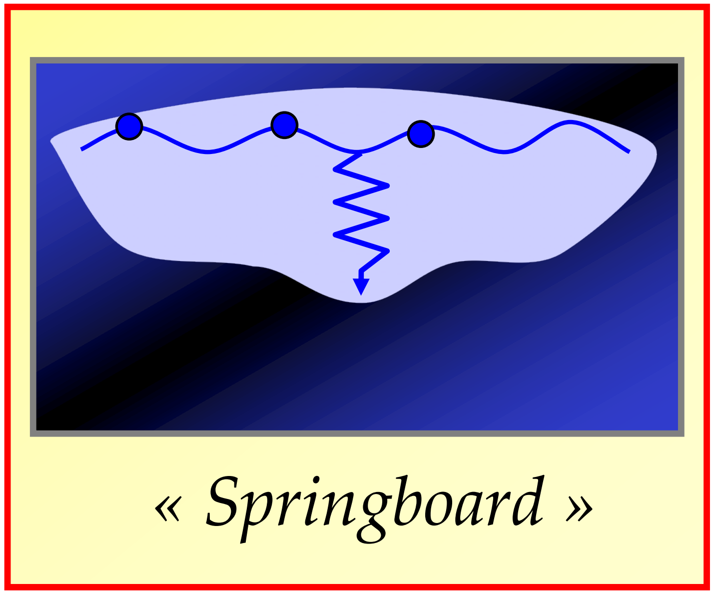




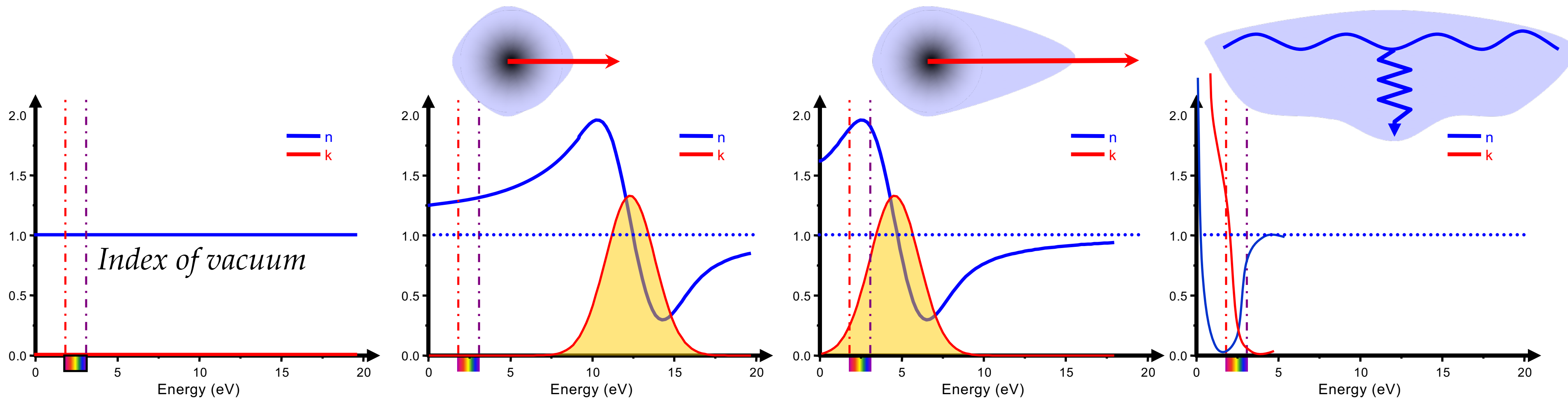
Collective answer of an optical excitation



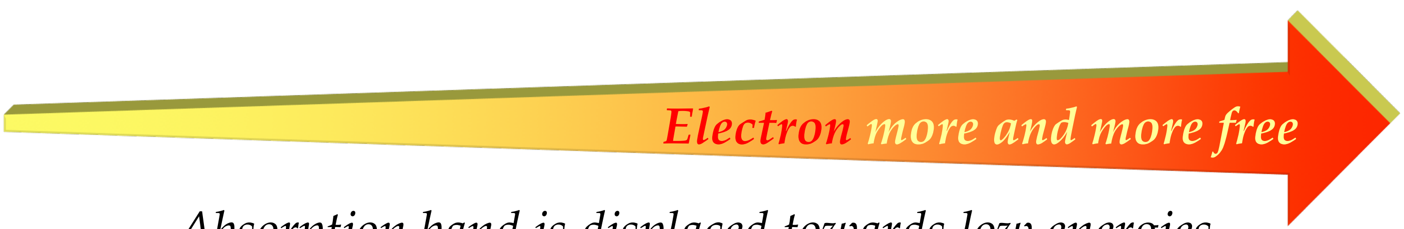




4 – LIGHT-MATTER INTERACTION



Vacuum *Insulator* *Semi-conductor* *Metal*

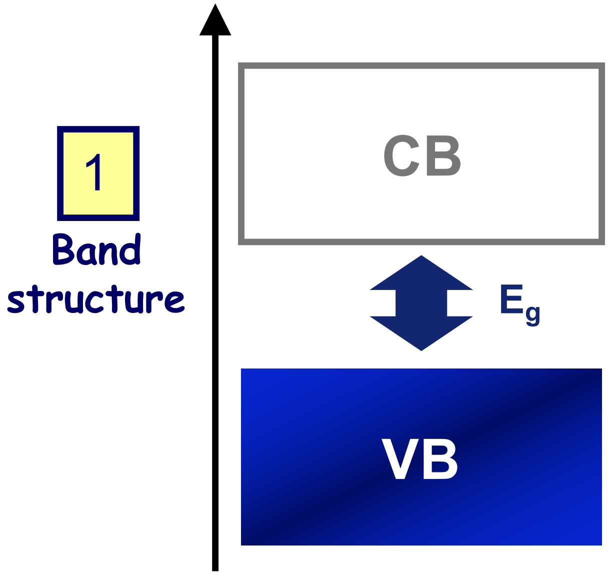


Absorption band is displaced towards low energies

Directly related to the oscillator strength

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:

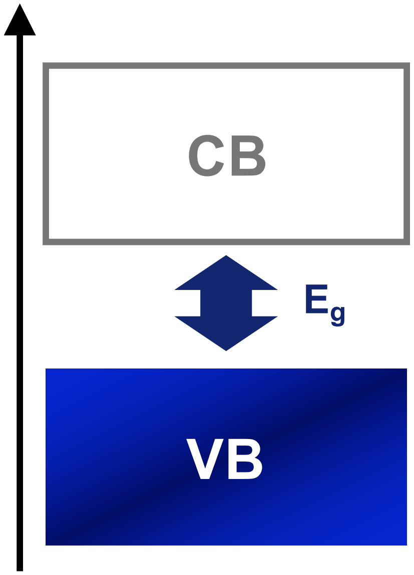


5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:

1

Band structure



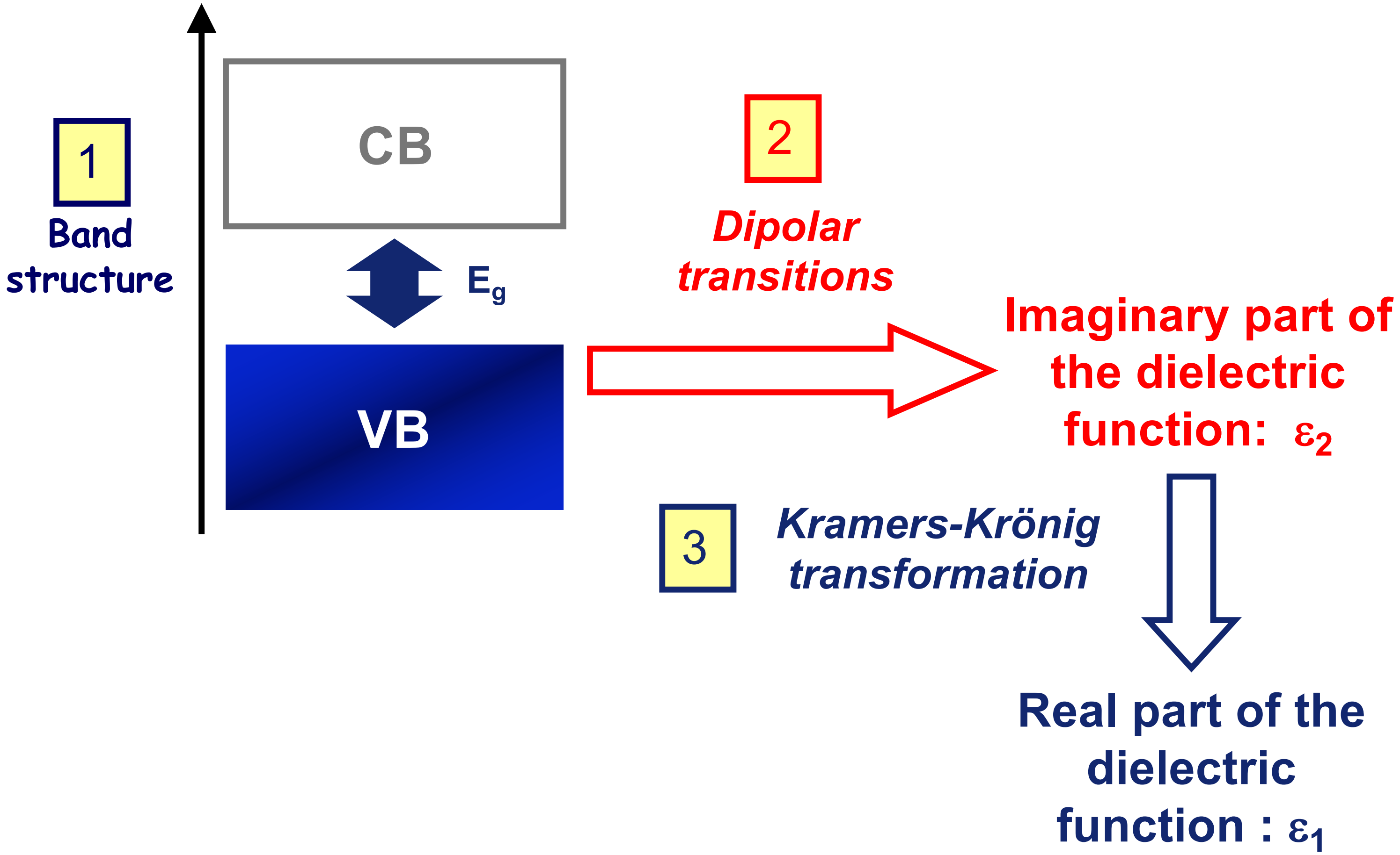
2

Dipolar transitions

Imaginary part of the dielectric function: ε_2

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

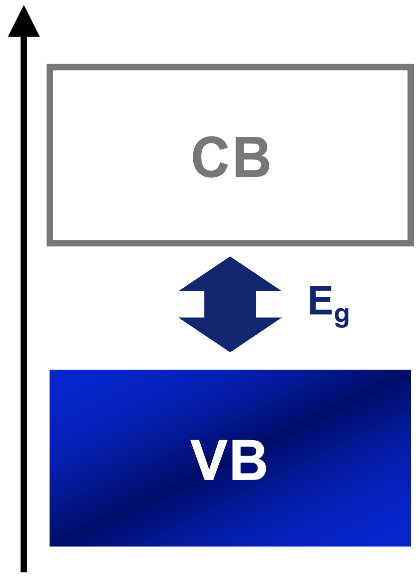
The different steps to calculate the optical properties:



5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:

1 **Band structure**



2 ***Dipolar transitions***

Imaginary part of the dielectric function: ε_2

3 ***Kramers-Krönig transformation***

Real part of the dielectric function : ε_1

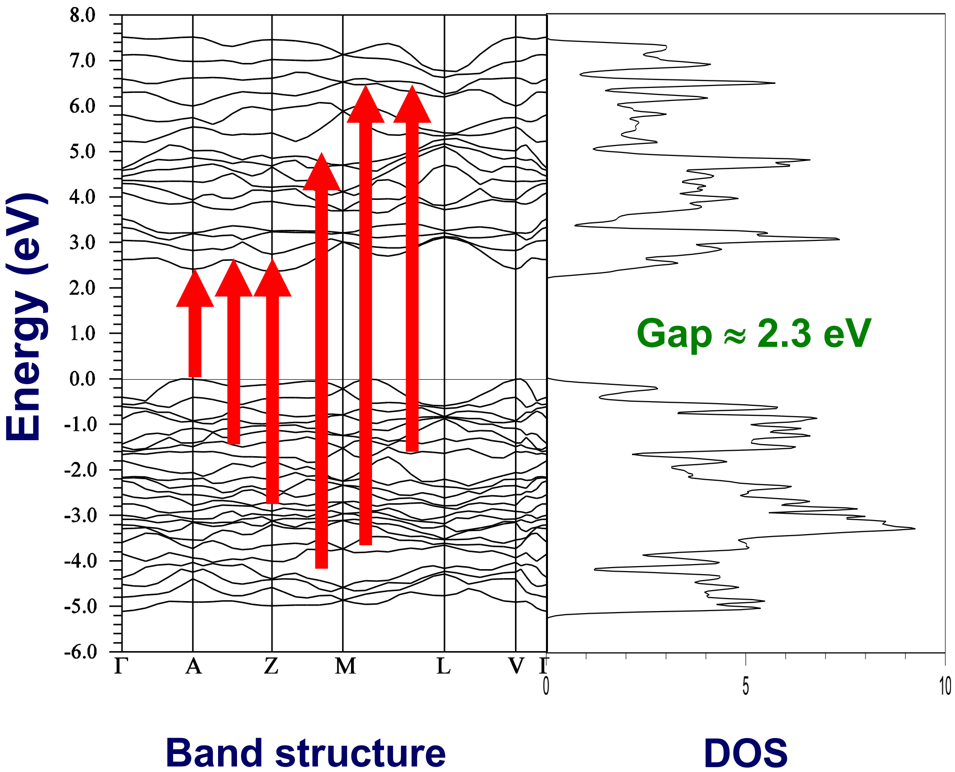
4 ***Determination pf n = f(E) & k = f(E)***

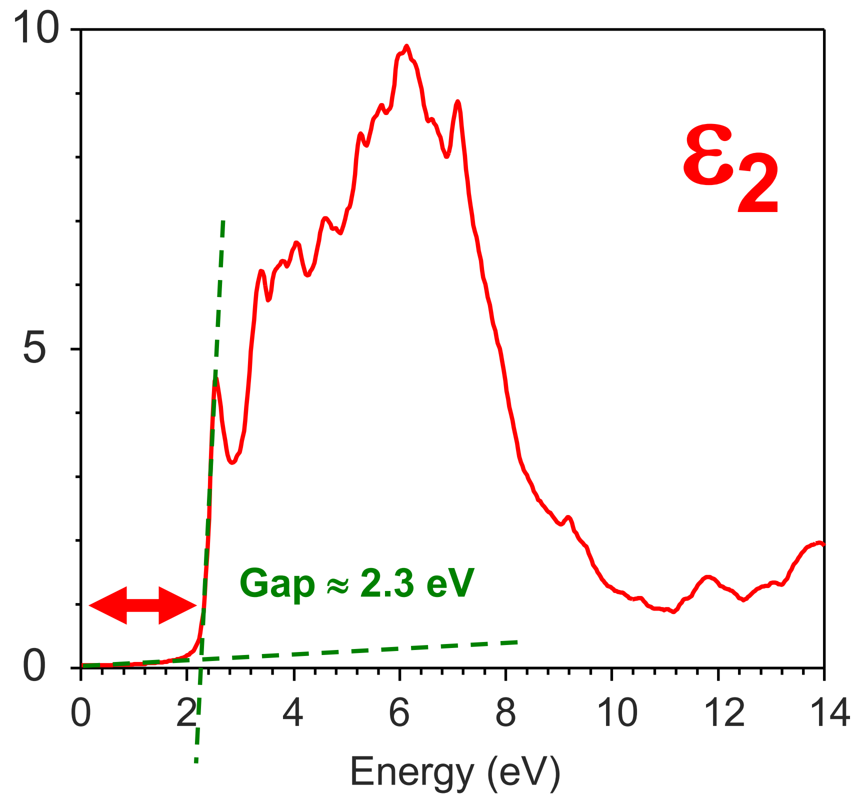
$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

Example of $BiVO_4$



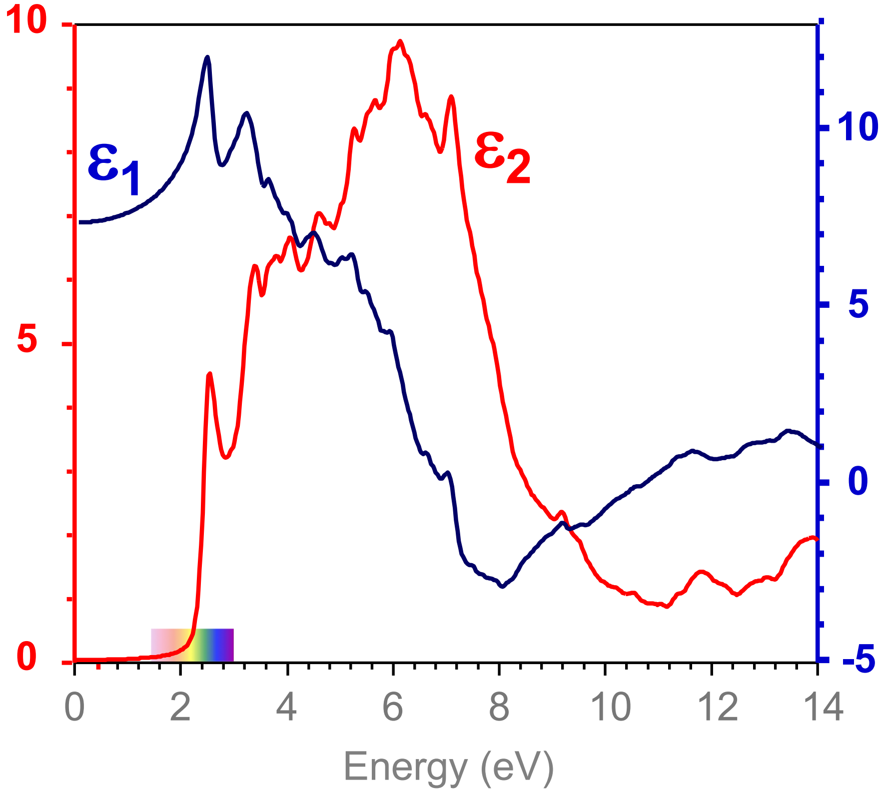


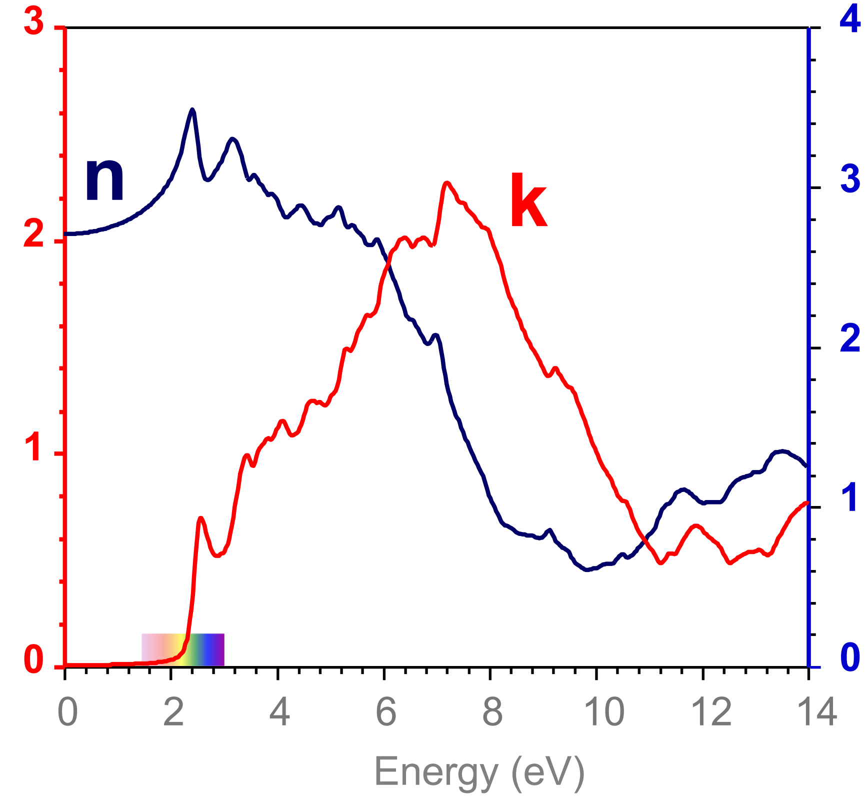
1 **Band structure calculation**

2 **Determination of ε_2**

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

Example of $BiVO_4$





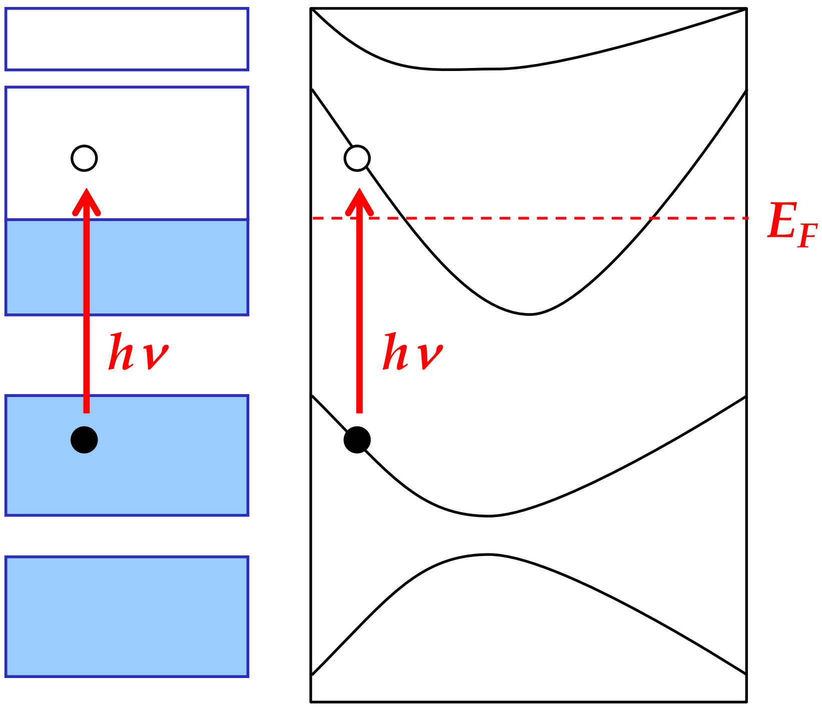
3 **Determination of ε_1**

4 ***Determination of $n = f(E)$ & $k = f(E)$***

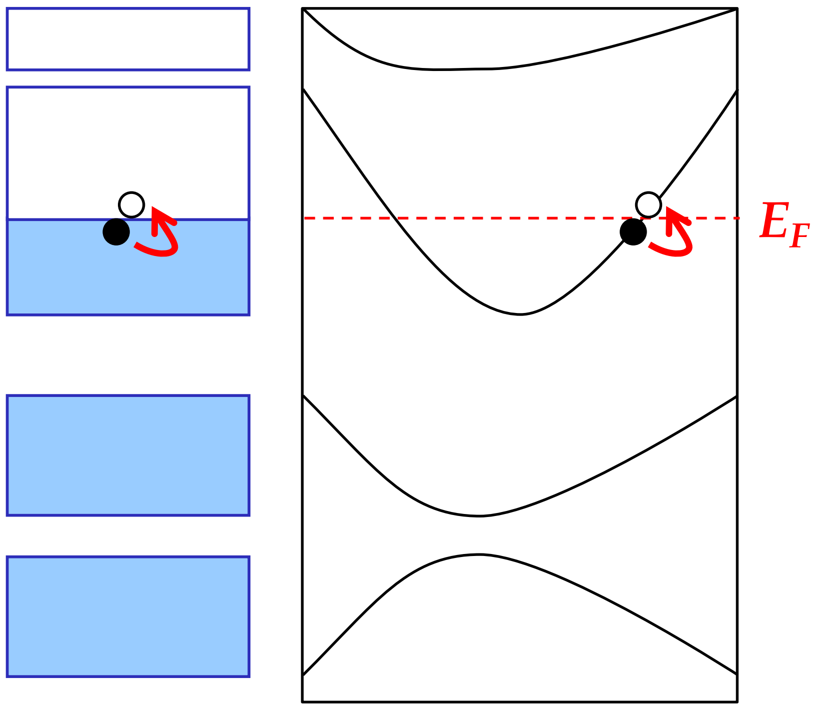
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

In WIEN2k, two types of contributions to the dielectric function ($\varepsilon = \varepsilon_1 + i.\varepsilon_2$) could be estimated:

Interband *contributions (based on IPA*)*



Intraband *contributions (using a Drude-like term)*



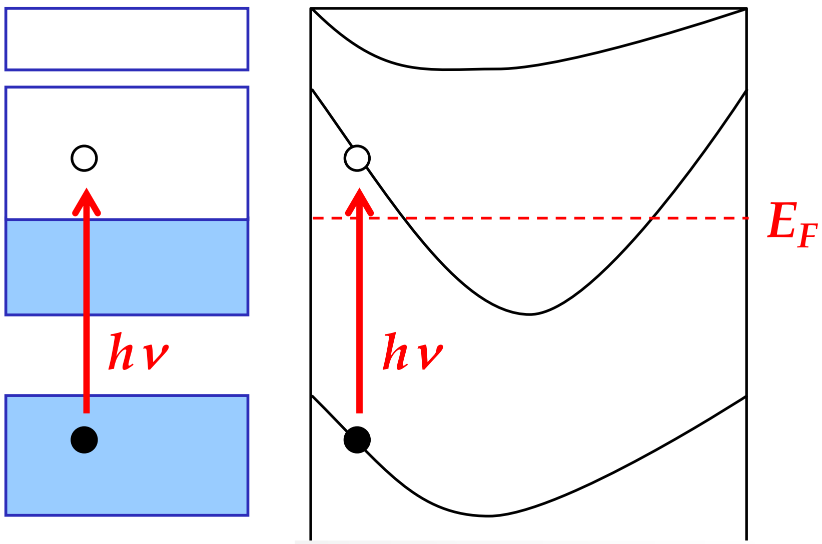
→ Dielectric tensor / Optical conductivity / Refractive index / Reflectivity / Absorption coefficient / Loss function (EELS)

**IPA: Independant Particle Approximation*

5 – INTERPRETATION: Interband transitions

In WIEN2k, two types of contributions to the dielectric function ($\varepsilon = \varepsilon_1 + i.\varepsilon_2$) could be estimated:

***Interband** contributions*
(based on IPA)*



Sum over all **v**alence and **c**onduction bands

joint density of states

$$\sum_{vck} \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

transition probability

$$\mathrm{Im}(\varepsilon_{ij}(\omega)) = \frac{16\pi^2}{\Omega\omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

IPA: Independant Particle Approximation

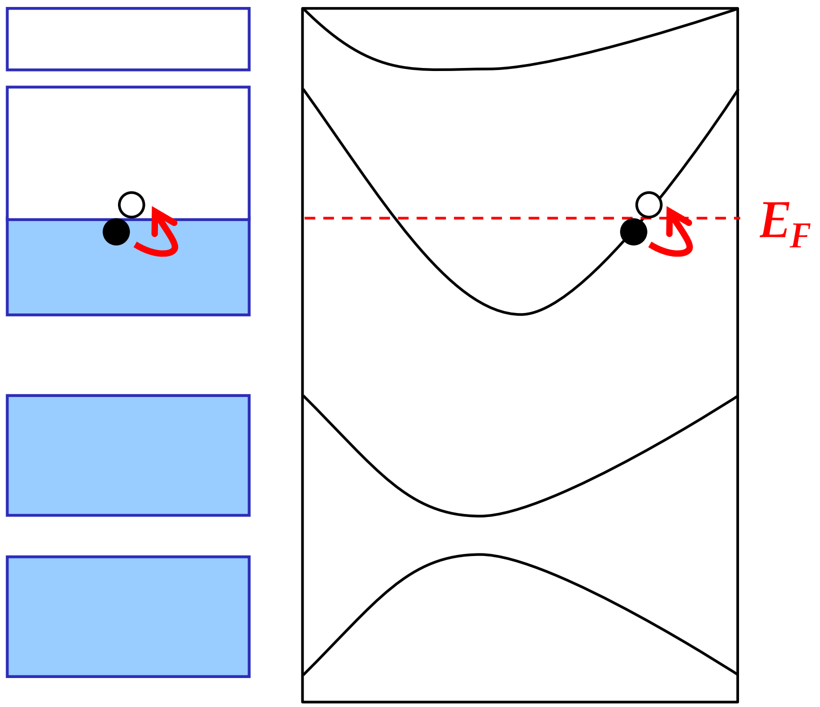
5 – INTERPRETATION: Intraband transitions (for metals)

In WIEN2k, two types of contributions to the dielectric function ($\varepsilon = \varepsilon_1 + i.\varepsilon_2$) could be estimated:

intraband: Drude model,
(ω_p: plasma frequency)

$$\mathrm{Im}\,\varepsilon^{\mathrm{intra}} = \frac{\Gamma {\omega_p}^2}{\omega\,(\omega^2 + \Gamma^2)}$$

Intraband contributions (using a Drude-like term)



Plasma frequency: (longitudinal oscillations of the electron gas)

$$\omega^2_{p,\alpha\beta} = \frac{4\pi e^2}{\Omega^2}\left(\frac{n}{m}\right)_{\alpha\beta} = \frac{e^2}{m^2\pi^2}\sum_l \int d\mathbf{k}\ \langle l|p^\alpha|l\rangle_\mathbf{k}\langle l|p^\beta|l\rangle_\mathbf{k}\ \delta(\varepsilon_l - \varepsilon_F)$$

5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Optical functions:

- Dielectric tensor

$$\Im \epsilon_{ij} = \frac{16\pi^2}{\Omega \omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

$$\Re \epsilon_{ij} = \delta_{ij} \frac{2}{\pi} P \int_0^\infty \frac{\omega' \Im \epsilon_{ij}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

- Optical conductivity

$$\Re \sigma_{ij}(\omega) = \frac{\omega}{4\pi} \Im \epsilon_{ij}(\omega)$$

- Refractive index

$$n_{ii} = \sqrt{\frac{|\epsilon_{ii}(\omega)| + \Re \epsilon_{ii}(\omega)}{2}} \qquad k_{ii}(\omega) = \sqrt{\frac{|\epsilon_{ii}(\omega)| - \Re \epsilon_{ii}(\omega)}{2}}$$

- Reflectivity

$$R_{ii}(\omega) = \frac{(m_{ii} - 1)^2 + k_{ii}^2}{(n_{ii} + 1)^2 + k_{ii}^2}$$

- Absorption

$$A_{ii}(\omega) = \frac{2\omega k_{ii}(\omega)}{c}$$

- Loss function

$$L_{ii}(\omega) = -\Im\left(\frac{1}{\epsilon_{ii}(\omega)}\right)$$

5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Symmetry of the dielectric tensor

triclinic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{xz} \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & \mathrm{Im}\,\epsilon_{yz} \\ \mathrm{Im}\,\epsilon_{xz} & \mathrm{Im}\,\epsilon_{yz} & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

monoclinic ($\alpha,\beta = 90°$)

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & 0 \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

orthorhombic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

tetragonal, hexagonal

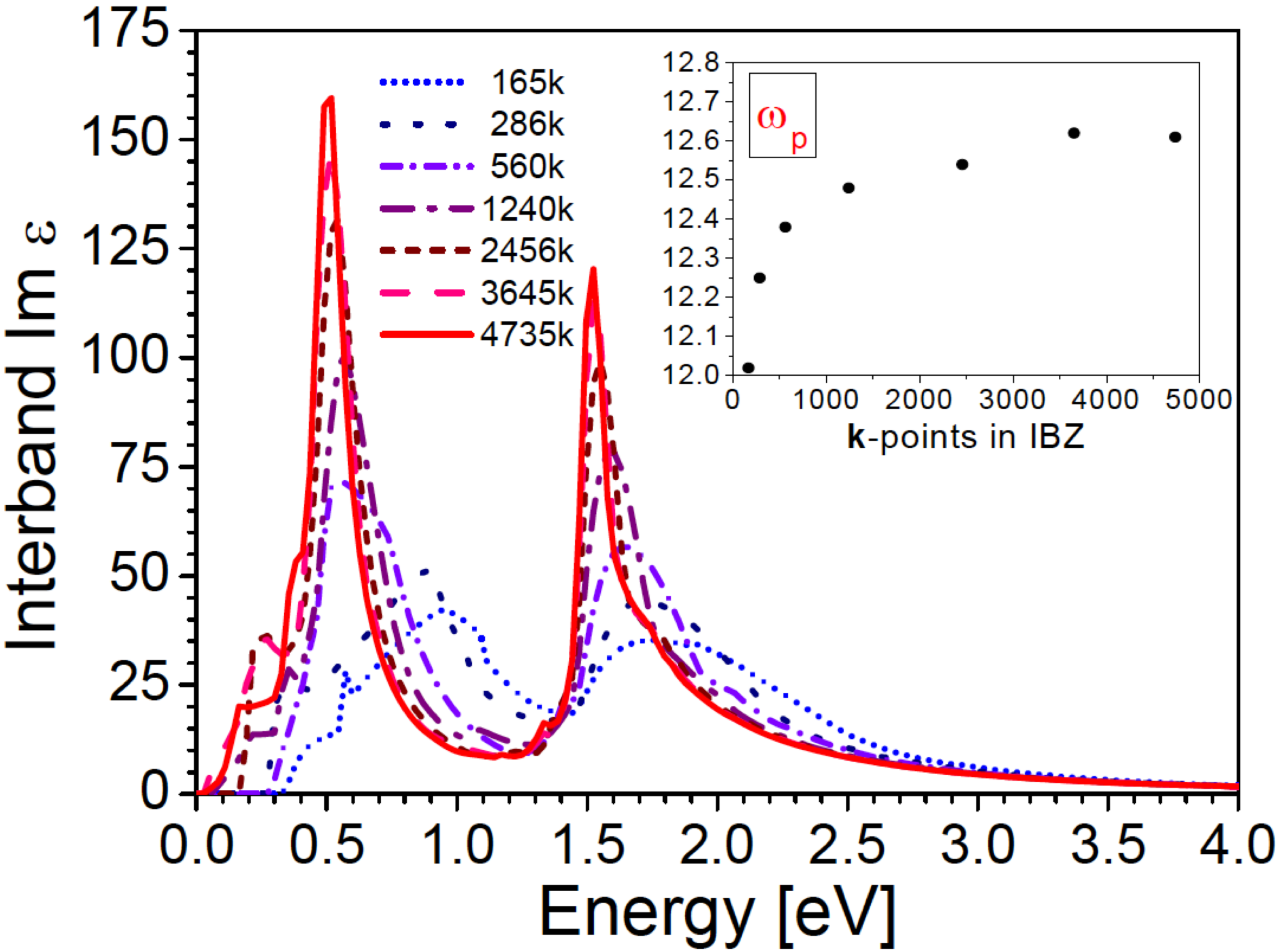
$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

cubic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{xx} \end{pmatrix}$$

5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Convergence with k-mesh (expl.: Al)



5 – OPTICS IN WIEN2k

⓿ normal SCF run ⟶ converged density

❶ x kgen ⟶ dense k-mesh (check convergence!)

❷ x lapw1 *-options* ⟶ eigenvectors on dense mesh

❸ x lapw2 -fermi *-options* ⟶ *case*.weight

- metals: "TETRA 101.0" in *case*.in2

❹ x optic *-options* ⟶ momentum matrix elements

case.symmat: $\langle c\mathbf{k}|\hat{p}_i|v\mathbf{k}\rangle \langle v\mathbf{k}|\hat{p}_j|c\mathbf{k}\rangle$

❺ **x joint** → **Im** $\varepsilon_{ij}(\omega)$ **(case.joint)**

❻ **x kram** → **Re** $\varepsilon_{ij}(\omega)$**, other optical funct.**

❼ **opticplot**

5 – SOME ADDITIONAL DETAILS

spin-polarized calculations

1. `x joint -up && x joint -dn`
2. `addjoint-updn`
3. `x kram`

procedure for metals

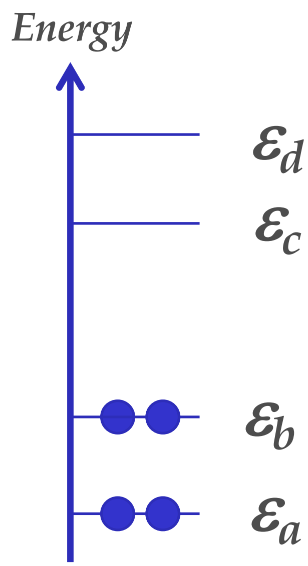
1. `x joint (mode=6)` $\longrightarrow$ plasma frequencies $\omega_{\mathrm{p}_{ij}}$
2. `x joint (mode=4)` $\longrightarrow$ interband $\mathrm{Im}\,\varepsilon$
3. `x kram (intra=1,` insert ω_{p}`)`

Kramers-Kronig needs $\mathrm{Im}\,\varepsilon$ in a large energy range

$$\mathrm{Re}\,\varepsilon_{ij} = \delta_{ij} + \frac{2}{\pi}\mathcal{P}\int_0^\infty \mathrm{d}\Omega\,\frac{\Omega}{\Omega^2 - \omega^2}\,\mathrm{Im}\,\varepsilon_{ij}$$

5 – INTERPRETATION: Band gap problem

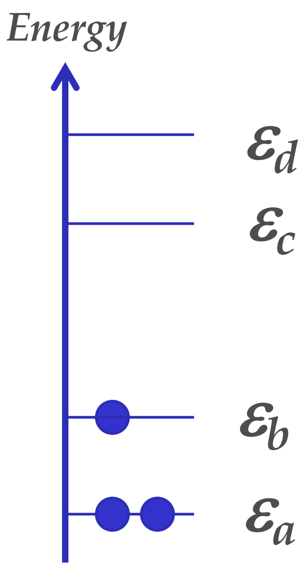
The band gap problem → Necessity to go beyond DFT

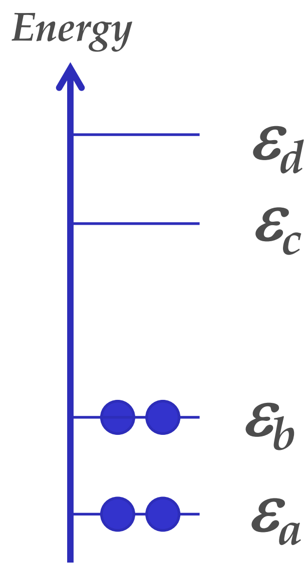


$$E(N) = 2\varepsilon_a + 2\varepsilon_b$$

5 – INTERPRETATION: Band gap problem

The band gap problem → Necessity to go beyond DFT





$E(N\text{-}1) = 2\varepsilon_a + \varepsilon_b$

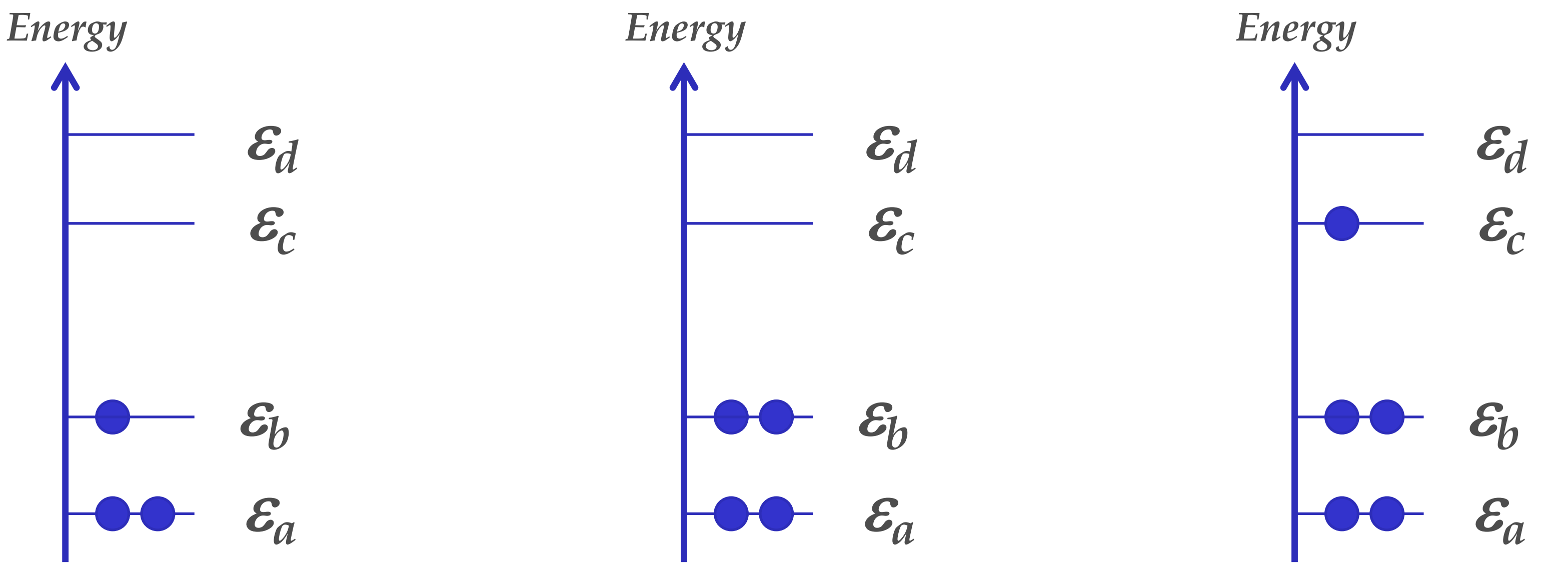
$E(N) = 2\varepsilon_a + 2\varepsilon_b$

$IP = E(N\text{-}1) - E(N)$

IP: Ionization potential

5 – INTERPRETATION: Band gap problem

The band gap problem → Necessity to go beyond DFT



$E(N\text{-}1) = 2\varepsilon_a + \varepsilon_b$ $E(N) = 2\varepsilon_a + 2\varepsilon_b$ $E(N+1) = 2\varepsilon_a + 2\varepsilon_b + \varepsilon_c$

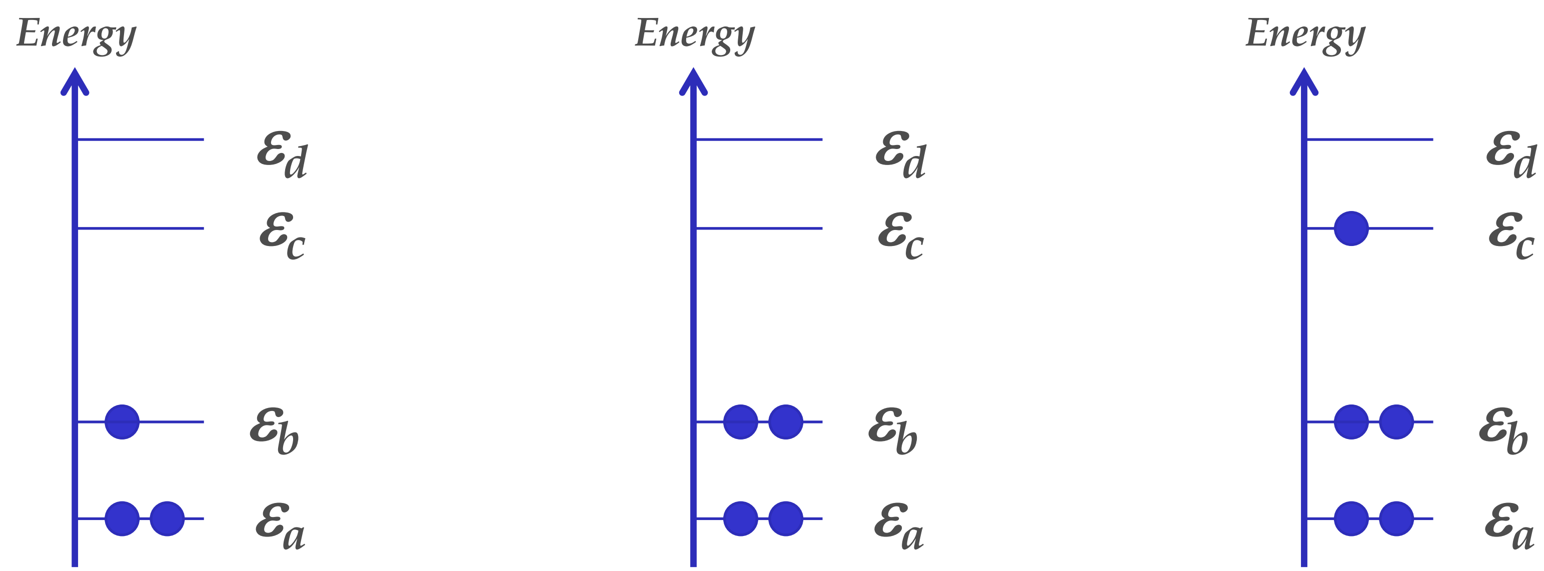
$IP = E(N\text{-}1) - E(N)$

$EA = E(N) - E(N+1)$

IP: Ionization potential *EA: Electron affinity*

5 – INTERPRETATION: Band gap problem

The band gap problem → Necessity to go beyond DFT



$E(N\text{-}1) = 2\varepsilon_a + \varepsilon_b$ $\quad$ $E(N) = 2\varepsilon_a + 2\varepsilon_b$ $\quad$ $E(N+1) = 2\varepsilon_a + 2\varepsilon_b + \varepsilon_c$

$IP = E(N\text{-}1) - E(N)$

$EA = E(N) - E(N+1)$

Fundamental energy gap

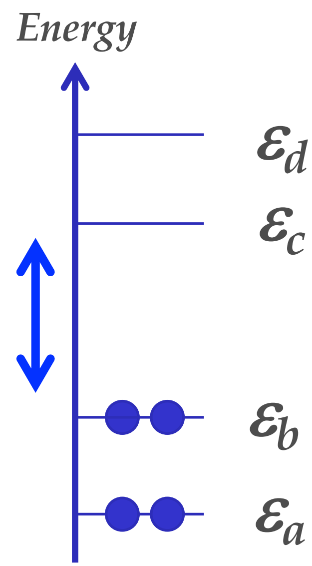
$$G = IP - EA = E(N\text{-}1) + E(N+1) - 2E(N)$$

IP: Ionization potential *EA: Electron affinity* J. P. Perdew et al. PNAS 114(11):2801 (2017)

5 – INTERPRETATION: Band gap problem

The band gap problem → Necessity to go beyond DFT

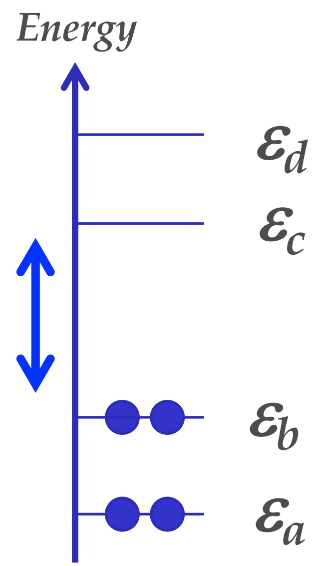
« Band gap » $g = \varepsilon_c - \varepsilon_b$



J. P. Perdew et al. PNAS 114(11):2801 (2017)

5 – INTERPRETATION: Band gap problem

The band gap problem → Necessity to go beyond DFT



« Band gap » $g = \varepsilon_c - \varepsilon_b$

$G = g + \Delta_{xc}$

Δ_{xc} *: exchange-correlation discontinuity*

Scissor Operator / GW / hybrid…

Fundamental energy gap

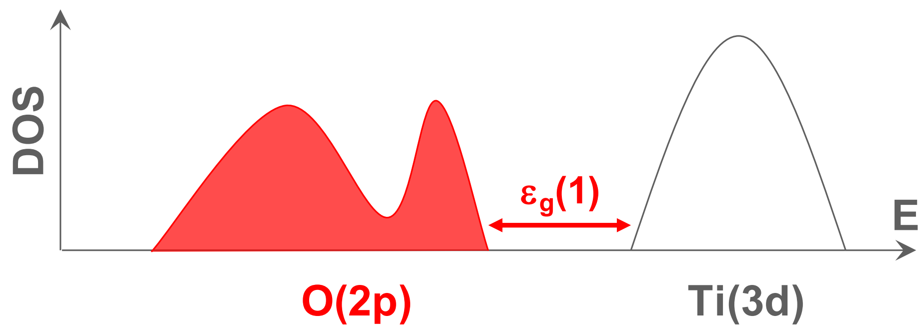
$$G = IP - EA$$
$$= E(N\text{-}1) + E(N\text{+}1) - 2E(N)$$

IP: Ionization potential *EA: Electron affinity* J. P. Perdew et al. PNAS 114(11):2801 (2017)

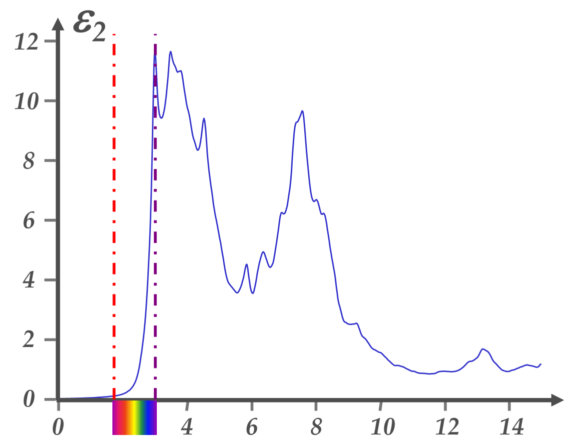
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Fundamental gap: electronic gap ≠ optical gap

Deduced from the band structure



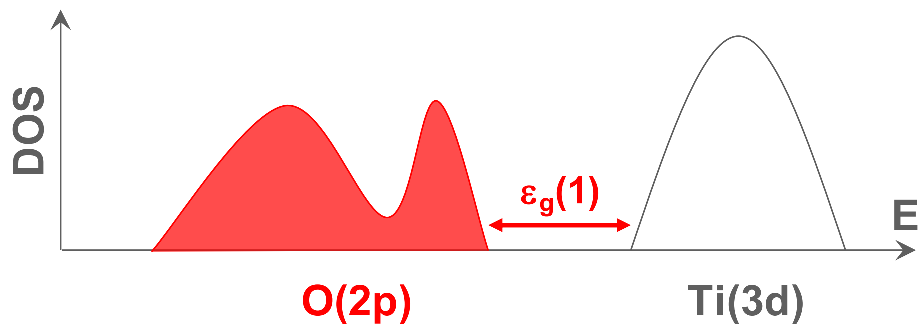
Dipolar transitions



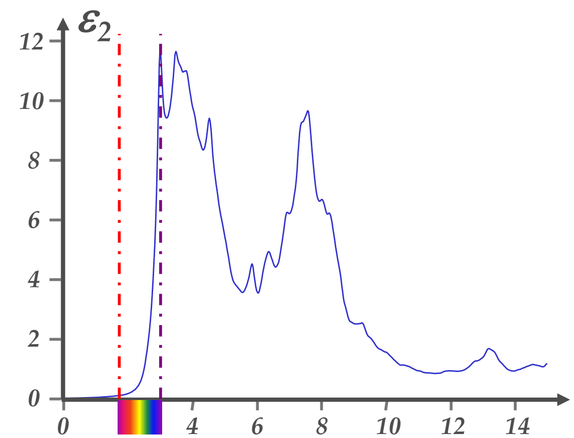
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

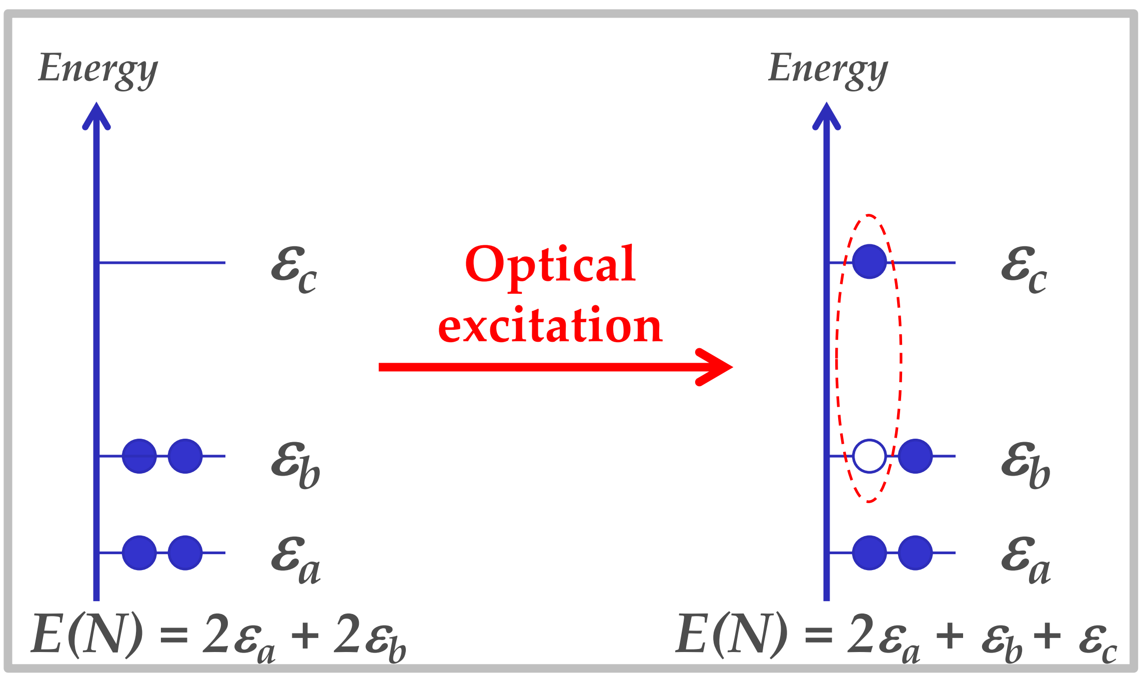
Fundamental gap: electronic gap ≠ optical gap

Deduced from the band structure

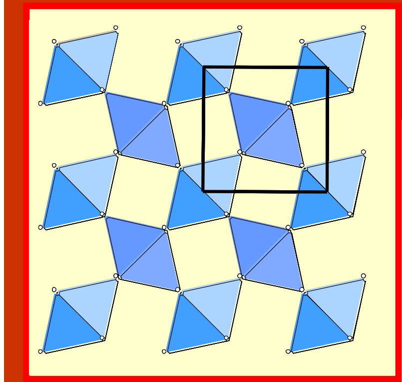


Dipolar transitions





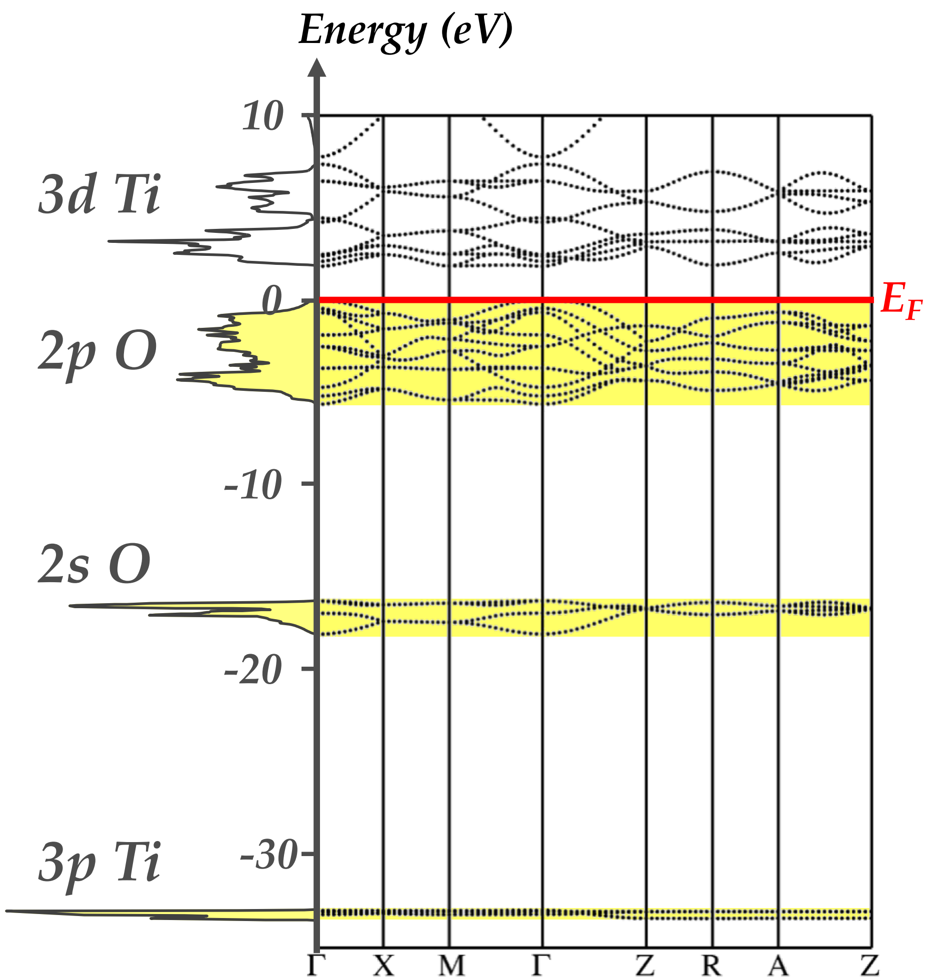
If excitonic effects:
we should go beyond
(TDDFT / BSE)



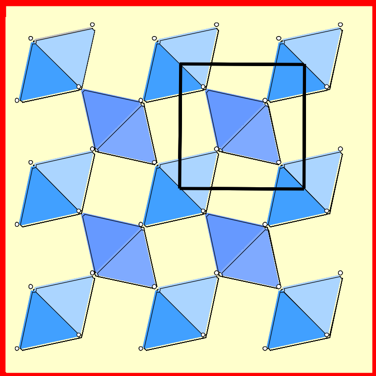
6 – ILLUSTRATIONS: TiO_2 series

Example of the rutile phase

Atomic structure → *Electronic structure* → *Dielectric function*

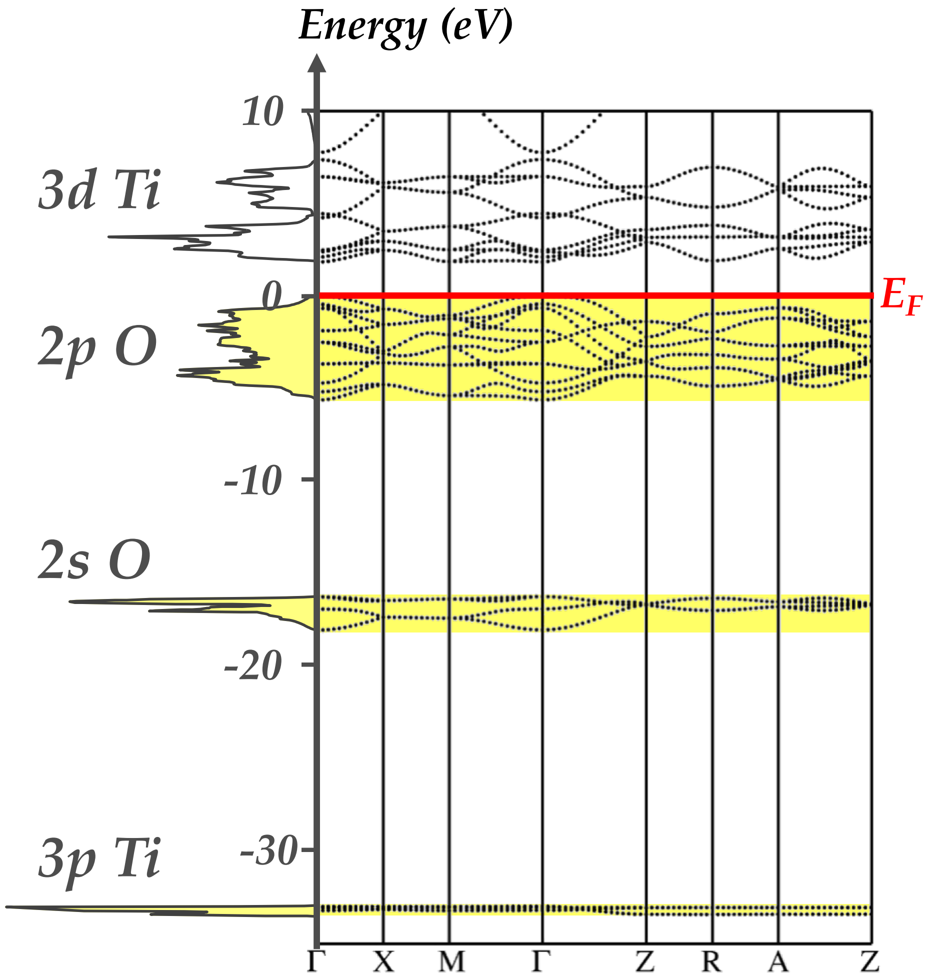


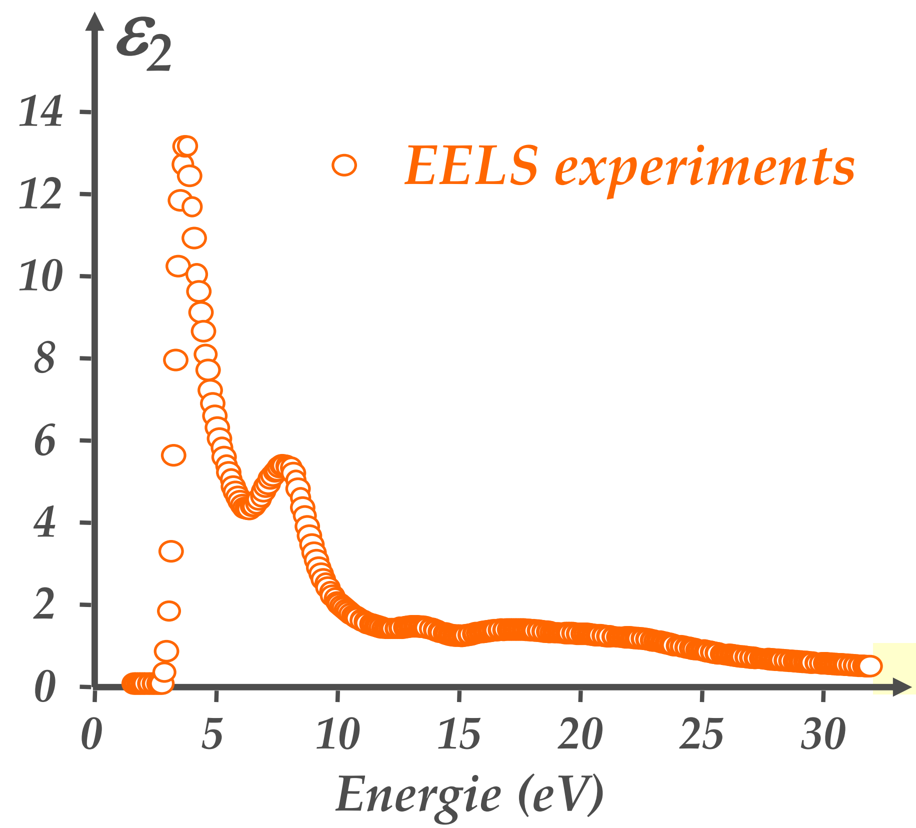
6 – ILLUSTRATIONS: TiO_2 series

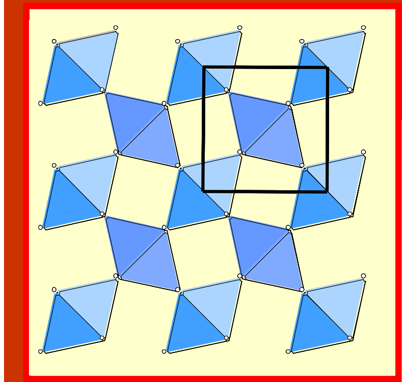


Example of the rutile phase

Atomic structure ⇒ *Electronic structure* ⇒ *Dielectric function*



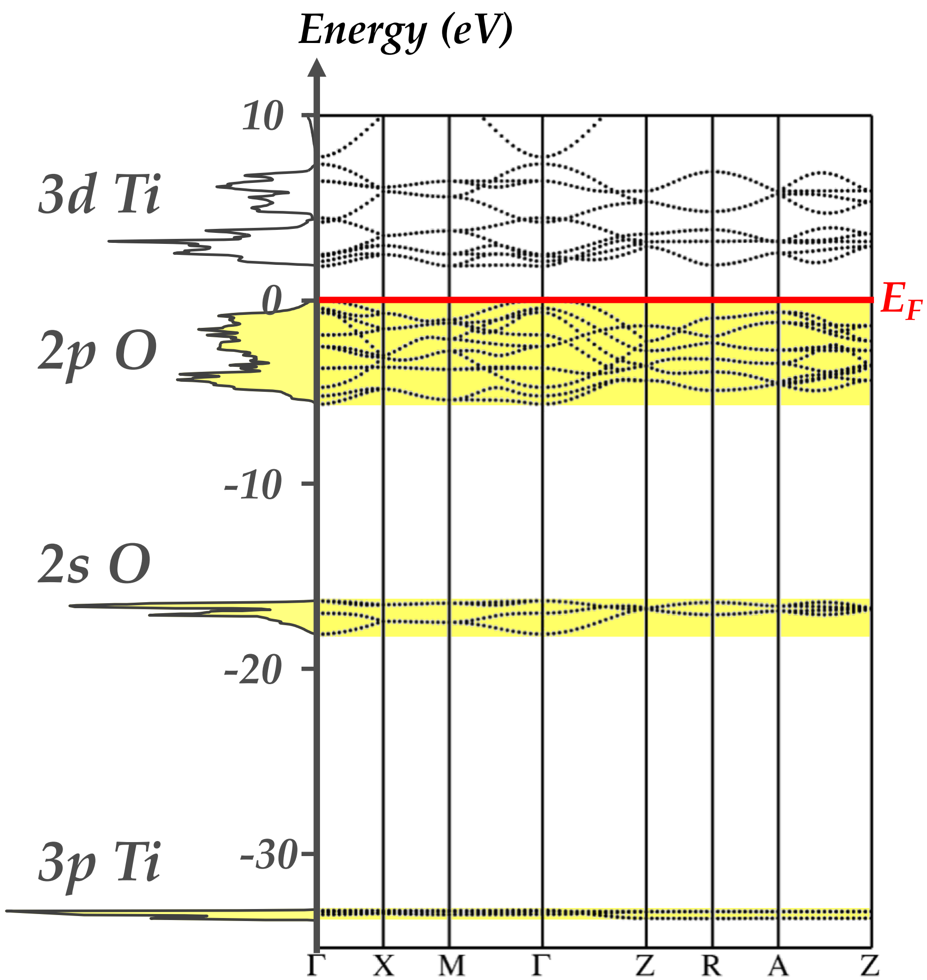


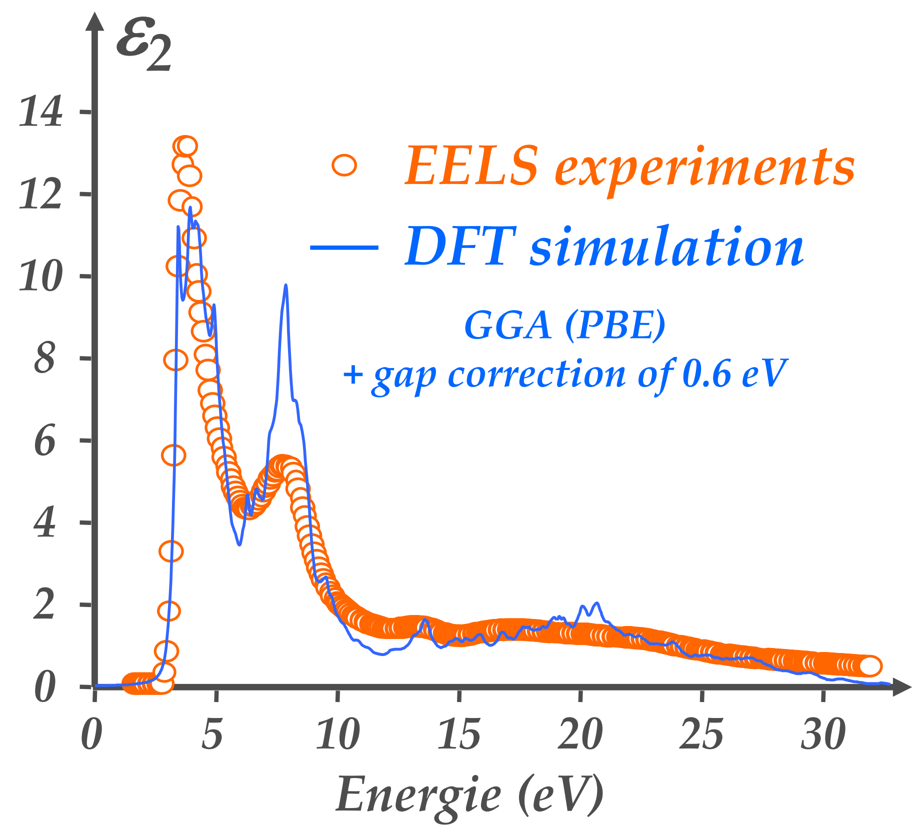


6 – ILLUSTRATIONS: TiO_2 series

Example of the rutile phase

Atomic structure → Electronic structure → Dielectric function





Program flow

SCF cycle → converged potential

x kgen → *denser k-mesh*

x lapw1 → *Kohn-Sham states for the denser k-mesh and higher E_{max}*

x lapw2 -fermi → *Fermi distribution*

x optic → *momentum matrix elements (dipolar transitions)*

x joint → *dielectric tensor components: ε_2*

x kram → *Kramers-Krönig transformation: $\varepsilon_2 \rightarrow \varepsilon_1$*
→ *Optical constants / broadening / scissors operator*

6 – ILLUSTRATIONS: TiO_2 series

TiO2-RUT.inop

```
2000    1        number of k-points, first k-point
-5.0   5.0       Emin, Emax in Ry for matrix elements
2                number of choices (columns in *outmat)
1                Re xx
3                Re zz
OFF              write unsymmetrized matrix elements to file?

Choices:
1......Re <x><x>
2......Re <y><y>
3......Re <z><z>
4......Re <x><y>
5......Re <x><z>
6......Re <y><z>
7......Im <x><y>
8......Im <x><z>
```

6 – ILLUSTRATIONS: TiO_2 series

TiO2-RUT.injoint

```
1   261                         LOWER AND UPPER BANDINDEX
0.0000   0.00100  10.0000       EMIN DE EMAX FOR ENERGYGRID IN ryd
    eV                          output units  eV / ryd  / cm-1
    4                           SWITCH
    2                           NUMBER OF COLUMNS
  0.1  0.1  0.3                 BROADENING (FOR DRUDE MODEL - switch 6,7 -ONLY)

SWITCH:

  0...JOINTDOS FOR EACH BAND COMBINATION
  1...JOINTDOS AS SUM OVER ALL BAND COMBINATIONS
  2...DOS FOR EACH BAND
  3...DOS AS SUM OVER ALL BANDS
  4...Im(EPSILON)
  5...Im(EPSILON) for each band combination
  6...INTRABAND contributions
  7...INTRABAND contributions including band analysis
```

TiO2-RUT.inkram

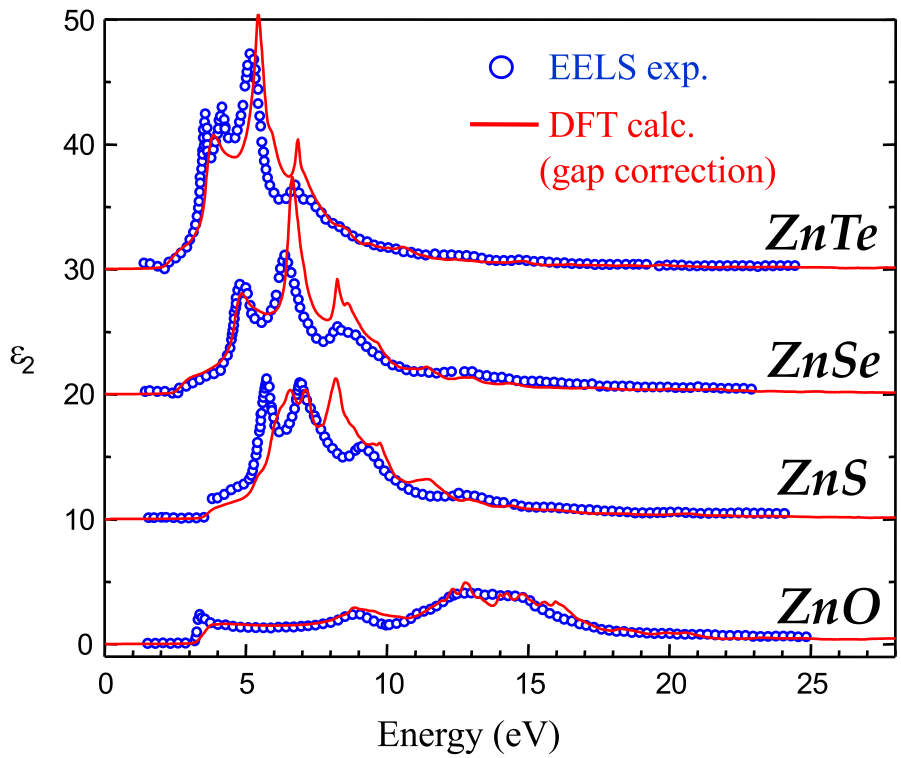
```
 0.1          Gamma: broadening of interband spectrum
  0.6         energy shift (scissors operator)
  0           add intraband contributions? yes/no: 1/0
 12.60        plasma frequencies  (from joint, opt 6)
  0.20        Gammas for Drude terms
```

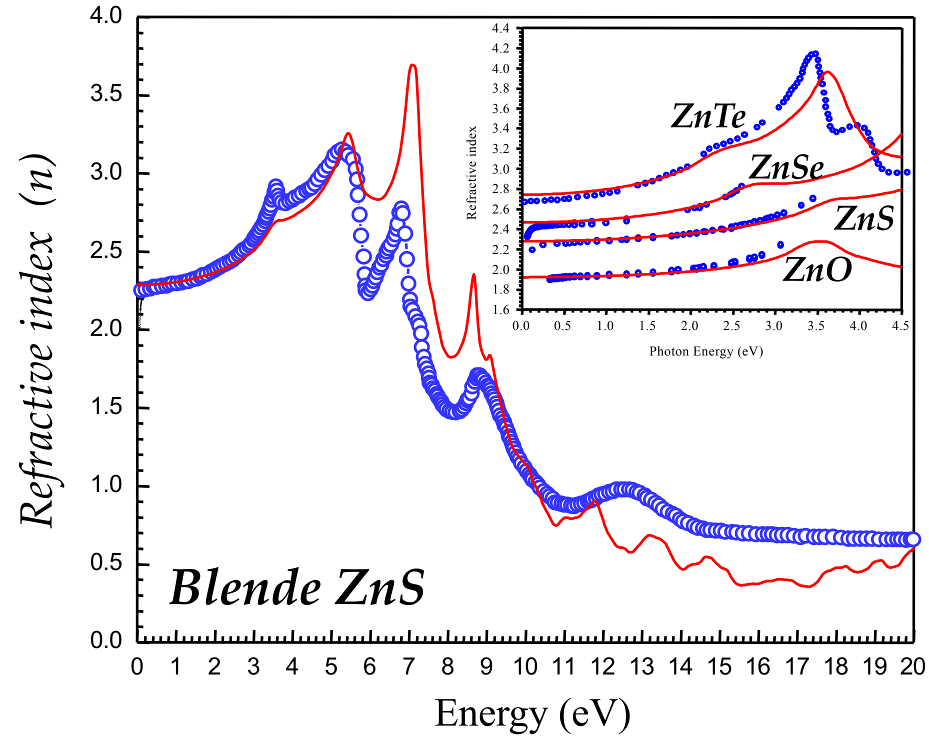
6 – ILLUSTRATIONS: TiO_2 series

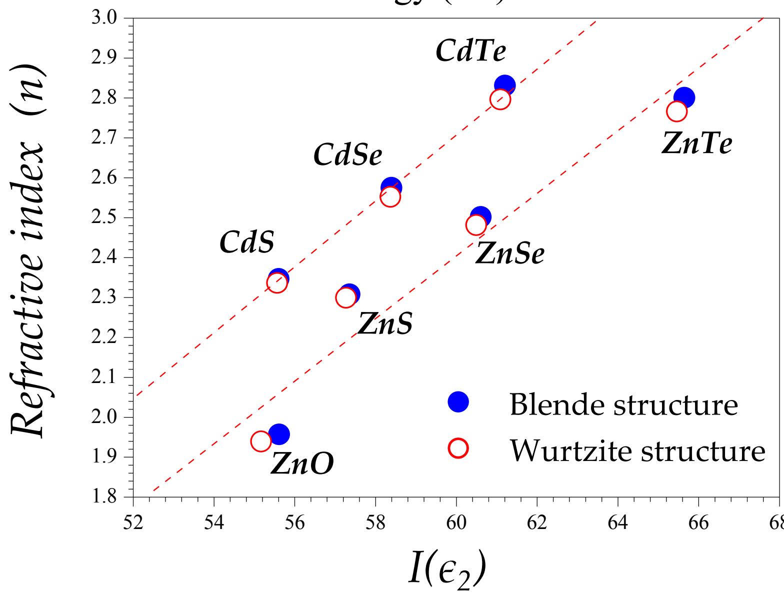
Files generated by:

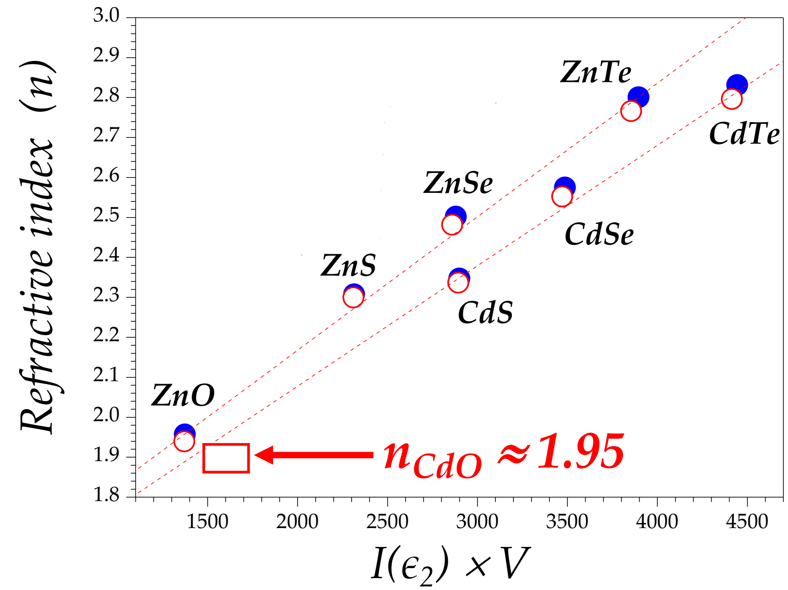
- **optic** → TiO2-RUT.symmat
  → TiO2-RUT.mommat
- **joint** → TiO2-RUT.joint
- **kram** → TiO2-RUT.epsilon
  → TiO2-RUT.sigmak
  → TiO2-RUT.refraction
  → TiO2-RUT.absorption
  → TiO2-RUT.eloss

6 –ILLUSTRATIONS: MQ series (M = Zn, Cd & Q = O, S, Se, Te)









7 – Some limitations of DFT simulation of optical properties

- Kohn-Sham eigenstates interpreted as excited states

Use of a scissors operator

- Independent-particle approximation (no e^-—h^+ interaction)

Use of Bethe-Salpeter Equation (BSE) – Time-dependent DFT

- LDA/GGA are not exact

Use of hybrid DFT, effective potentials

Use of DFT+U, LDA+DMFT, GW…

WIEN2k allows to simulate a lot of "excited states" properties
BUT
you must be aware of the limitations and approximations to properly interpret your data.