TECHNISCHE UNIVERSITÄT WIEN

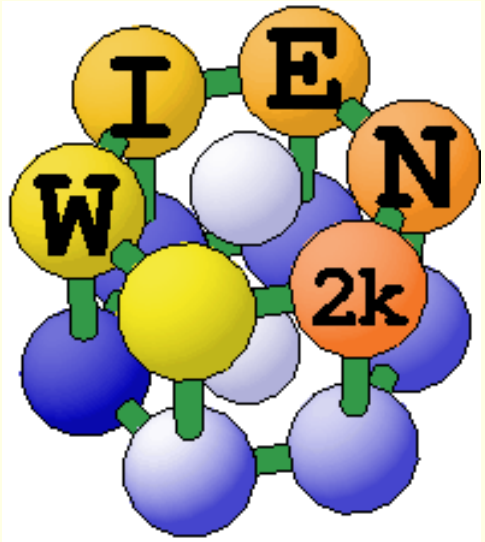
XPS, Optical properties

Peter Blaha

Institute of Materials Chemistry, TU Wien

(Xavier Rocquefelte)

University of Rennes



Photoemission spectroscopy, PES

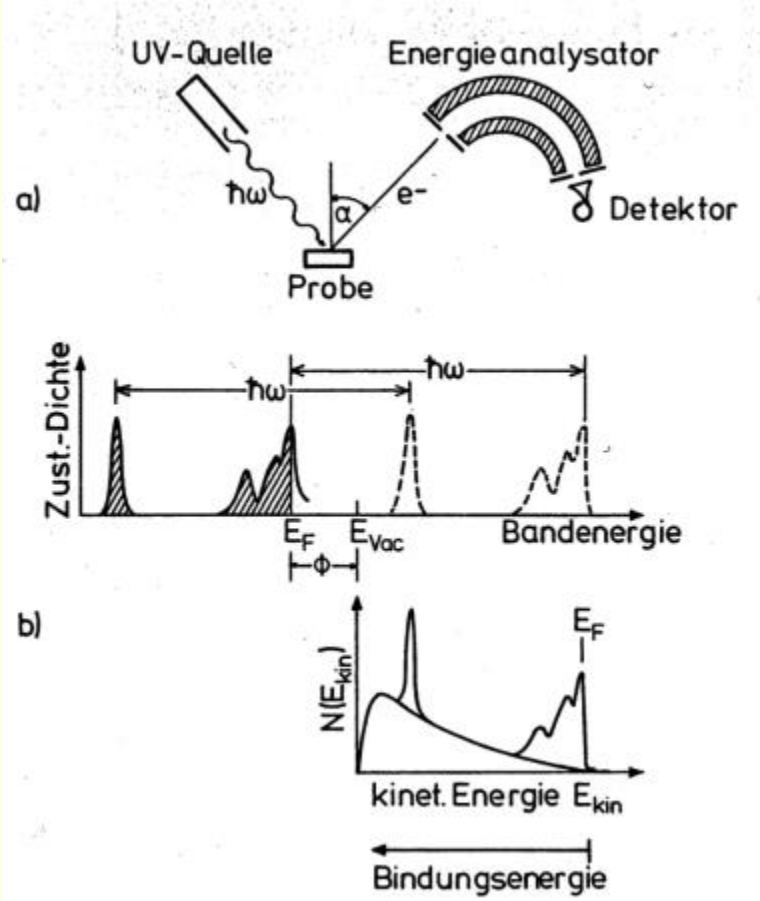
•Illuminate sample with light of known energy, measure kinetic E of emitted electrons e^-

→ core-e^-, Valence-DOS

- Energyconservation:

$$\hbar\omega = \phi + E_{kin} + E_b$$

  - ϕ: work function
  - E_{kin}: kinetic E of e^-
  - E_b: bindingenergy of e^-



- UPS: UV (He-light, 21.1 und 40.4 eV), for valence-electrons
- XPS, ESCA: X-rays (Al 1486 eV), for core and valence-electrons
- Synchrotronradiation: UV or X-rays of "any" wavelength

Work function

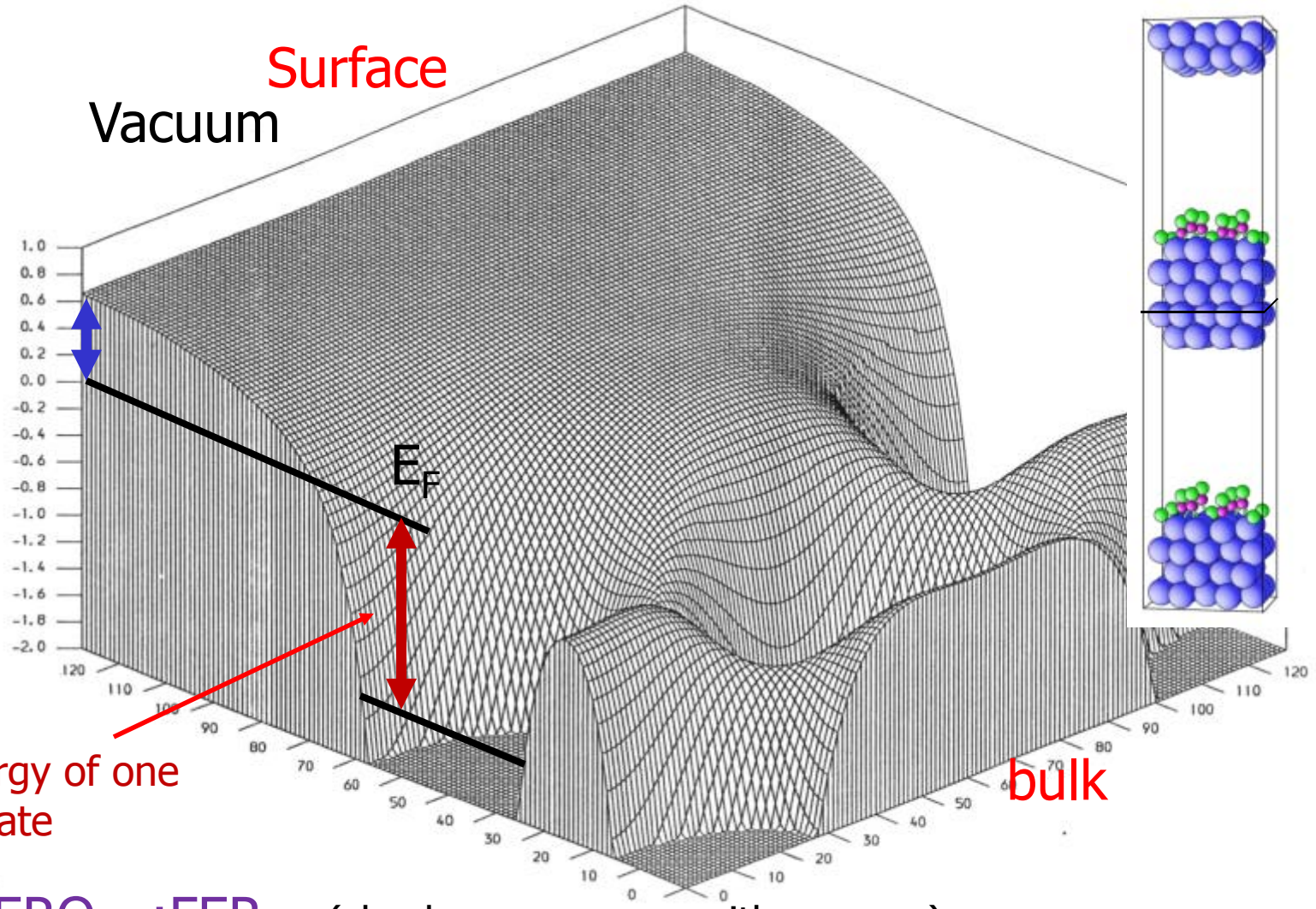
potential

supercell

Surface

Vacuum

Work-function

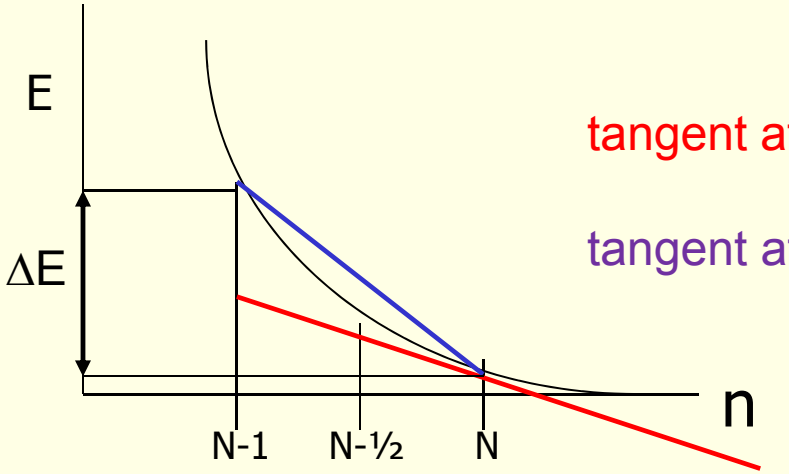


binding energy of one particular state

WF= :VZERO - :FER (check convergence with vacuum)

XPS, core-level shifts

- Ionizationpotential of core-e^-, IP= $E^{tot}(N) - E^{tot}(N-1)$
  - *gives information on charge state of the atom*
- core-eigenvalues ε_i are NOT a good approximation: $\varepsilon_i = dE/dn$
- **Slater's** "transition state": core-eigenvalues ε_i for half occupancy



tangent at N ≠ ΔE

tangent at N-½ ~ secant ~ ΔE

- Δ-SCF-calculation with and without core-hole: $E^{tot}(N) - E^{tot}(N-1)$
  - *supercells to reduce hole-hole interaction*

C,N 1s	exp.(eV)	ε_i	Δ-SCF
TiC	281.5	264.7	281.9
Ti_4C_4	281.5	263.3	281.1
TiN	397.0	377.5	397.1

valence e⁻: bandstructure via ARPES

Surface state
d-band
sp-band

Normalemission:

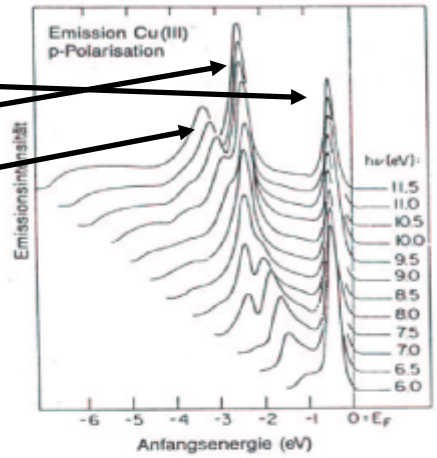
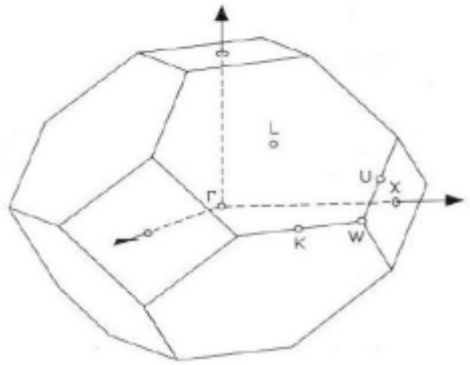


Abb. 3.11 a. UP-Spektren einer Cu(111)-Oberfläche bei Detektion normal zur Oberfläche und Variation der Photonenenergie von 6 bis 11,5 eV. Als Energieachse dient die Bindungsenergie bezogen auf die Fermi-Energie, hier als Anfangsenergie der Elektronen bezeichnet [29].

Brillouinzone fcc:



Volumenbandstruktur:

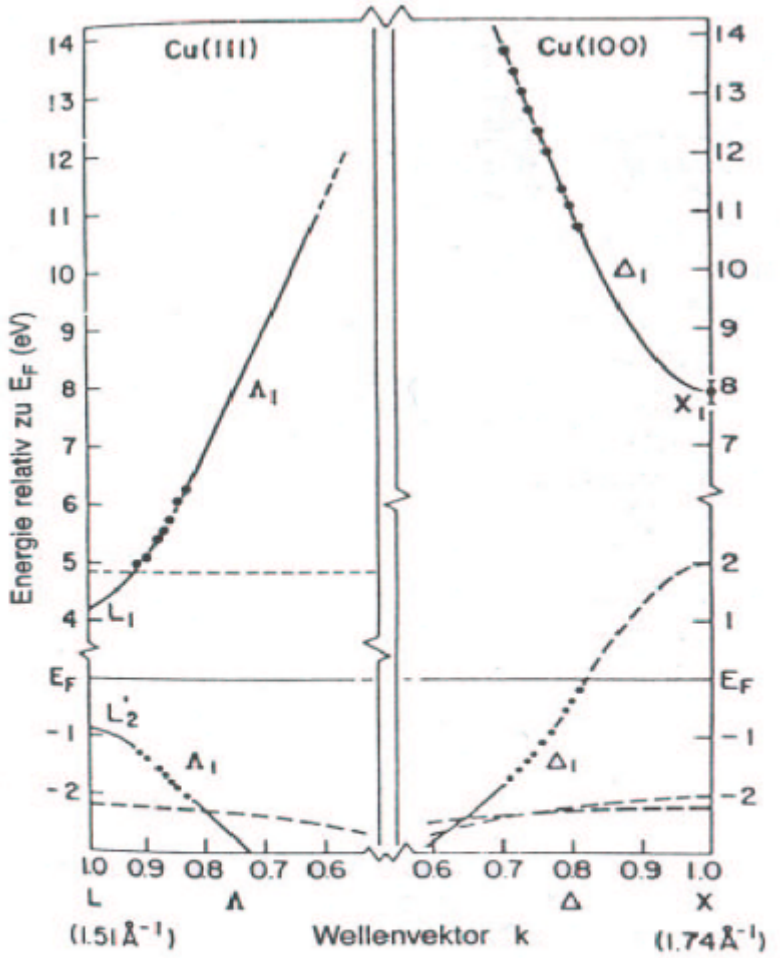
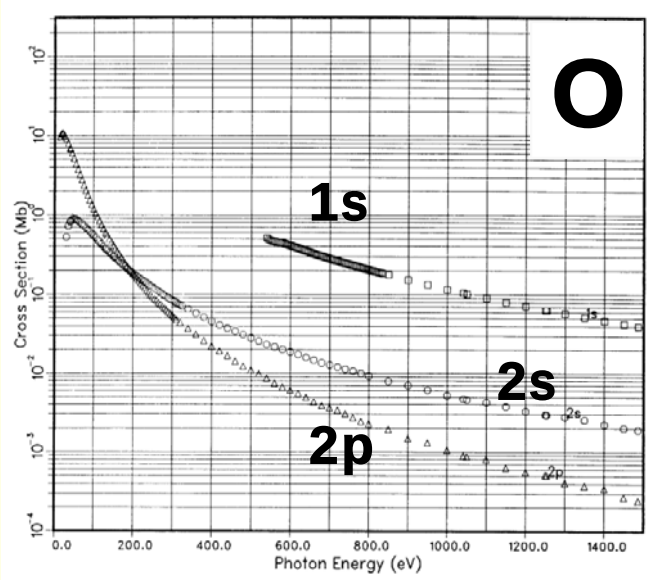
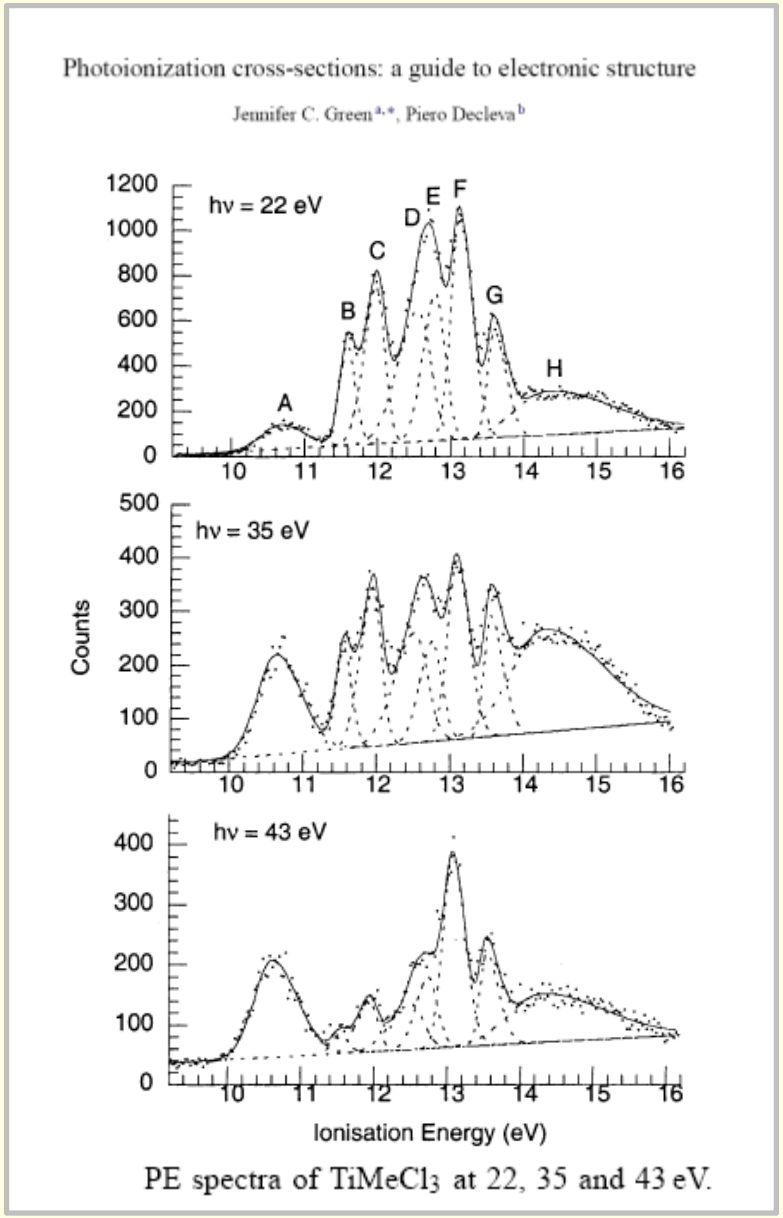


Abb. 3.11 b. Aus den Spektren von Abb. 3.11 a ermitteltes Bänderschema in den [111]-(Γ−L)- und [110]-(Γ−X)-Richtungen. Die Punkte geben die gemessenen Peakpositionen aus 3.11 a wieder, die Linien sind aus einer theoretischen Bandstruktur. Beim Vergleich mit der Cu-Bandstruktur in der Abb. 3.10 beachte man den unterbrochenen Energiemaßstab und den unterdrückten Γ-Punkt in Abb. 3.11 b [29].

valence PES: usually explained by DOS

- a single DOS cannot explain the E-dependency of PES
- $I = \sum_{atoms,l} N_{a,l} \sigma_{a,l}$
- $N_{a,l}$ = Partial DOS
- $\sigma_{a,l}$ = atomic cross section

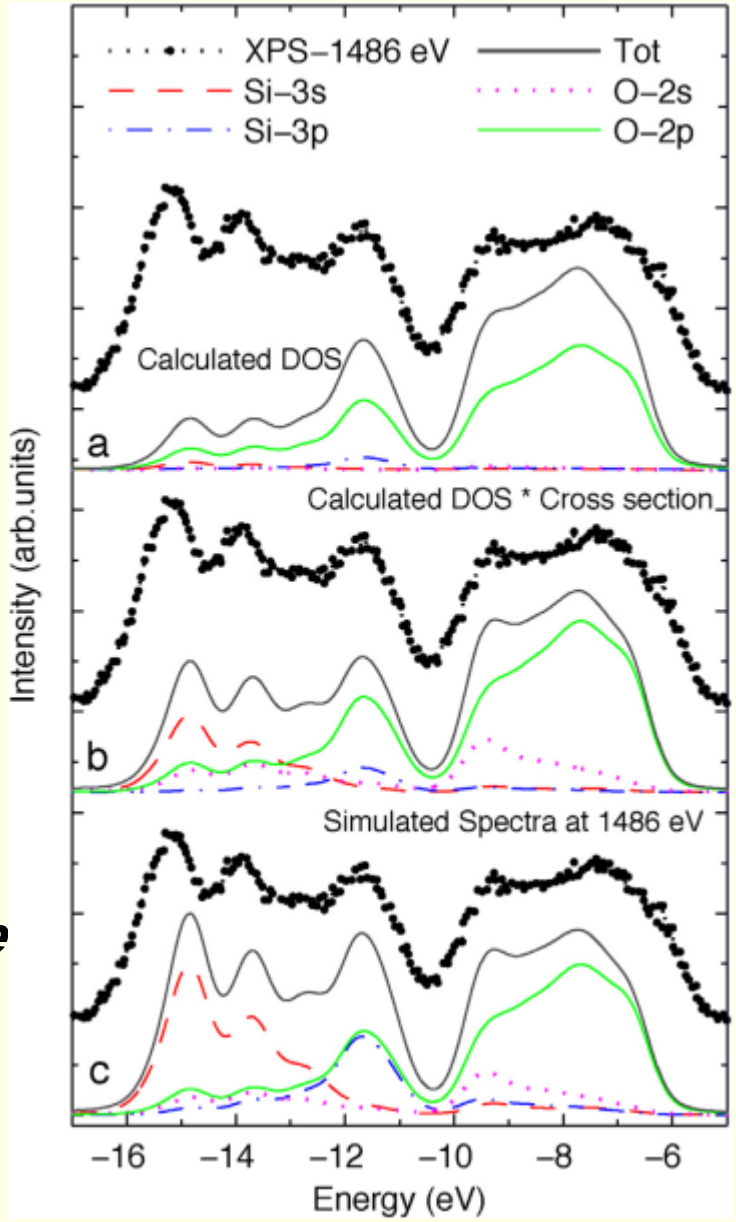




PE spectra of $TiMeCl_3$ at 22, 35 and 43 eV.

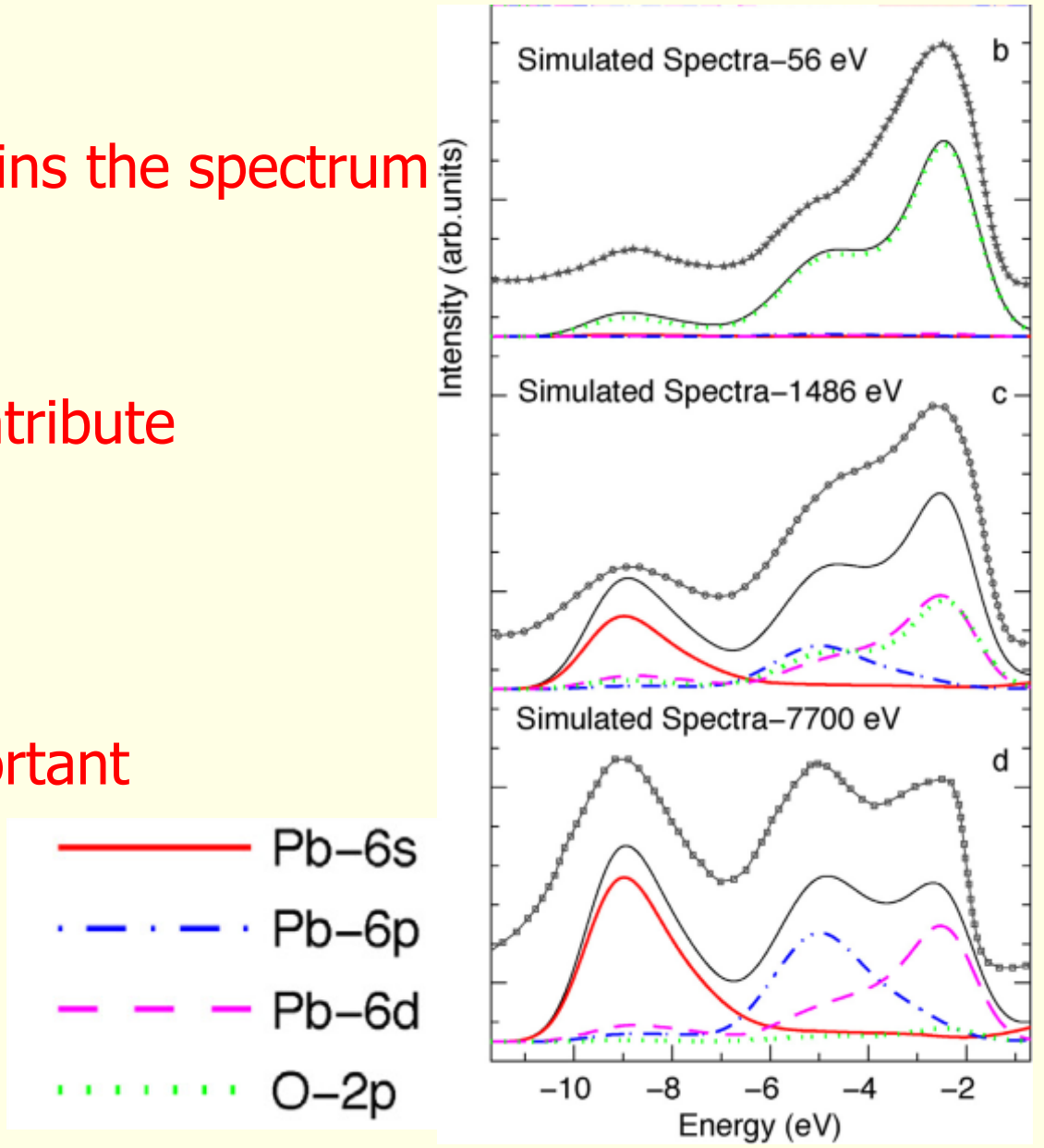
SiO_2 valence band XPS

- **Total DOS** gives 5 peaks, but wrong intensities
- **Cross section modulated PDOS** gives better intensities
- **Renormalized PDOS * σ** gives perfect intensities
  - *renormalization according to the **inverse charge fraction** of an orbital within the atomic sphere + removal of interstital DOS:* $N_{tot} = \sum_{atoms,l} N_{a,l} + N_{int}$



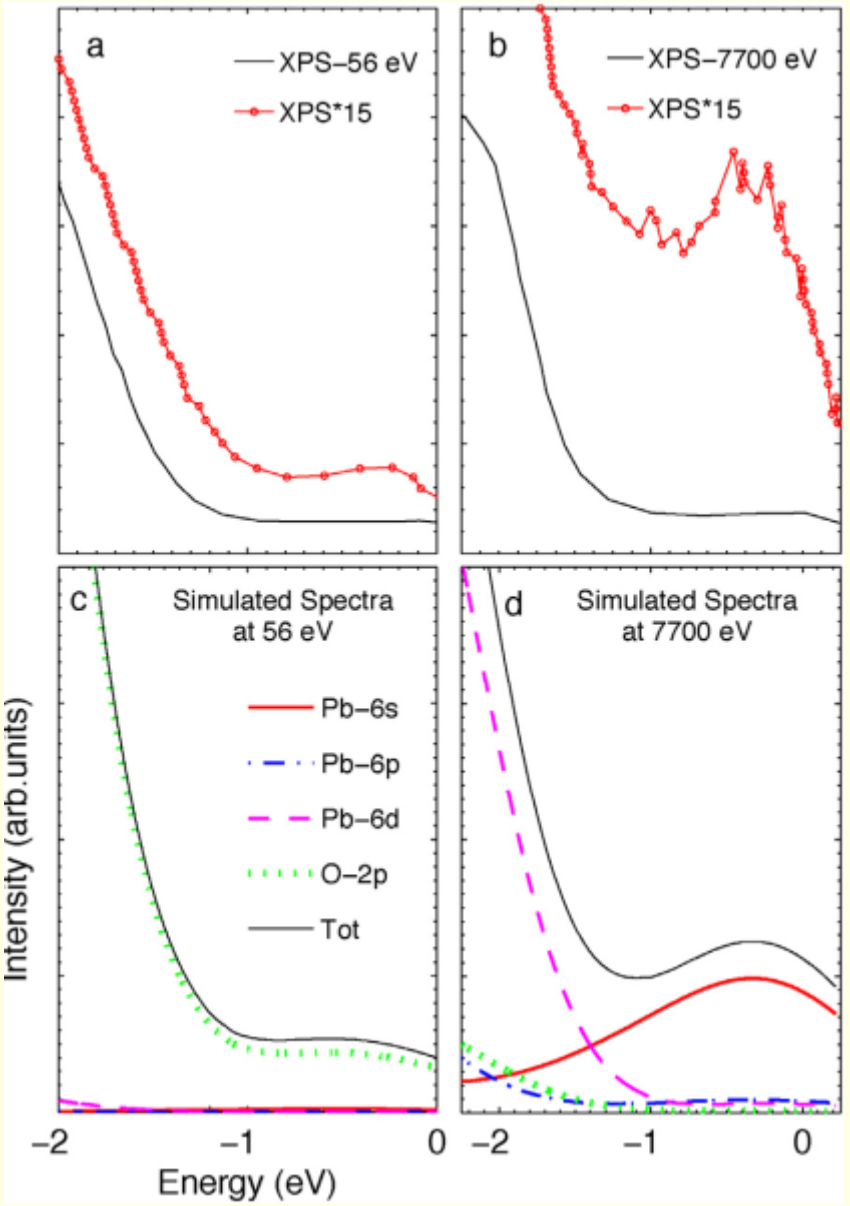
PbO_2 at 3 different energies

- 56eV: O-2p PDOS explains the spectrum
- 1486 eV: all orbitals contribute
- 7700 eV: O-2p not important



PBO_2 at very low BE

- 56 eV: almost no intensity till -1 eV
- 7700eV: strong contribution from antibonding Pb-6s



Modelling the Optical Properties of Inorganic Materials

1 – MULTIPLE FACETS OF COLOURED MATTER

2 – ELECTRONIC STRUCTURE OF A SOLID

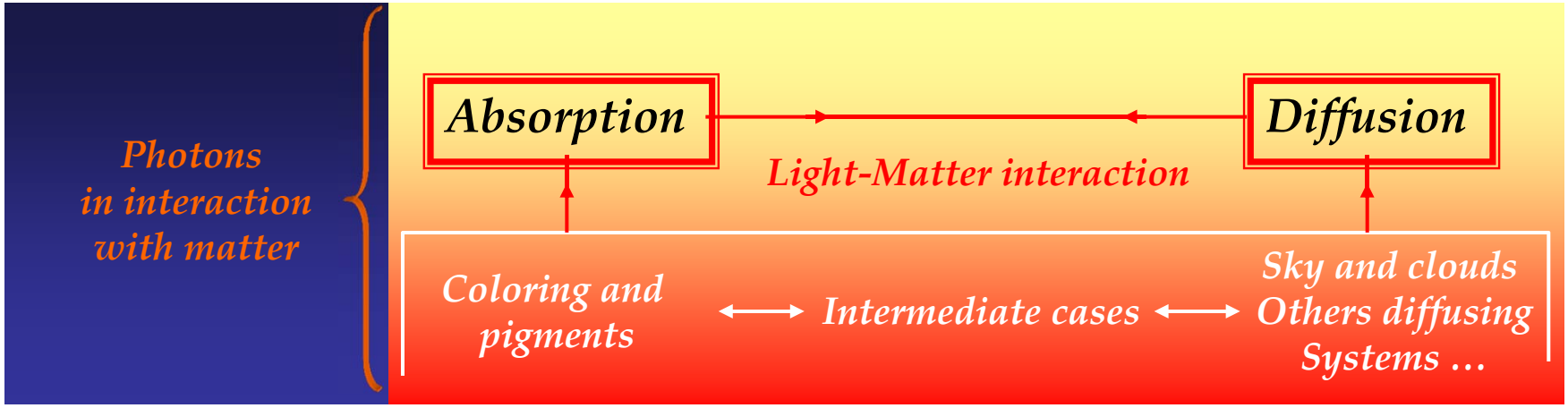
3 – UNDERSTANDING OF COLORS FROM BANDS

4 – LIGHT-MATTER INTERACTION

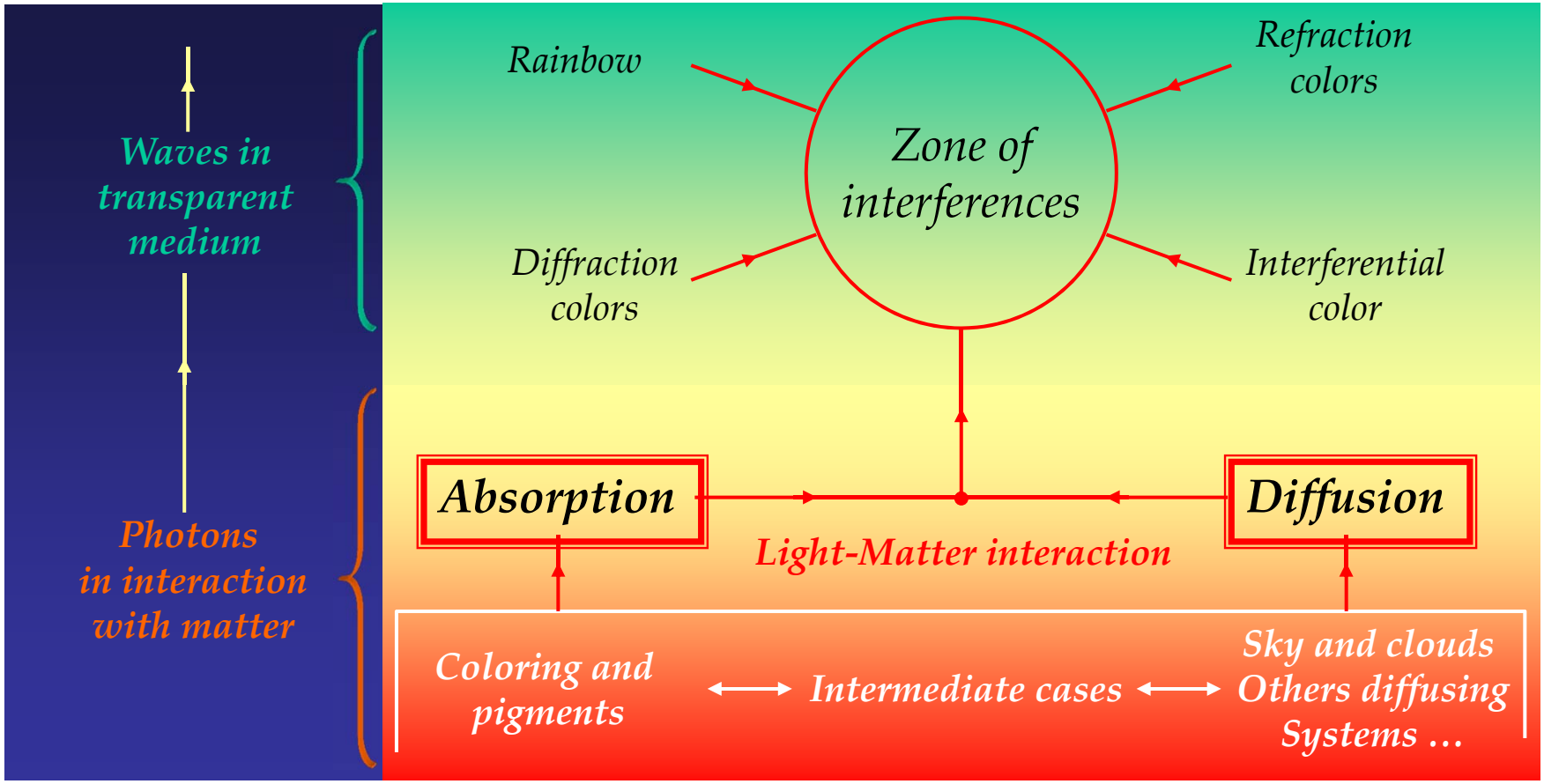
5 – OPTICAL PROPERTIES: WHICH TREATMENT?

6 – ILLUSTRATIONS

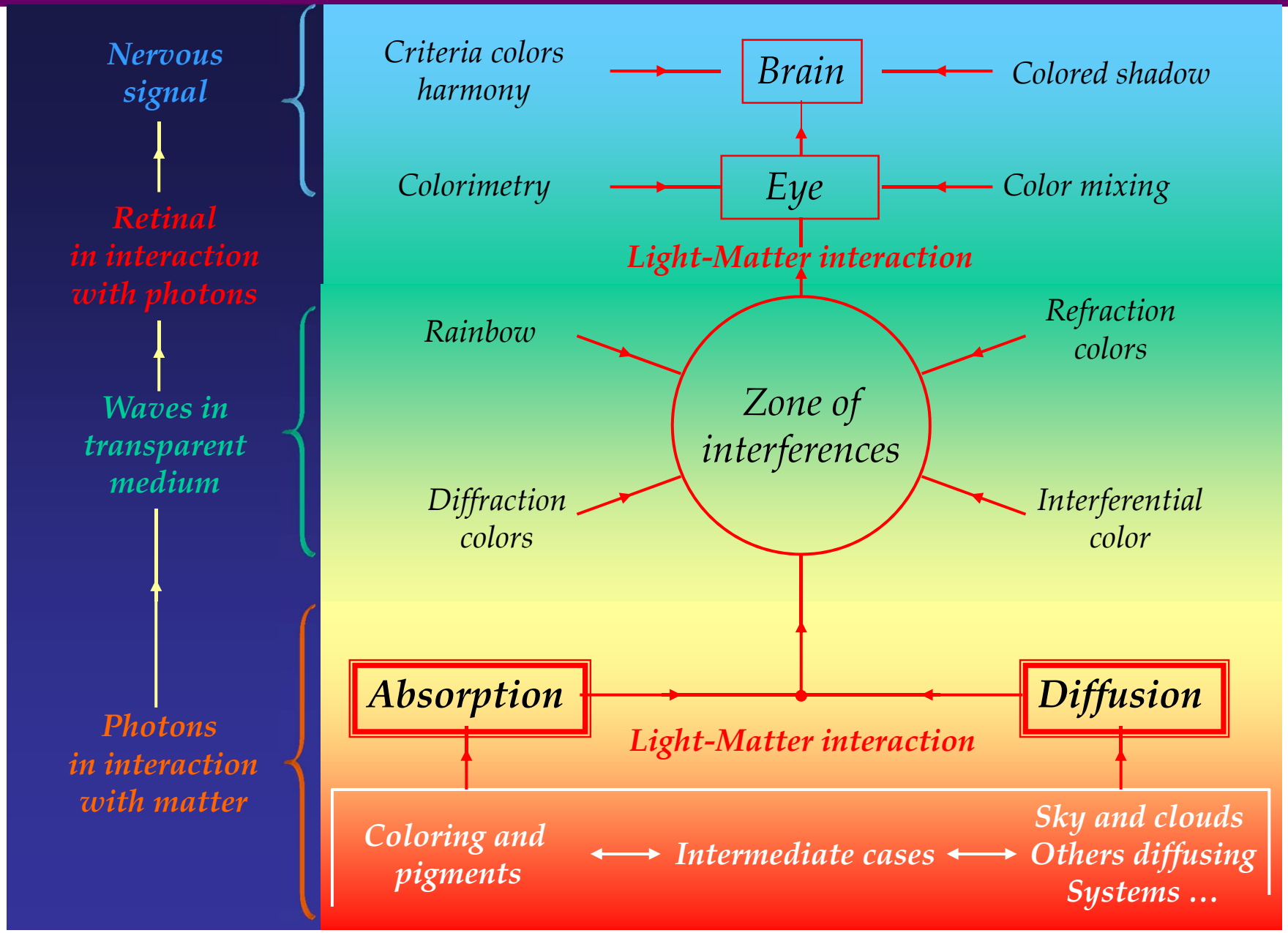
1 – MULTIPLE FACETS OF COLOURED MATTER



1 – MULTIPLE FACETS OF COLOURED MATTER



1 – MULTIPLE FACETS OF COLOURED MATTER



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

1 – MULTIPLE FACETS OF COLOURED MATTER

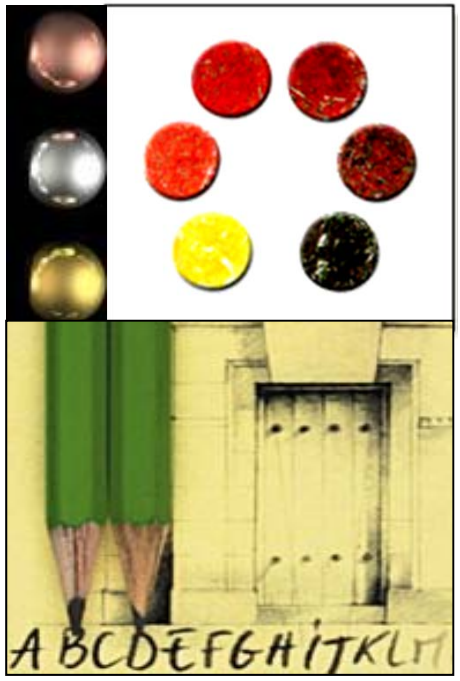
Interaction between the electromagnetic field and matter

Physical color

Diffusion et interferences
Dispersion / Reflection et Refraction / Scattering

Transparent matter

Chemical color



Absorption
Energy dissipation

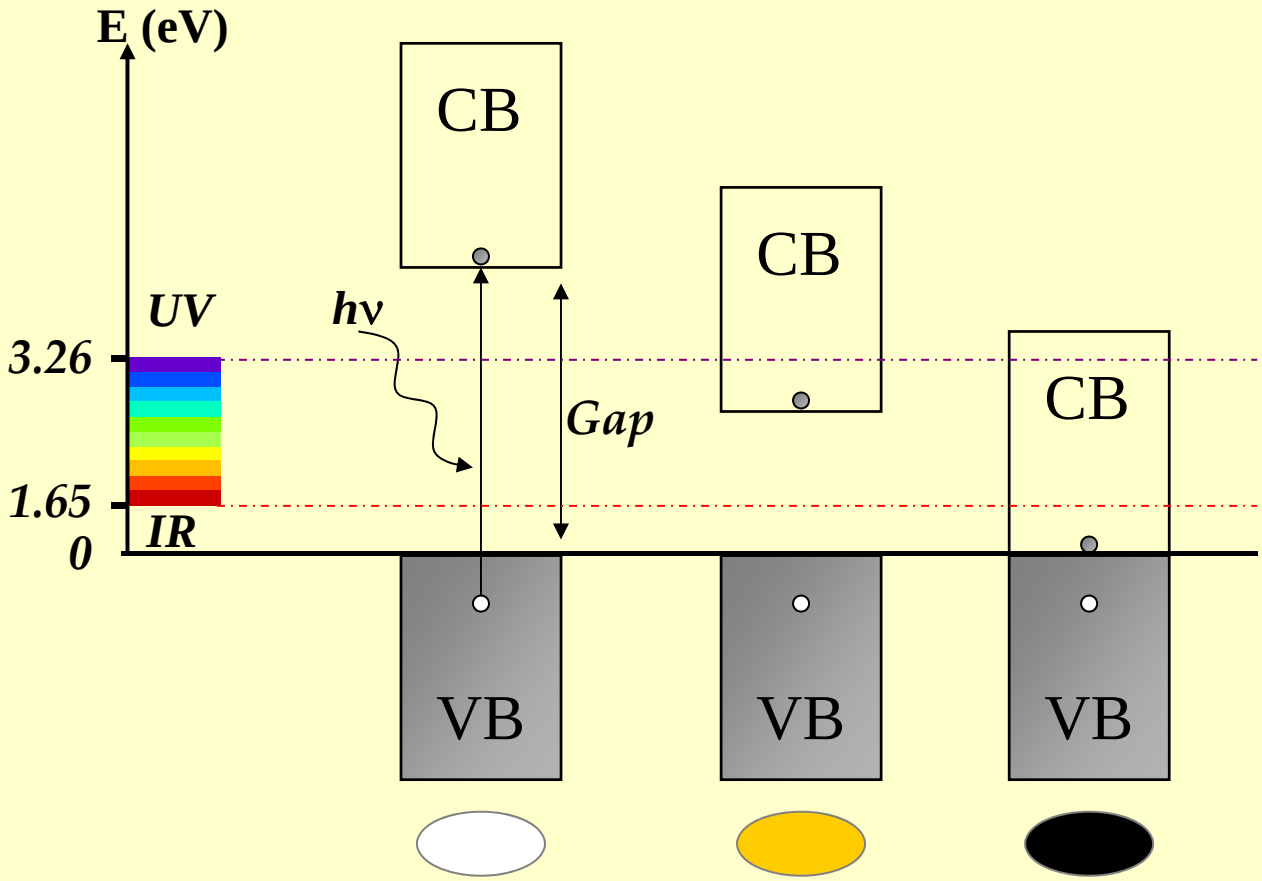
Opaque matter

1 – MULTIPLE FACETS OF COLOURED MATTER

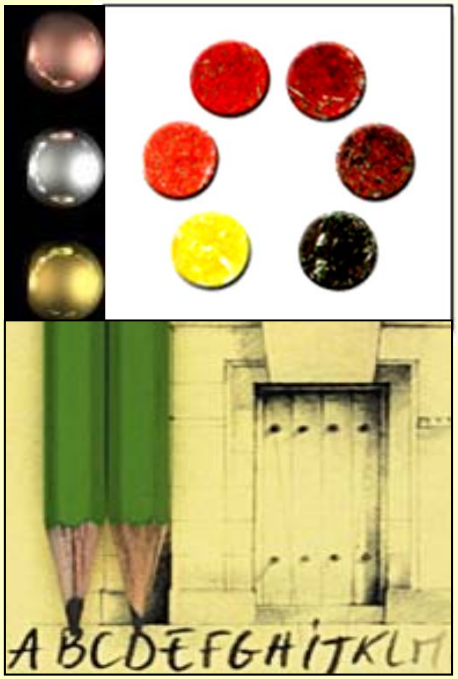
Chemical color → « Inelastic diffusion »

Acceptor electron levels ⇒ Dissipative absorption

From insulator to semiconductor to metal systems



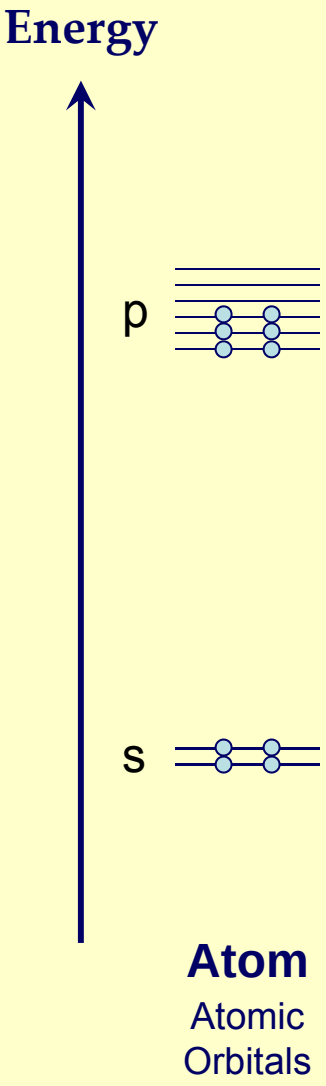
Chemical colors



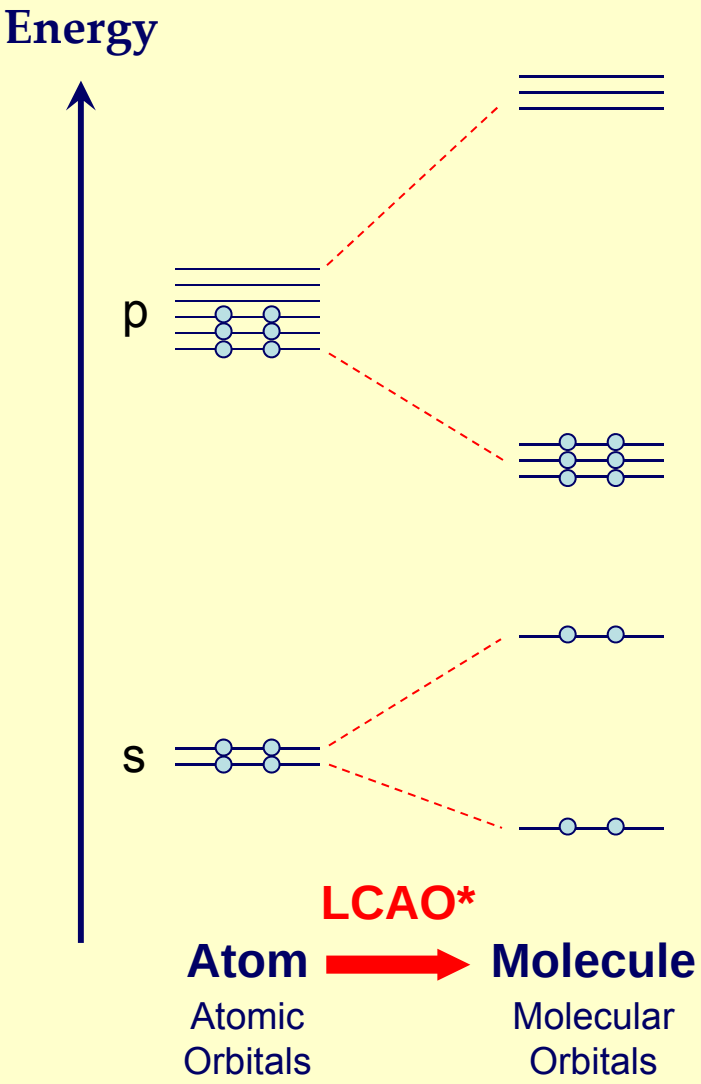
Absorption
Energy dissipation

Opaque Matter

From the atom to the molecule and to the solid



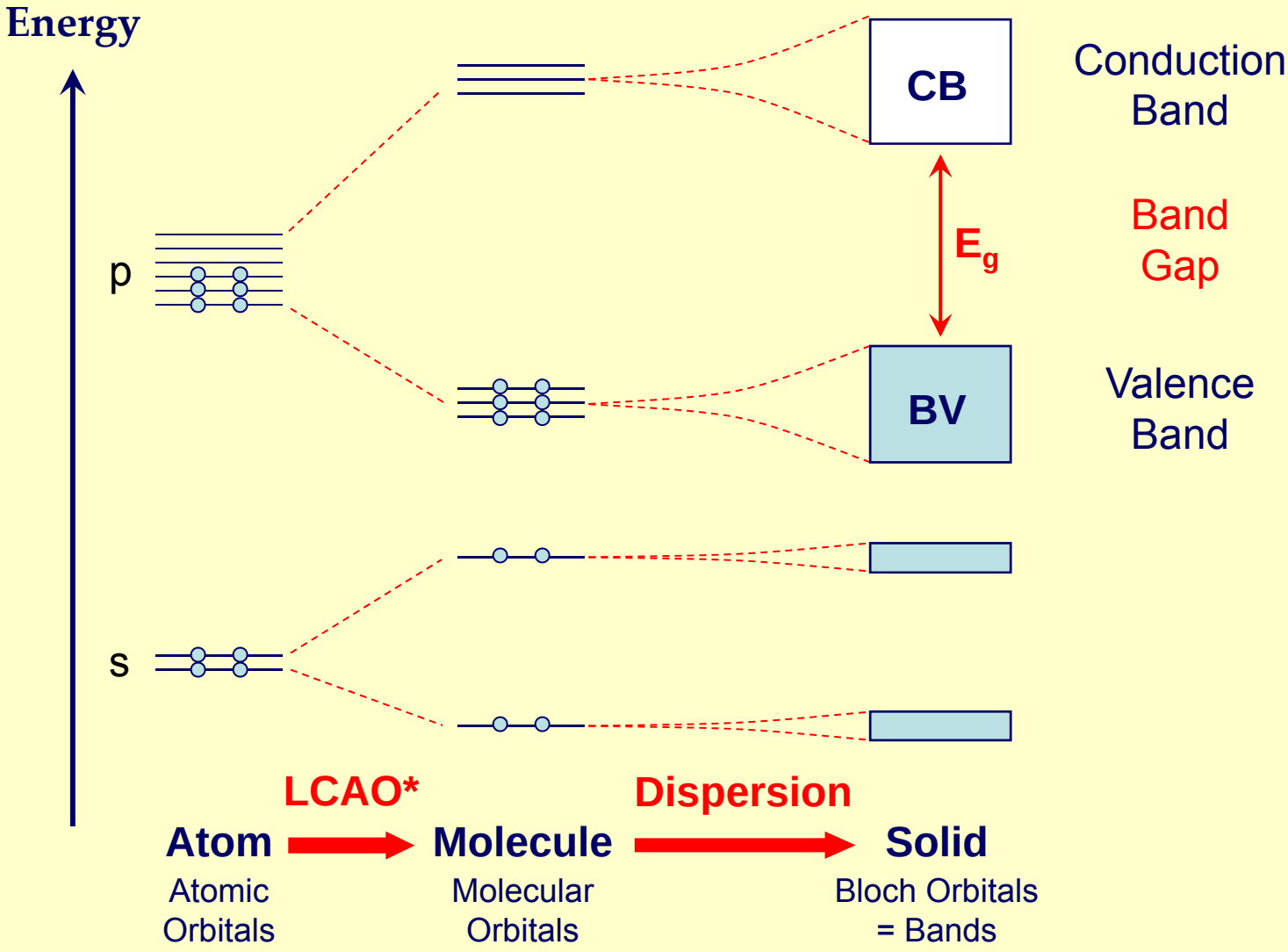
From the atom to the molecule and to the solid



*LCAO : Linear Combination of Atomic Orbitals

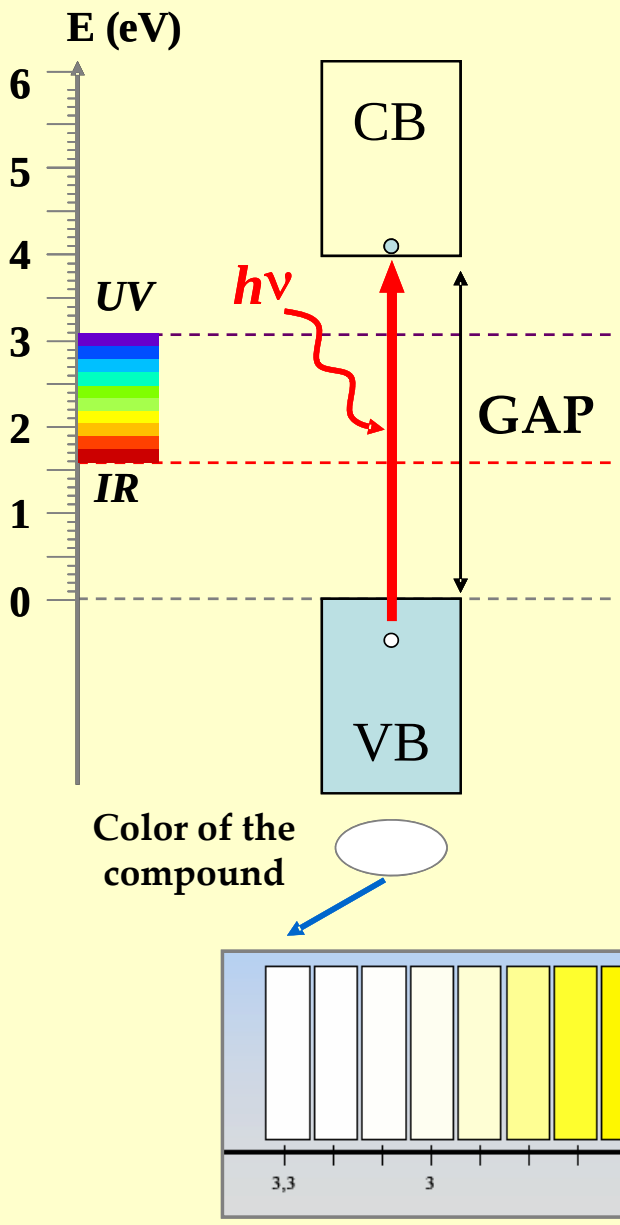
2 – ELECTRONIC STRUCTURE OF A SOLID

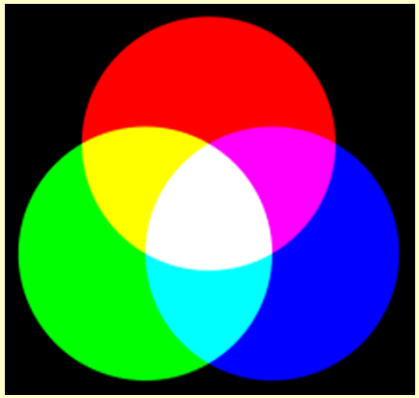
From the atom to the molecule and to the solid



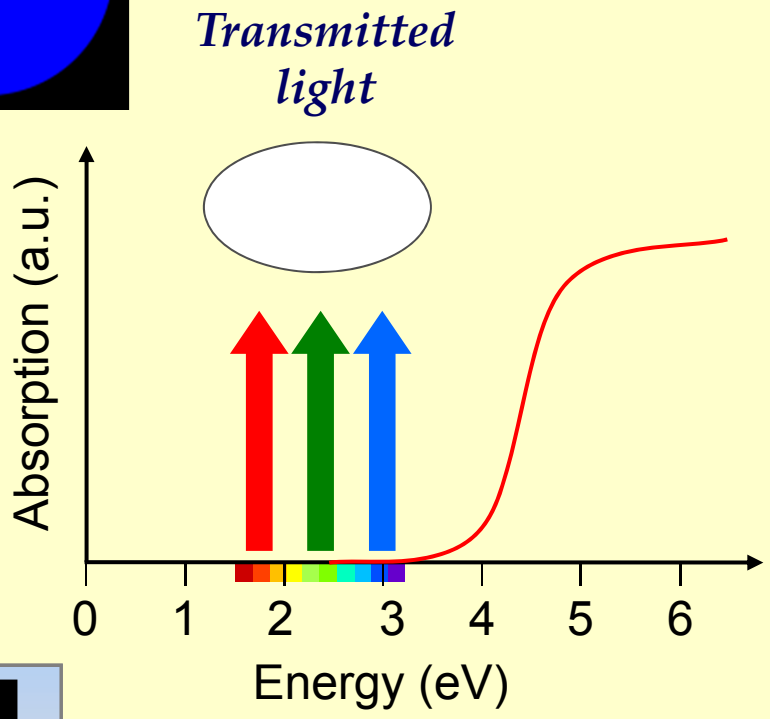
*LCAO : Linear Combination of Atomic Orbitals

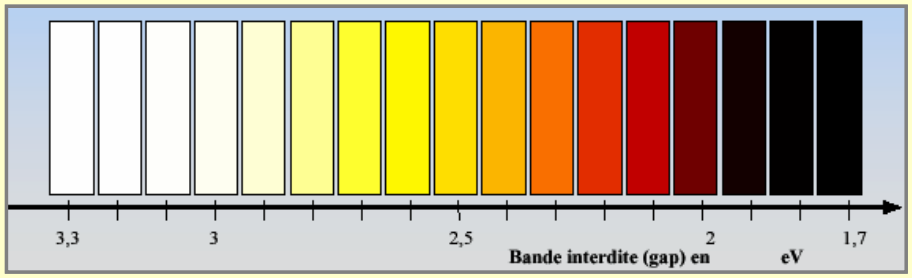
3 – UNDERSTANDING OF COLORS FROM BANDS





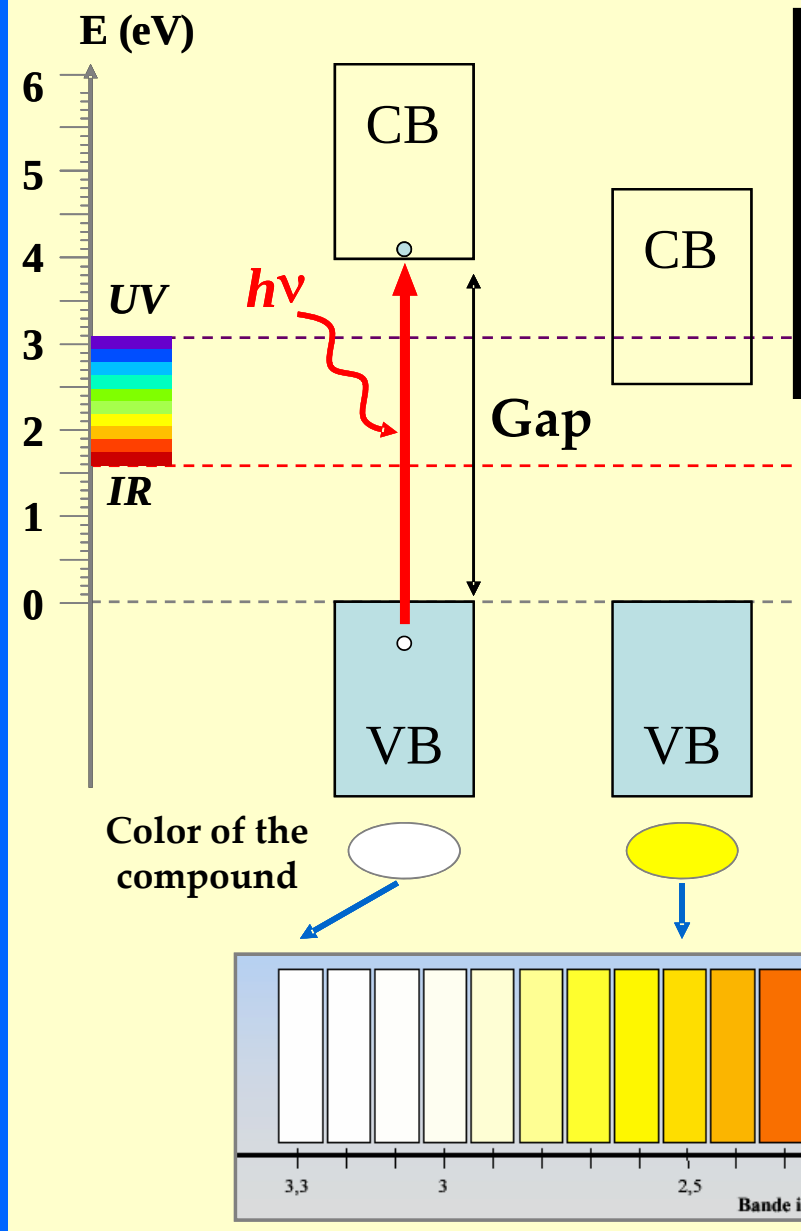
Color of a SC* with 1 gap

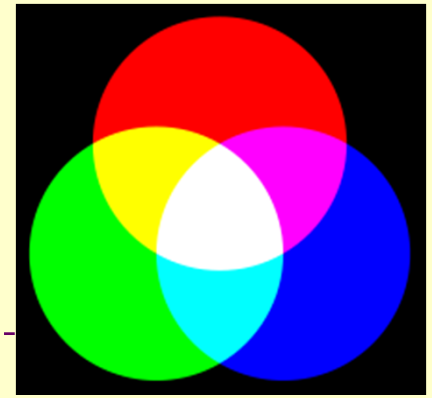




*SC : Semiconductor

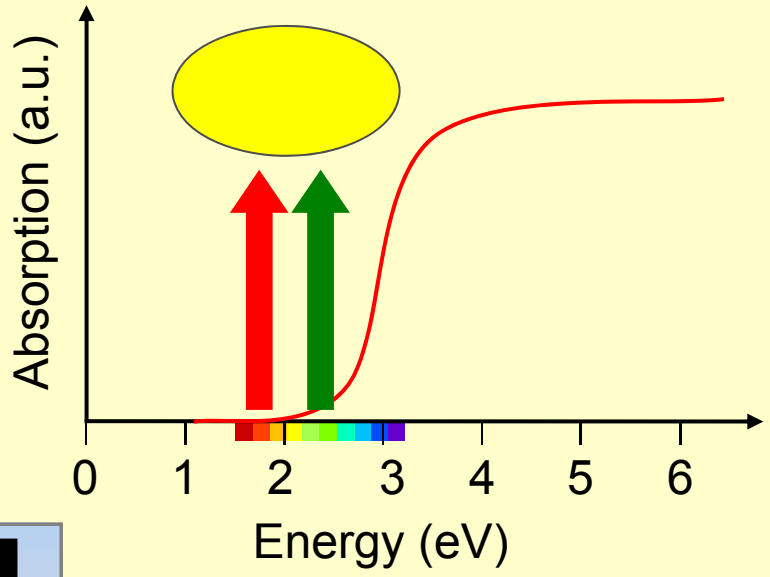
3 – UNDERSTANDING OF COLORS FROM BANDS





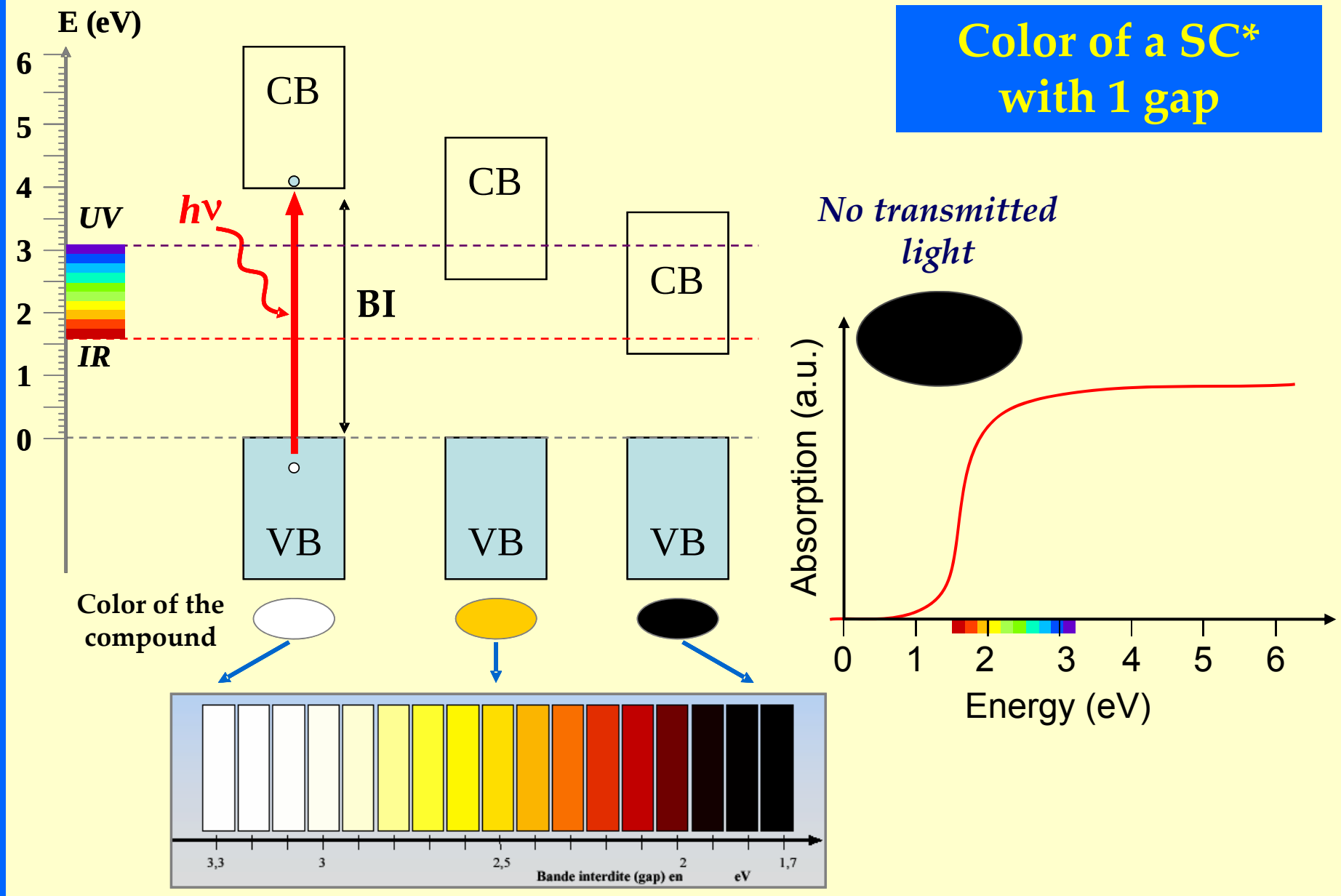
Color of a SC* with 1 gap

Transmitted light



*SC : Semiconductor

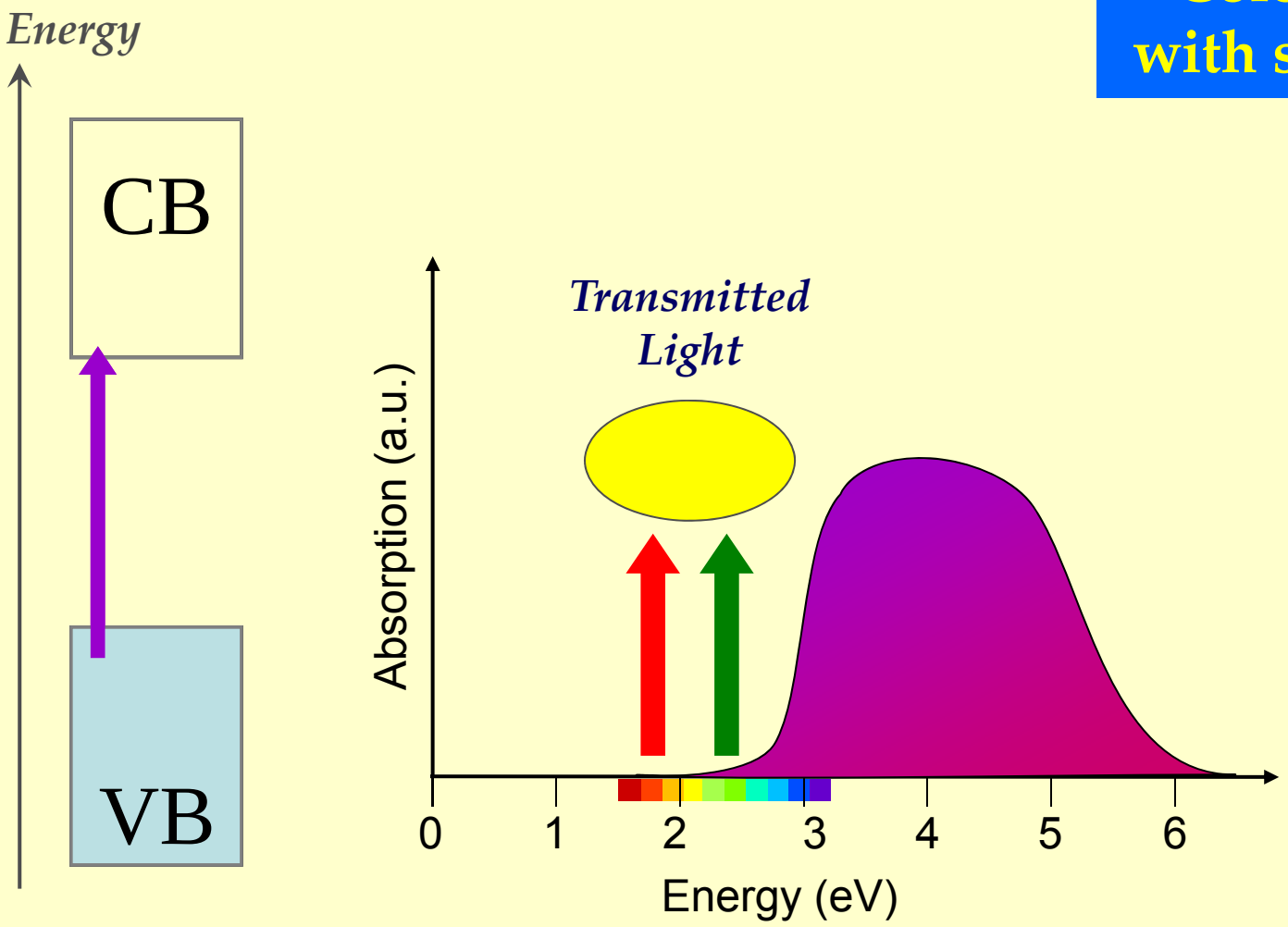
3 – UNDERSTANDING OF COLORS FROM BANDS



*SC : Semiconductor

3 – UNDERSTANDING OF COLORS FROM BANDS

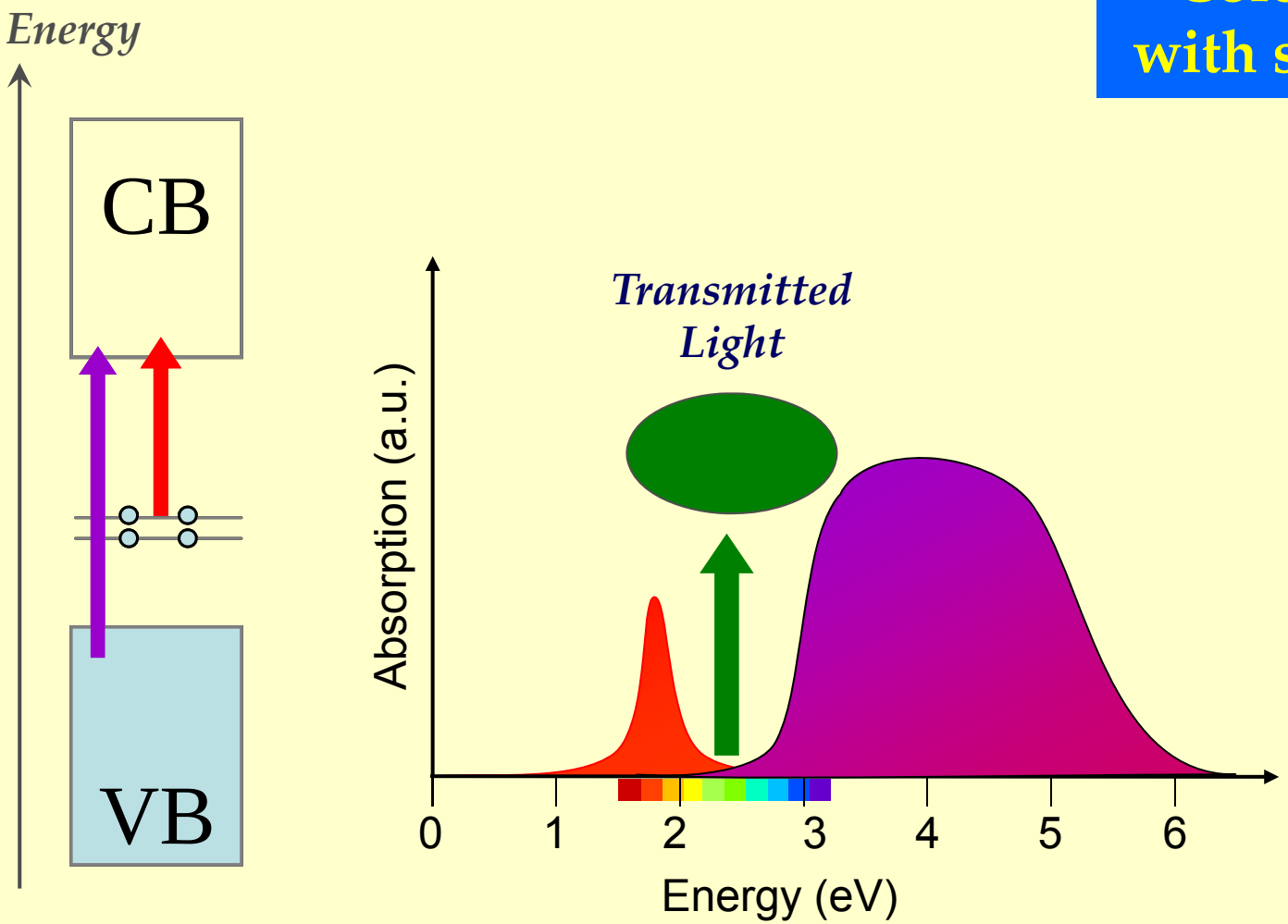
Color of a SC* with several gaps



*SC : Semiconductor

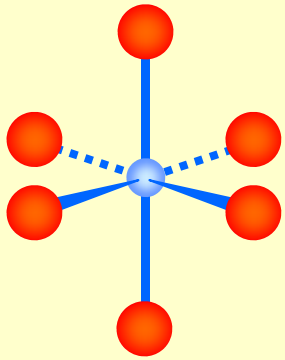
3 – UNDERSTANDING OF COLORS FROM BANDS

Color of a SC* with several gaps

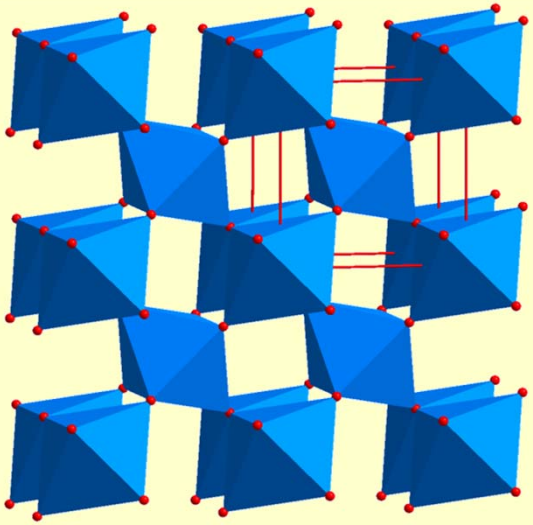


*SC : Semi-conducteur – BI : Bande interdite

3 – UNDERSTANDING OF COLORS FROM BANDS



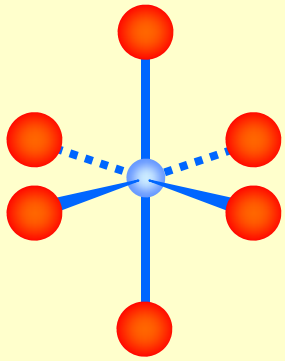
TiO_2



Powder sample of TiO_2 (rutile)

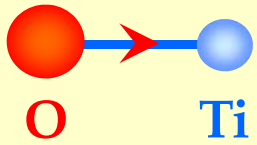
Charge transfer→ color

3 – UNDERSTANDING OF COLORS FROM BANDS

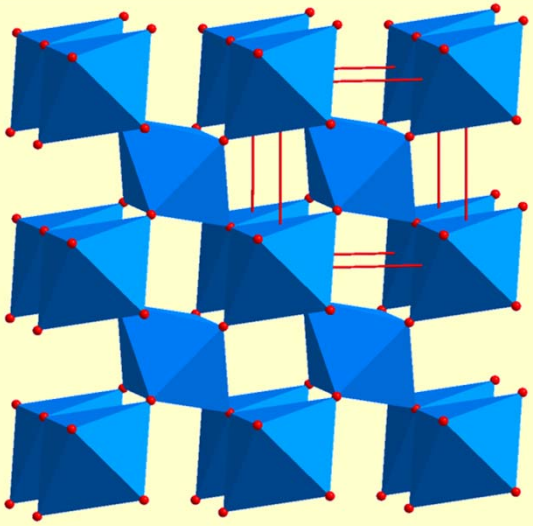


Powder sample of TiO_2 (rutile)

Charge transfer→ color

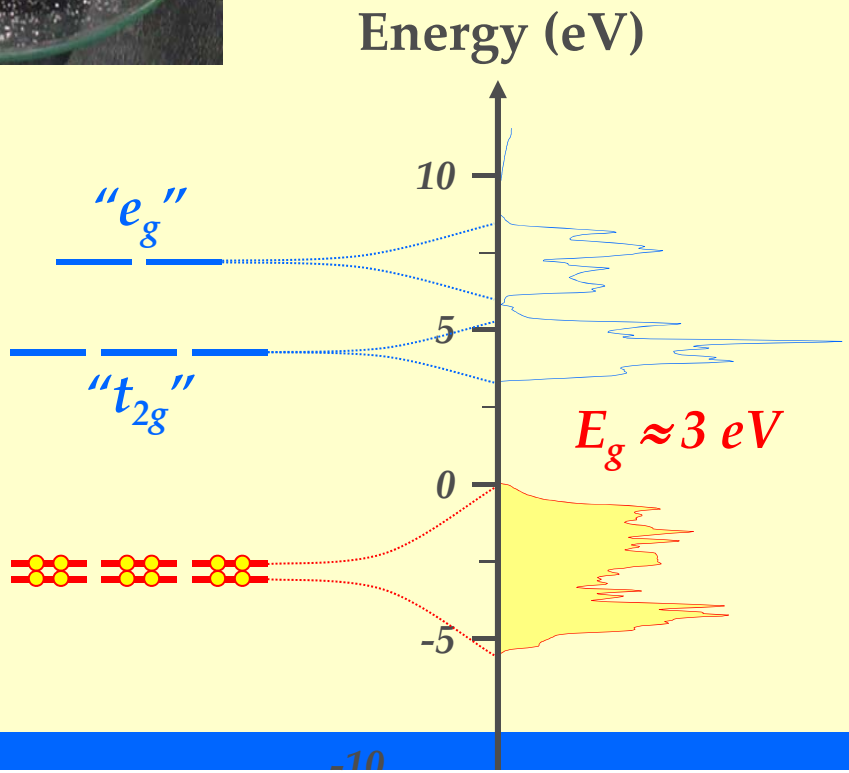


TiO_2



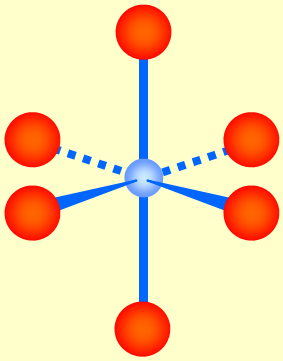
Ti^{4+} ($3d^0$)

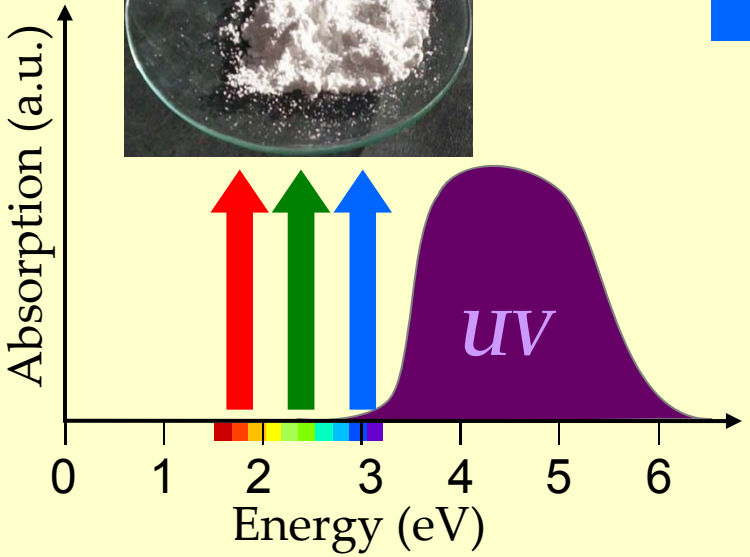
$2 \times O^{2-}$ ($2p^6$)

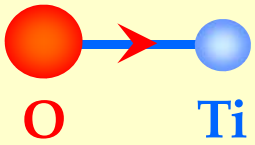


3 – UNDERSTANDING OF COLORS FROM BANDS

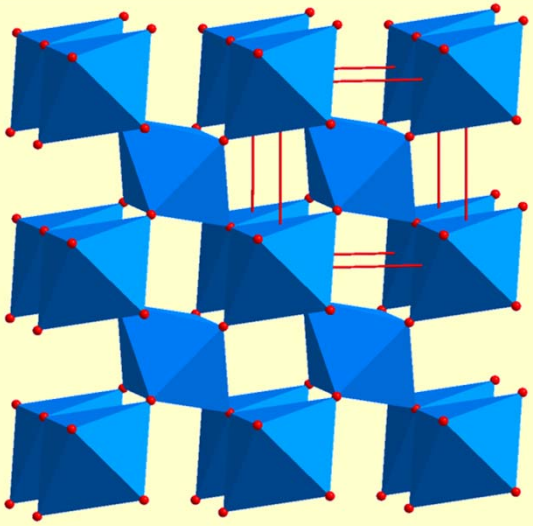
Charge transfer→ color





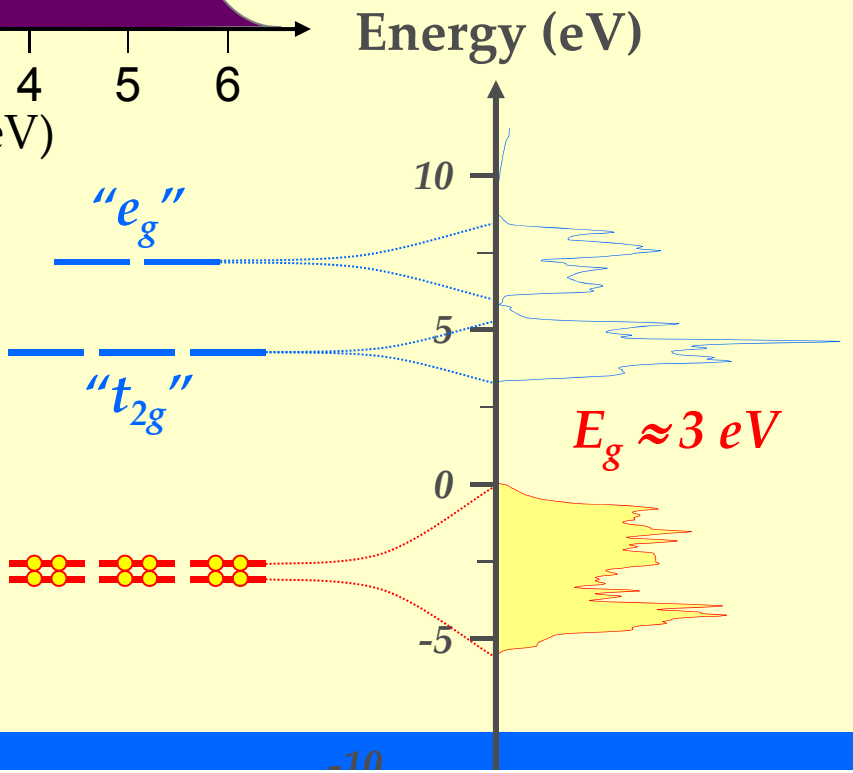


TiO_2



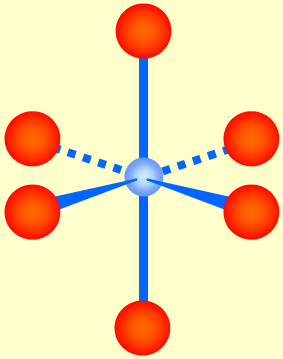
Ti^{4+} ($3d^0$)

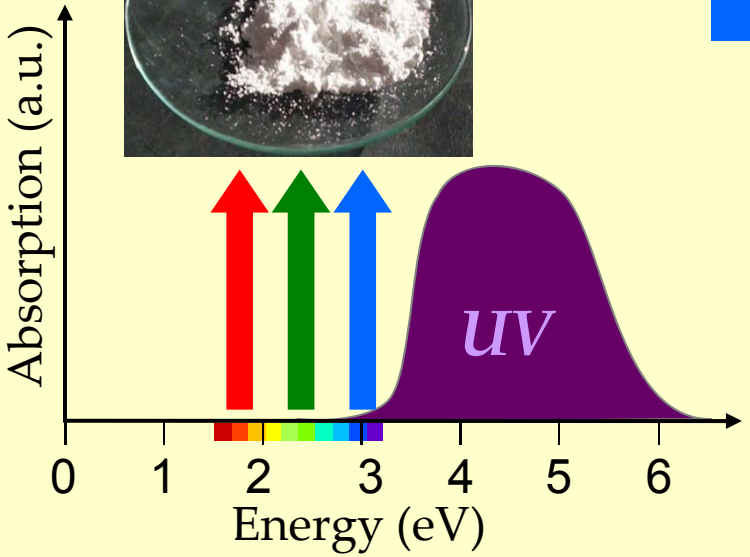
$2 \times O^{2-}$ ($2p^6$)

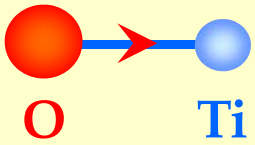


3 – UNDERSTANDING OF COLORS FROM BANDS

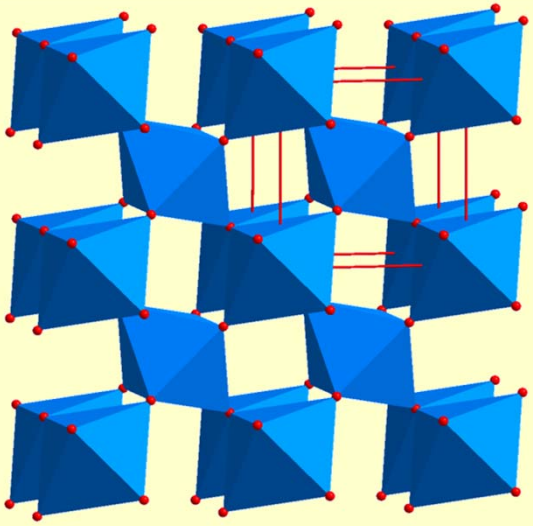
Charge transfer→ color





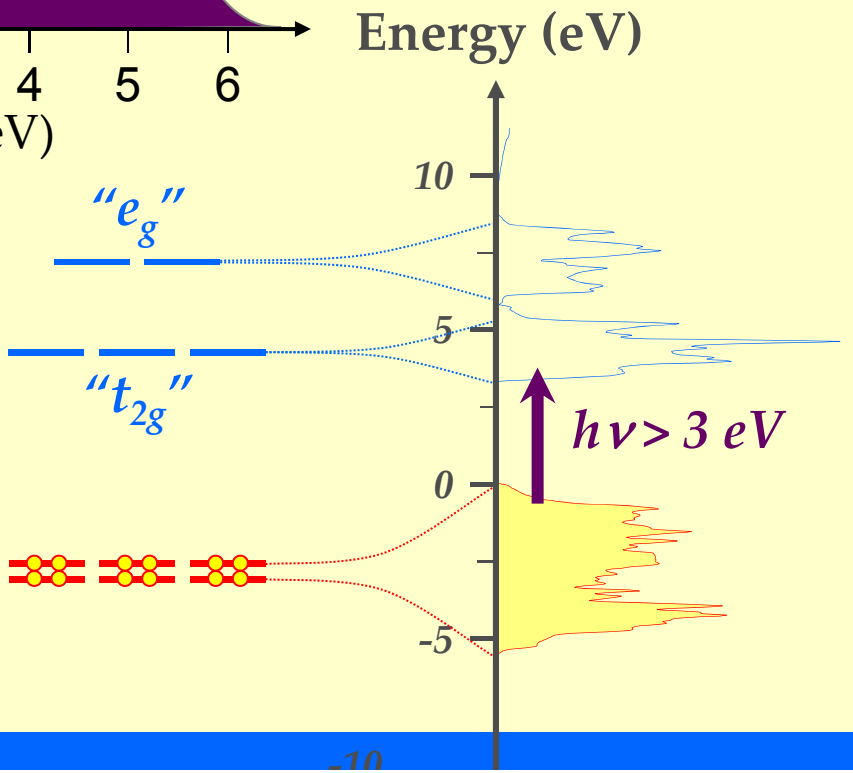


TiO_2

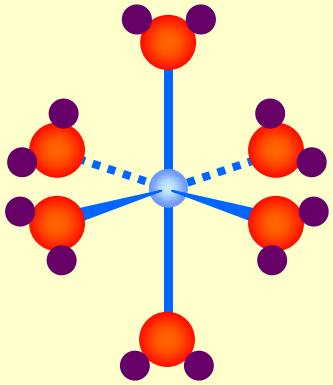


Ti^{4+} ($3d^0$)

$2 \times O^{2-}$ ($2p^6$)



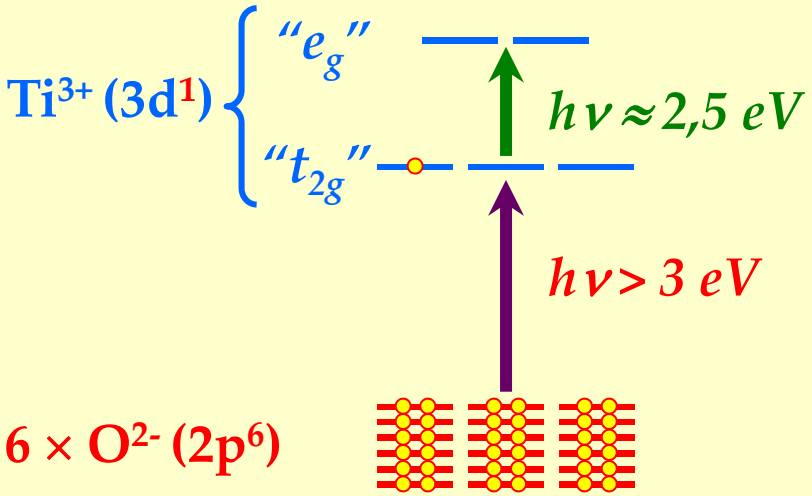
3 – UNDERSTANDING OF COLORS FROM BANDS



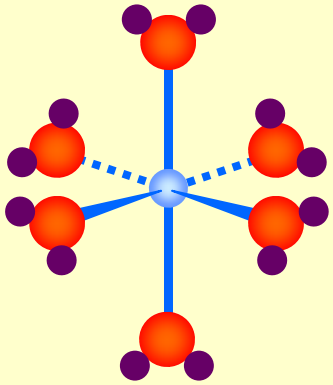
$Ti[H_2O]^{3+}$

$TiCl_3$
in solution

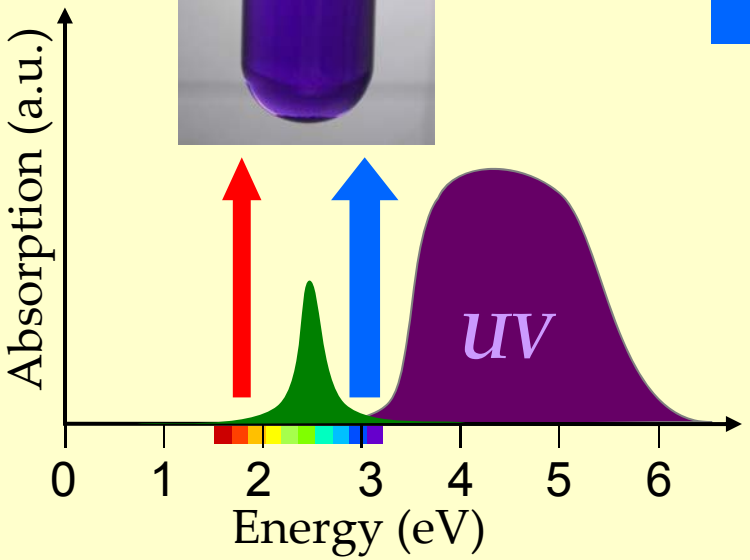
d-d transition → color



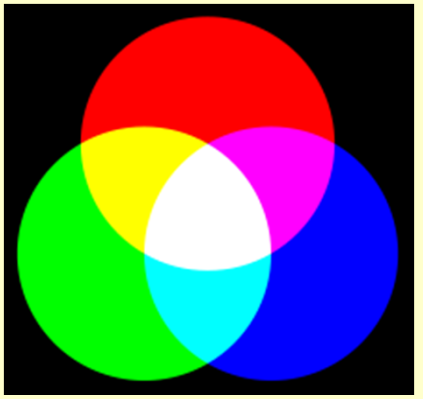
3 – UNDERSTANDING OF COLORS FROM BANDS

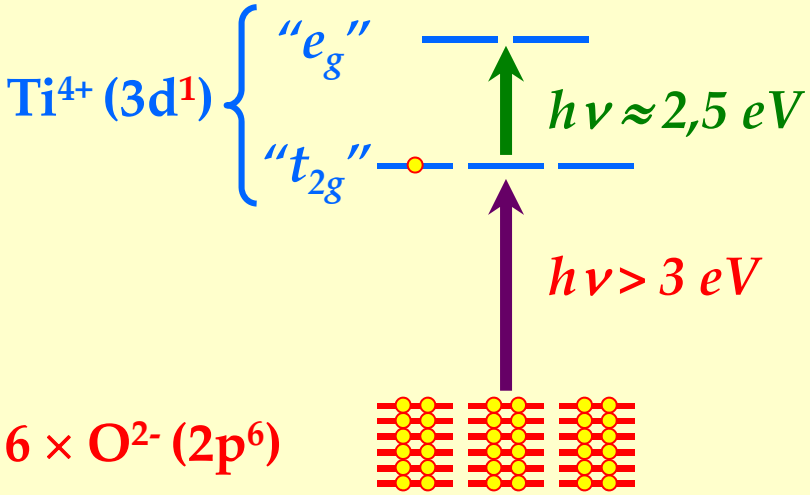


$Ti[H_2O]^{3+}$



d-d transition → color





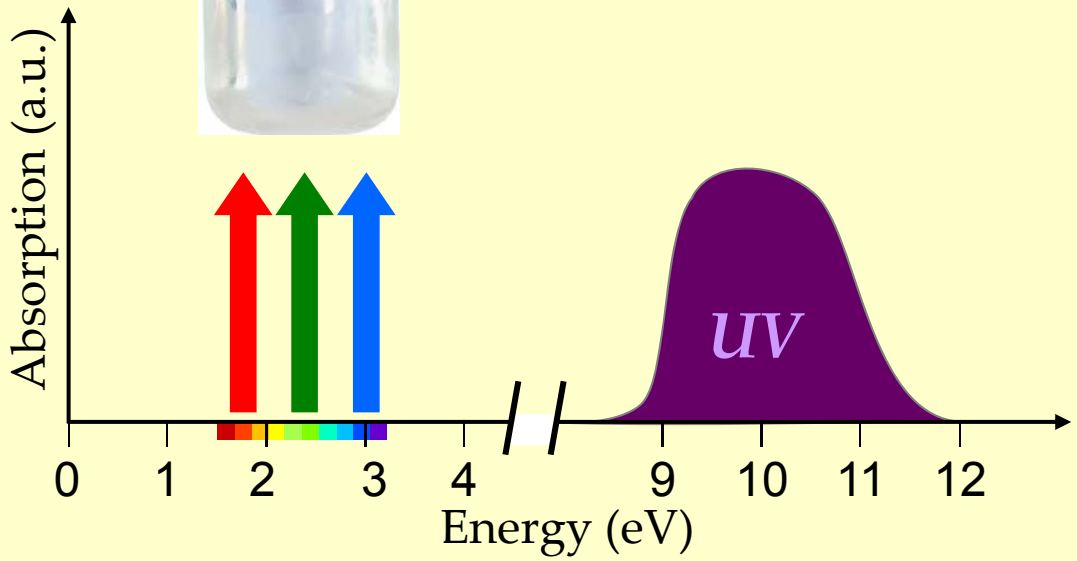
Rq. : For d^n with n > 1

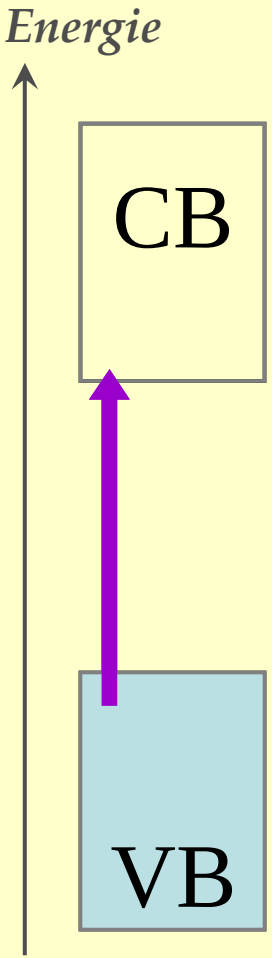
→ Interelectronic correlations must be taken into account

→Tanabe-Sugano diagrams (spectroscopic terms)

3 – UNDERSTANDING OF COLORS FROM BANDS

Alumine corindon (Al_2O_3)



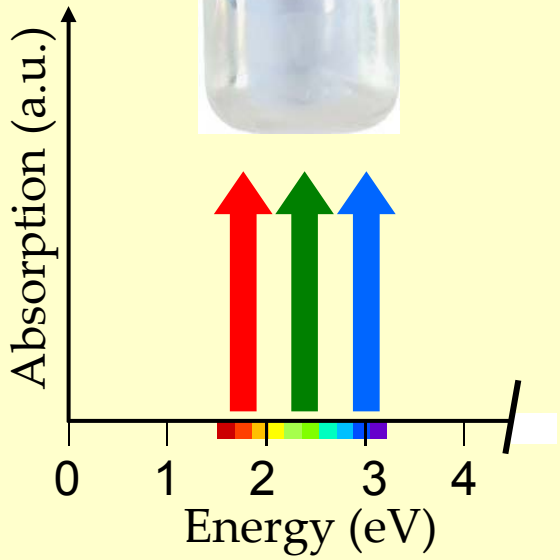


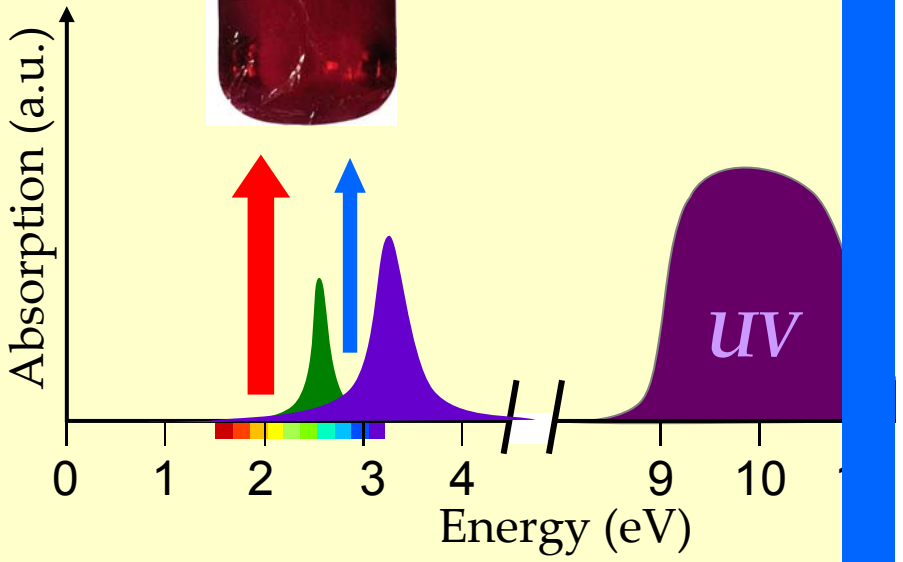
3 – UNDERSTANDING OF COLORS FROM BANDS

Alumine corindon (Al_2O_3)

+ 1% Cr^{3+}

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





3 – UNDERSTANDING OF COLORS FROM BANDS

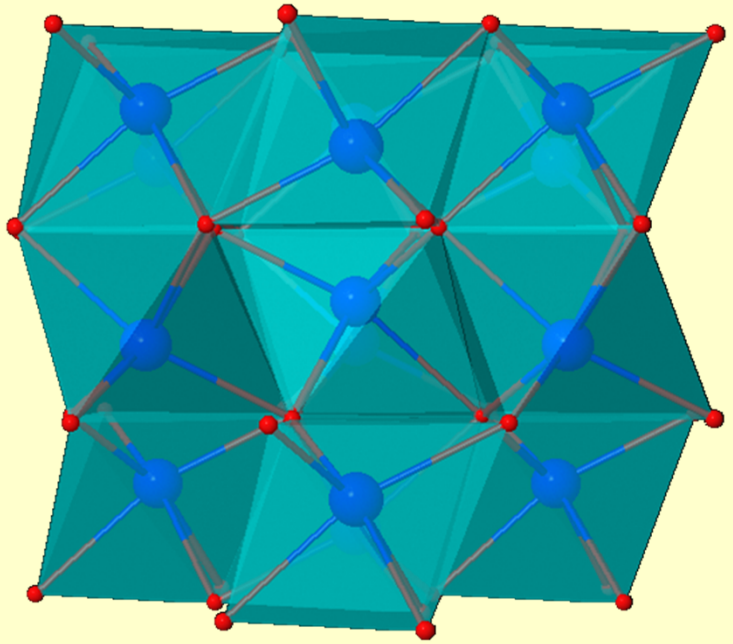
Rubis
(Al_2O_3:1%Cr^{3+})

Impurity (d-d)
→ color

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

→ Interelectronic correlations must be taken into account

→Tanabe-Sugano diagrams (spectroscopic terms)

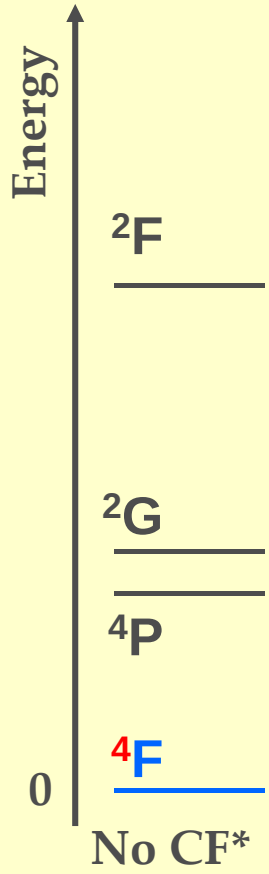


3 – UNDERSTANDING OF COLORS FROM BANDS

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

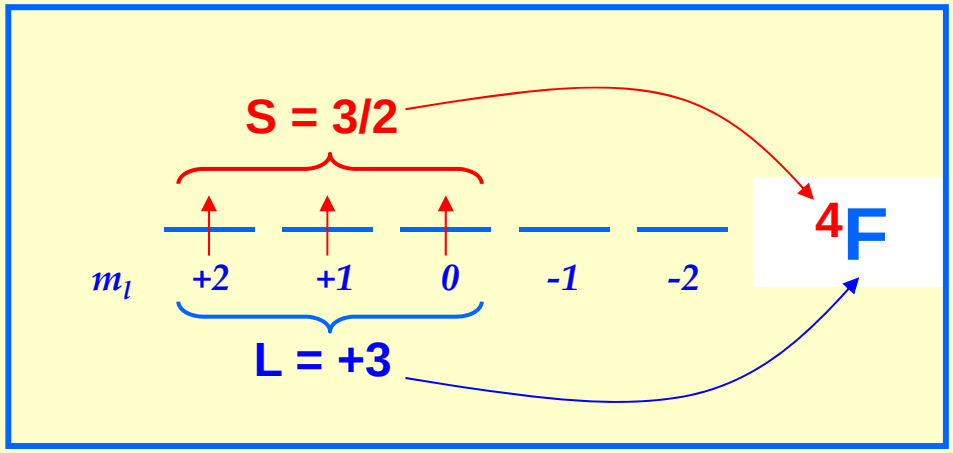
Impurity (d-d) → color

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



Free ion: we define the spectroscopic terms :

Multiplicity of spin → 2S+1X



*CF : Cristal Field

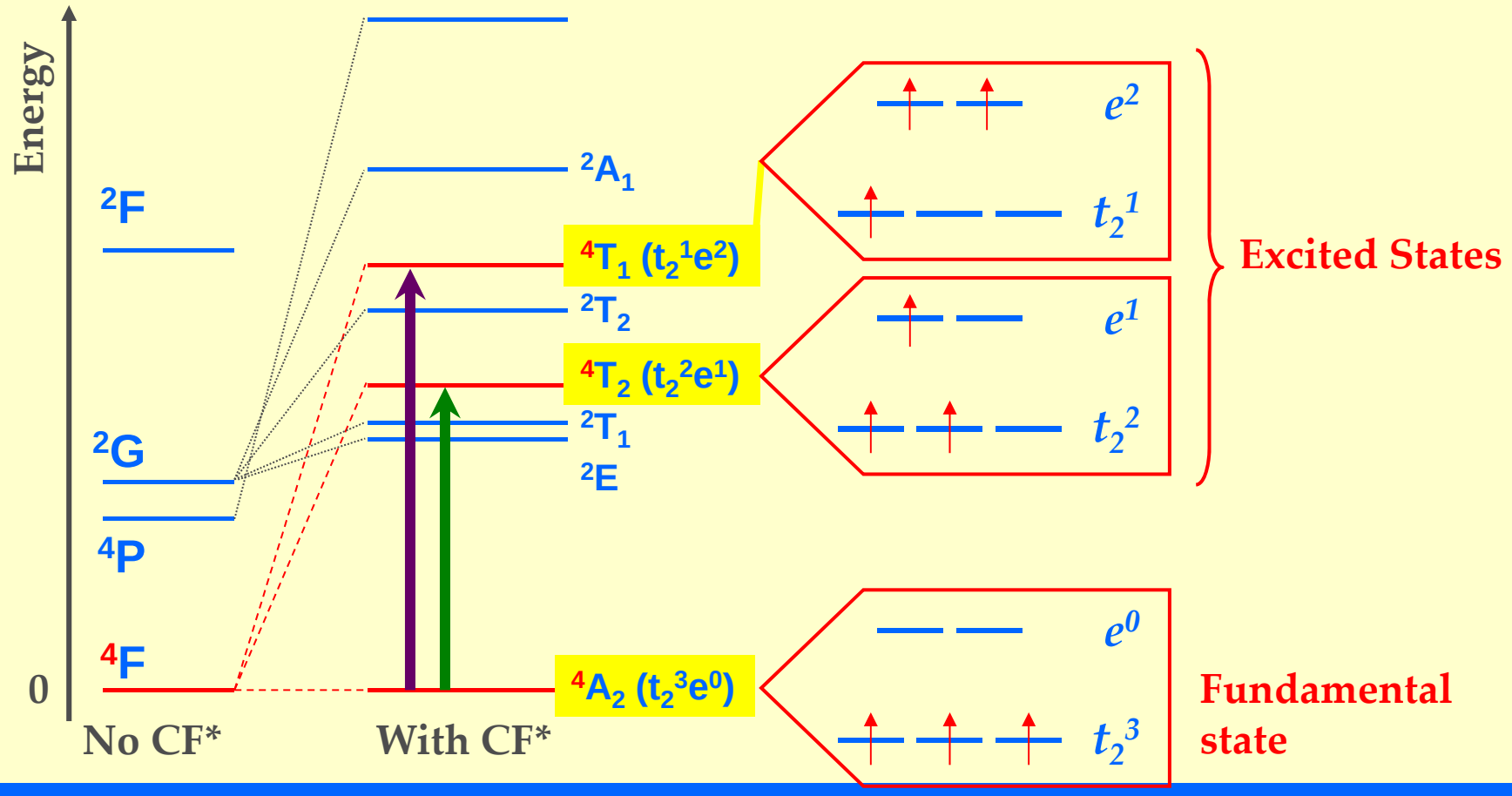
3 – UNDERSTANDING OF COLORS FROM BANDS

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

Impurity (d-d) → color

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

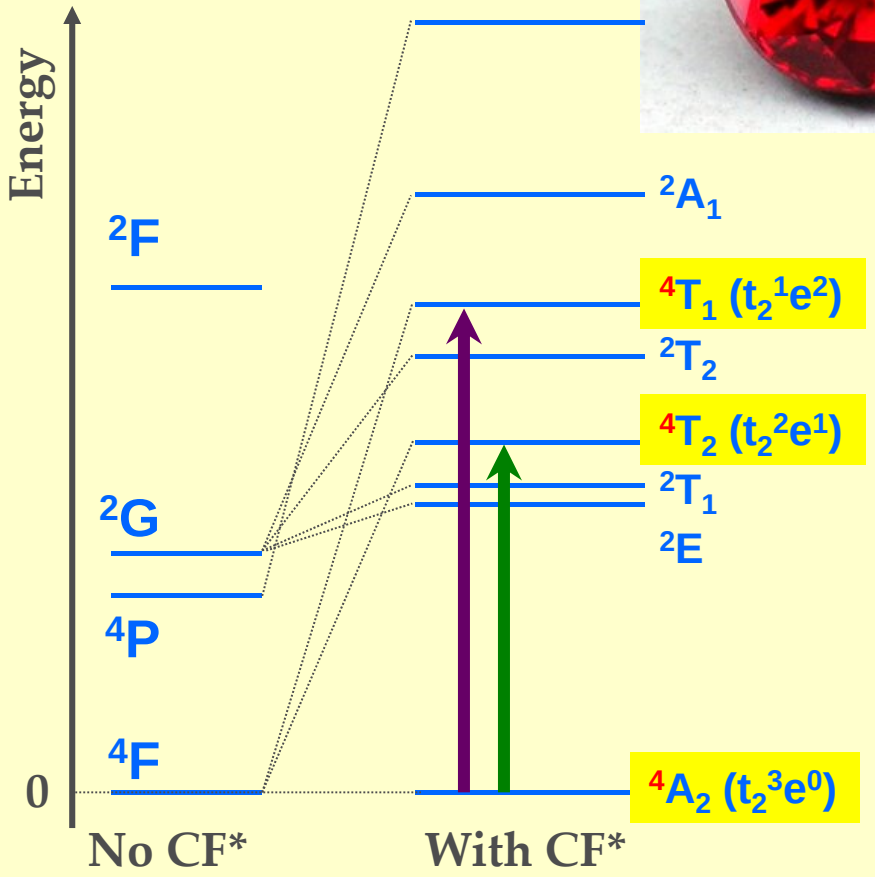
→ Degeneracy lifting due to the octahedral crystal field effect created by the ligands



*CF : Cristal Field

3 – UNDERSTANDING OF COLORS FROM BANDS

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

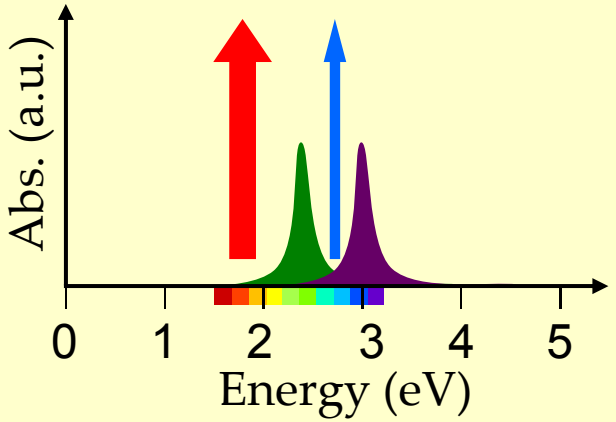


Impurity (d-d) → color

Red color

+

Slightly blue



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

→ Interelectronic correlations must be taken into account

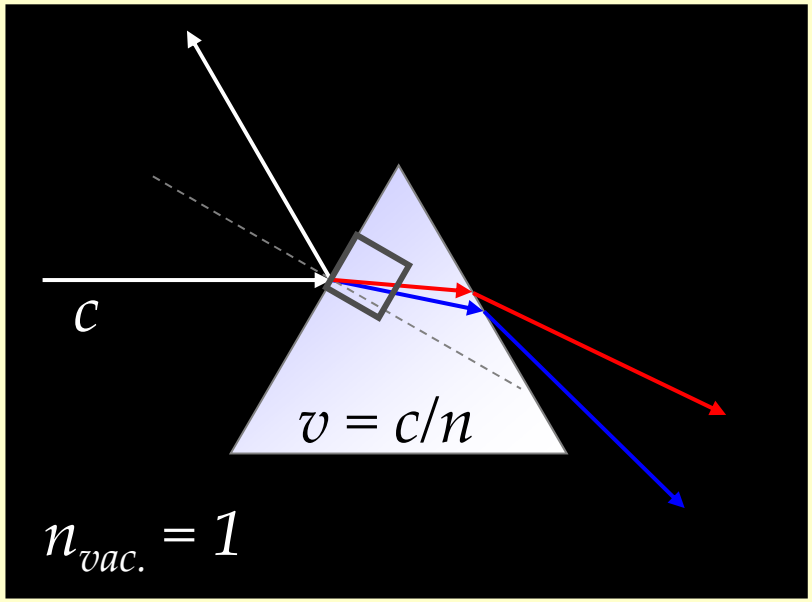
→Tanabe-Sugano diagrams (spectroscopic terms)

*CC : Champ Cristallin

4 – LIGHT-MATTER INTERACTION

Physical color → « Elastic diffusion »

Example of a prism



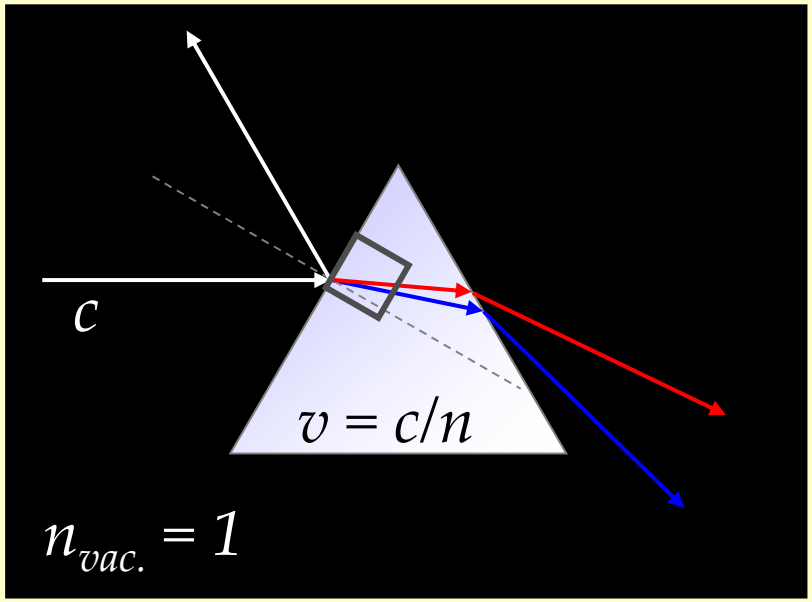
n : index of refraction

Propagation speed is changed

4 – LIGHT-MATTER INTERACTION

Physical color → « Elastic diffusion »

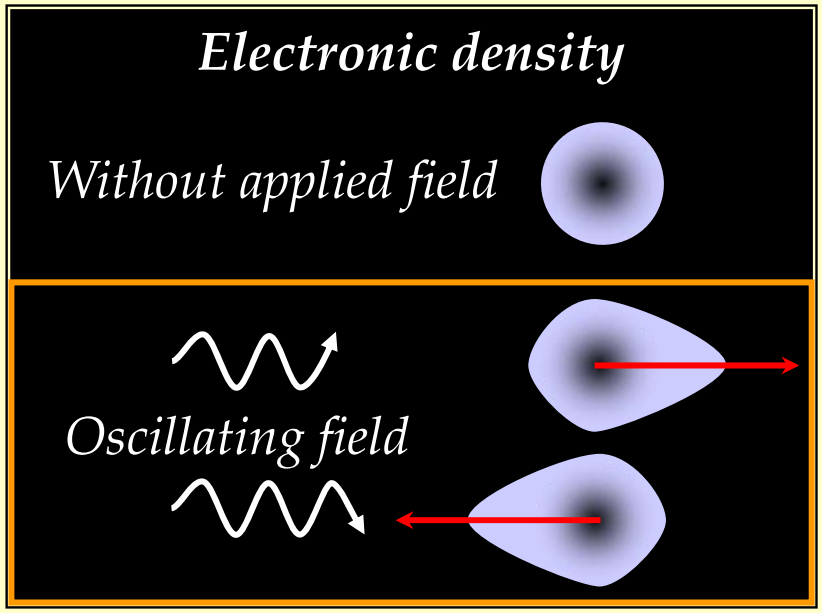
Example of a prism



Dipole moment

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

Elastic diffusion mechanism at the electronic level



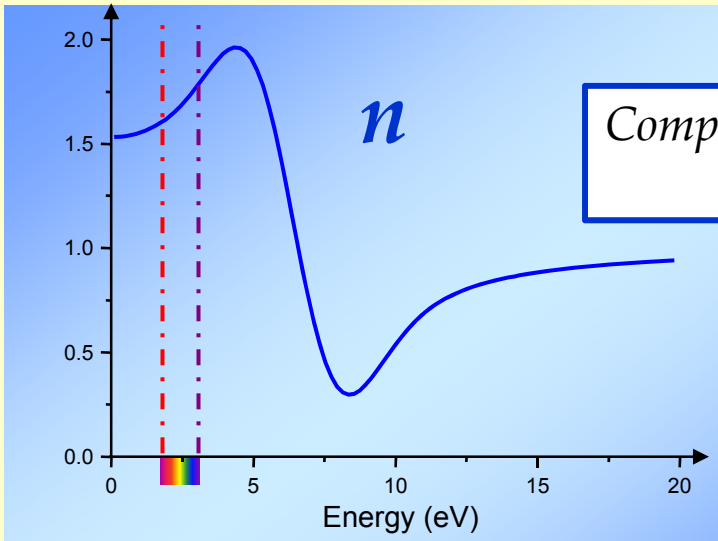
***Oscillating Electric Field** polarize ρ*

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

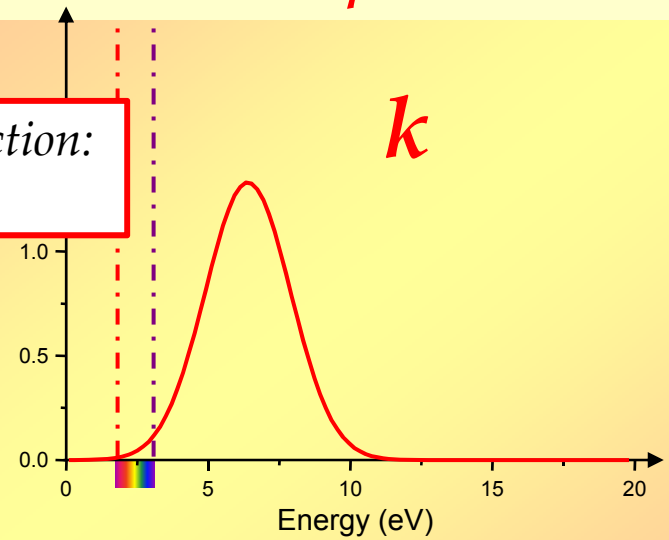
Succession of absorption and emission

4 – LIGHT-MATTER INTERACTION

Diffusion



Absorption



Complex index of refraction:

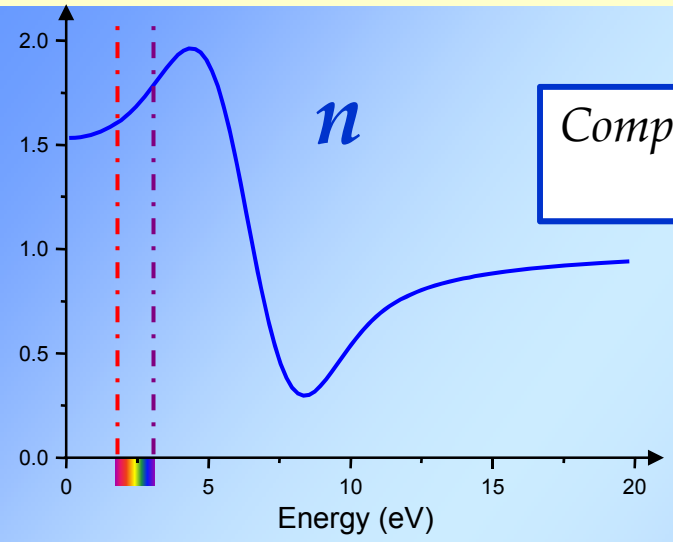
$N = n + i\,k$

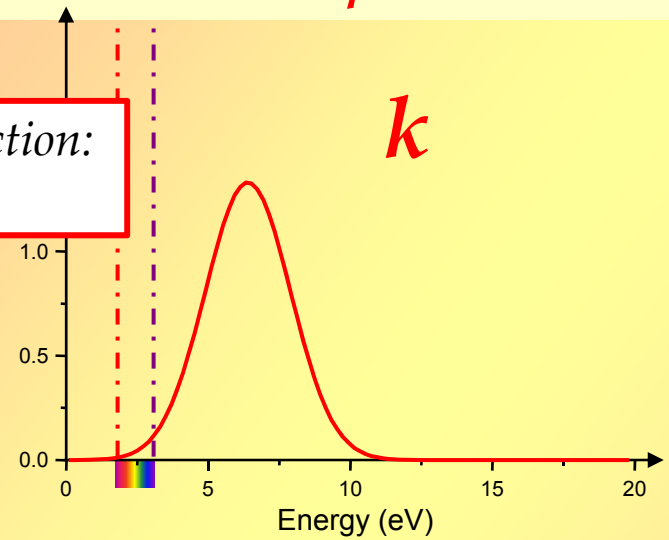
Kramers-Kronig

4 – LIGHT-MATTER INTERACTION

Diffusion

Absorption

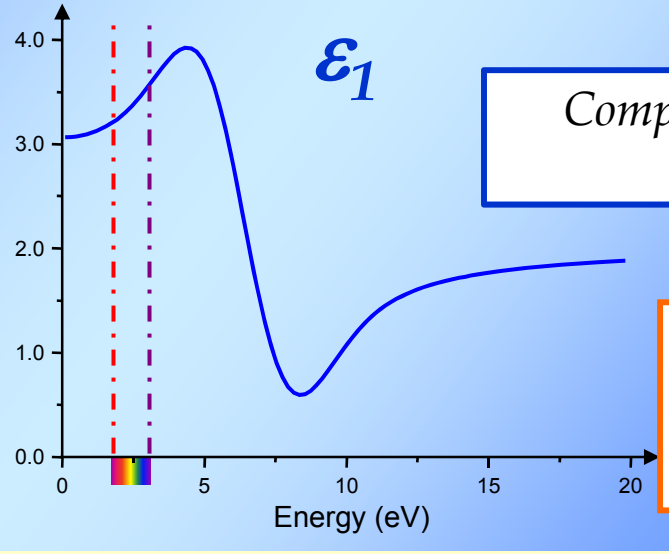


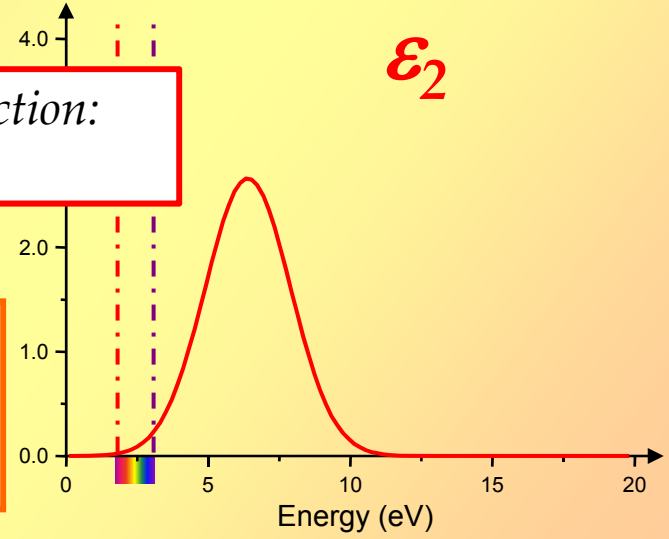


Complex index of refraction:

$N = n + i\,k$

Kramers-Kronig





Complex dielectric function:

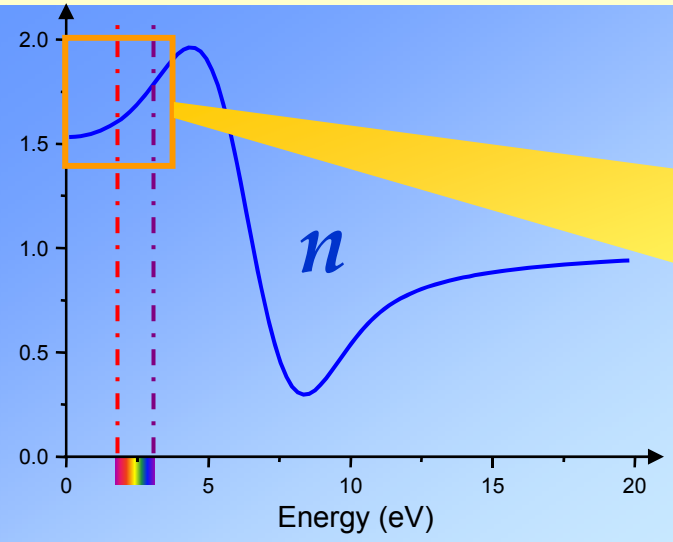
$\varepsilon = \varepsilon_1 + i\,\varepsilon_2$

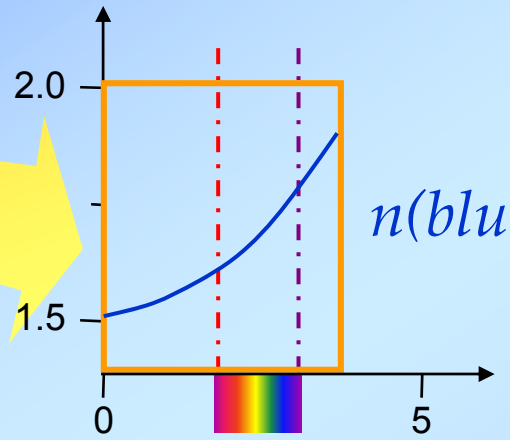
$\varepsilon_1 = n^2 - k^2$

$\varepsilon_2 = 2nk$

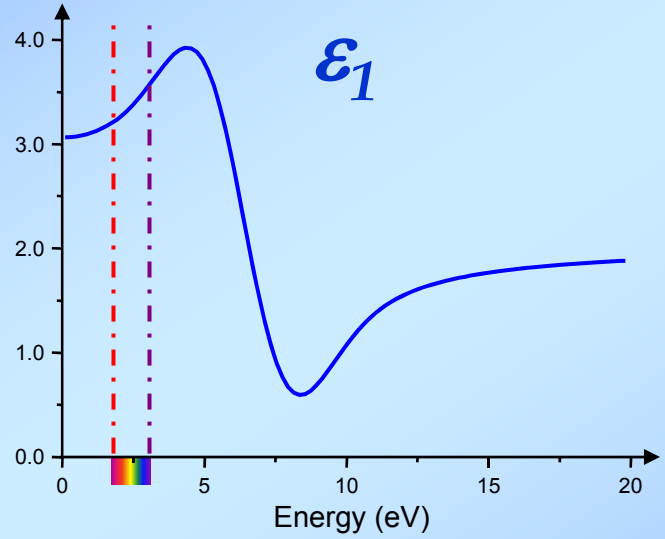
4 – LIGHT-MATTER INTERACTION

Diffusion in the case of a prism

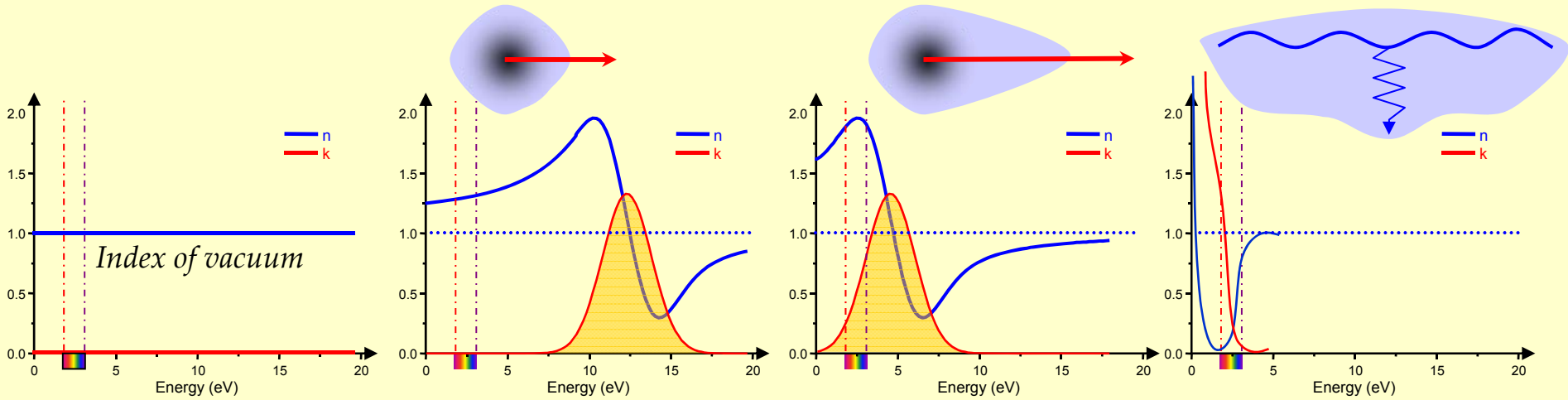




$n(blue) > n(red)$



4 – LIGHT-MATTER INTERACTION



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

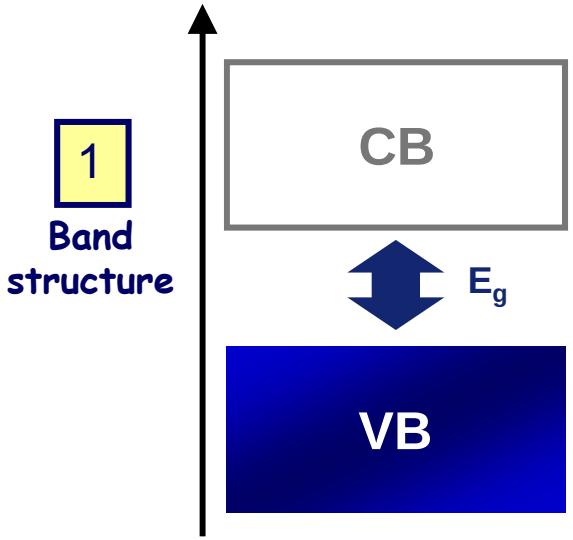
Electron *more and more free*

Absorption band is displaced towards low energies

Directly related to the oscillator strength

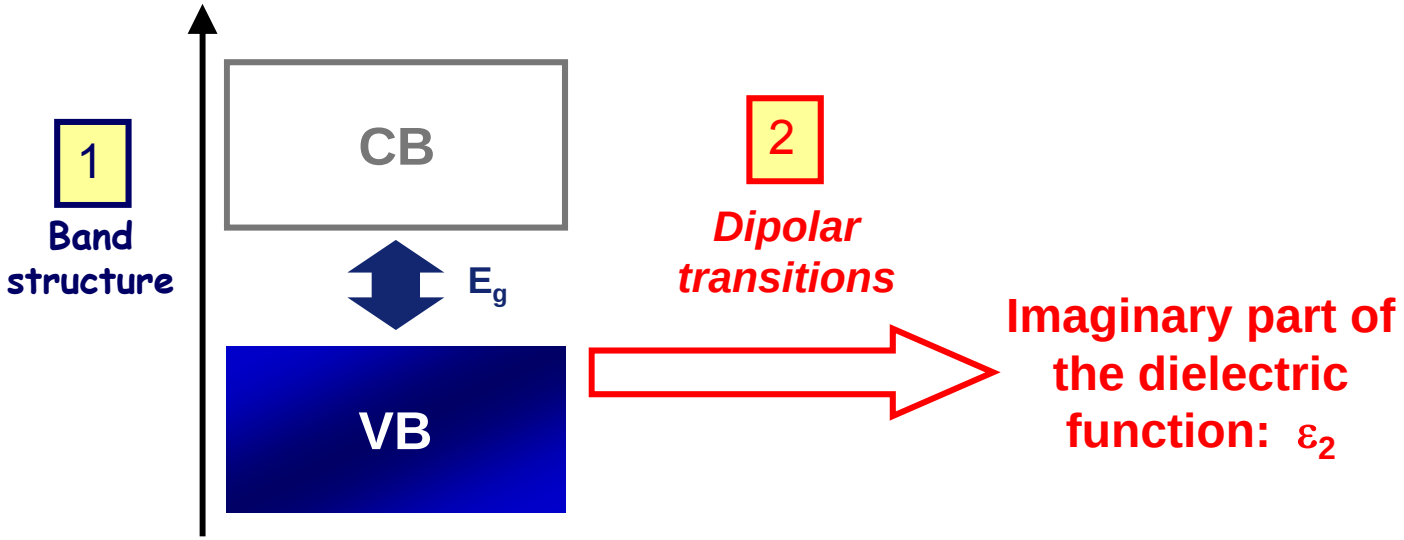
5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:



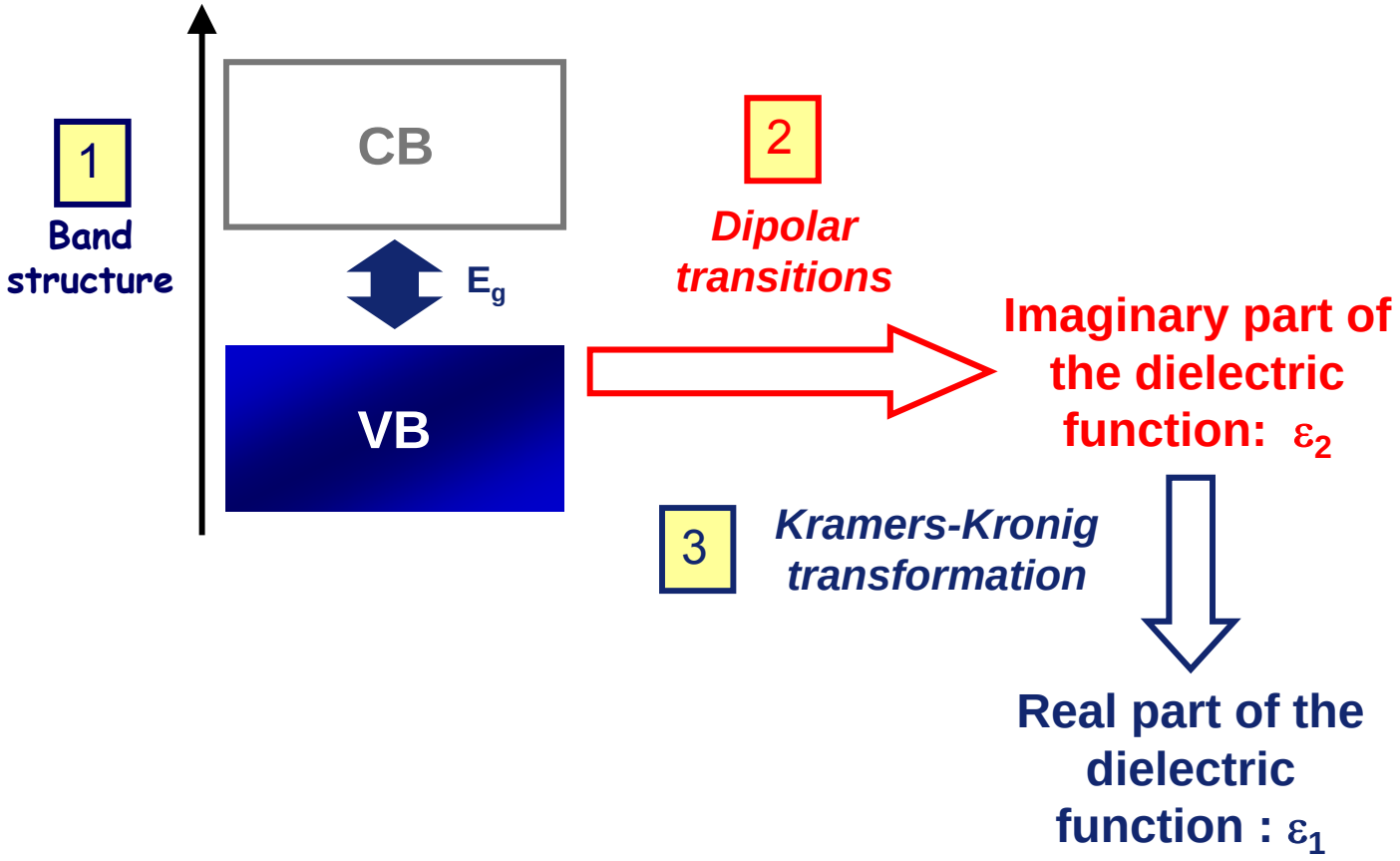
5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:



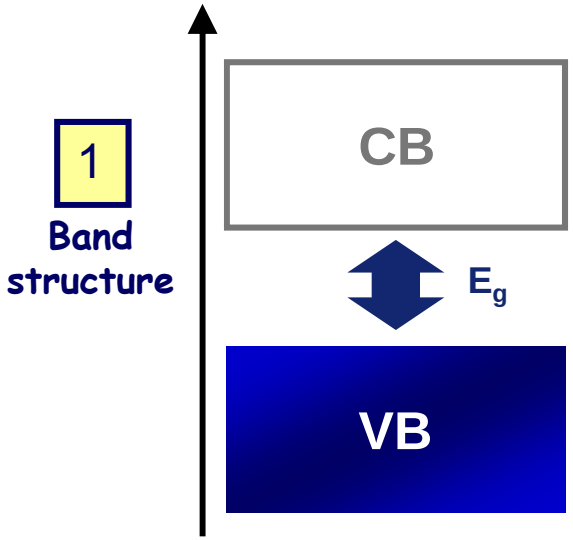
5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:



5 – OPTICAL PROPERTIES: WHICH TREATMENT?

The different steps to calculate the optical properties:



2

Dipolar transitions

Imaginary part of the dielectric function: ε_2

3 *Kramers-Krönig transformation*

Real part of the dielectric function : ε_1

4

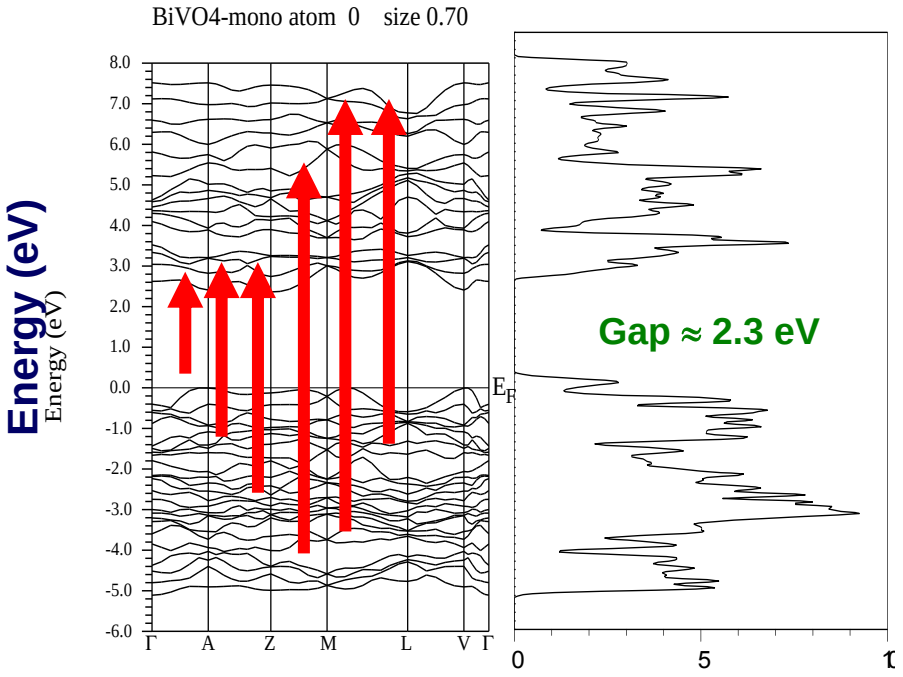
Determination of n = f(E) & k = f(E)

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

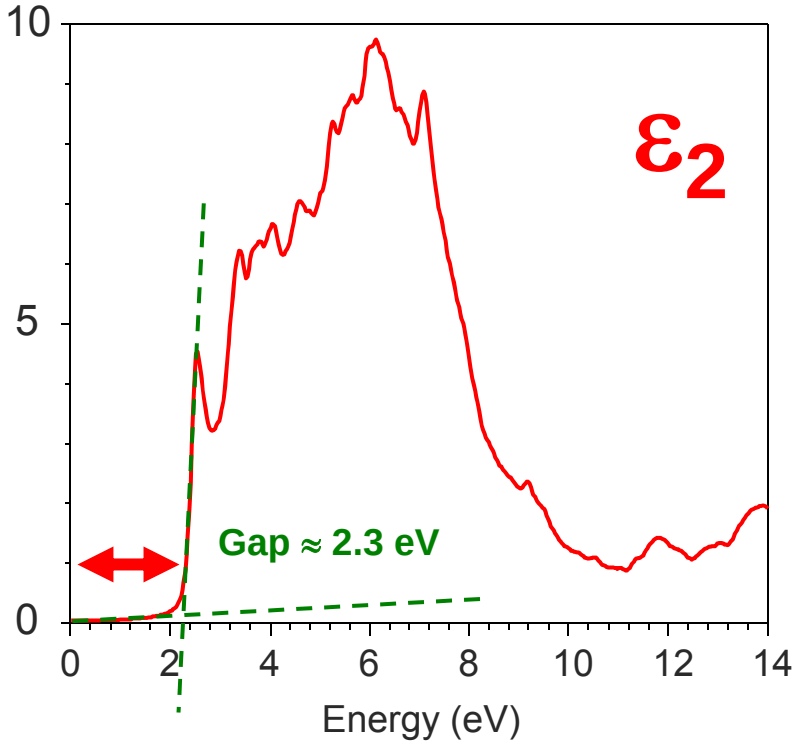
$$\varepsilon_2 = 2nk$$

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

Example of $BiVO_4$



Band structure **DOS**

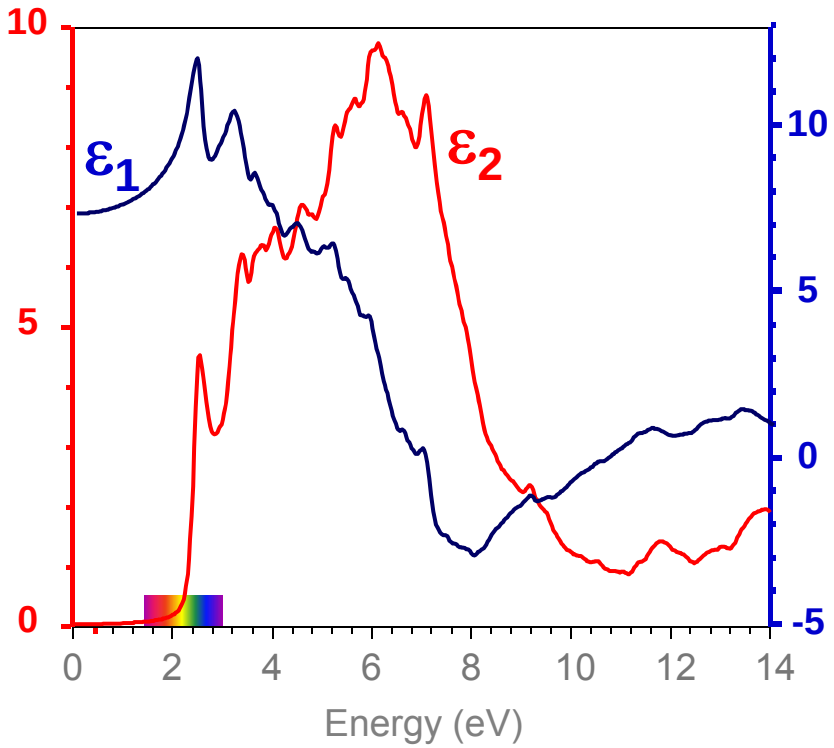


1 **Band structure calculation**

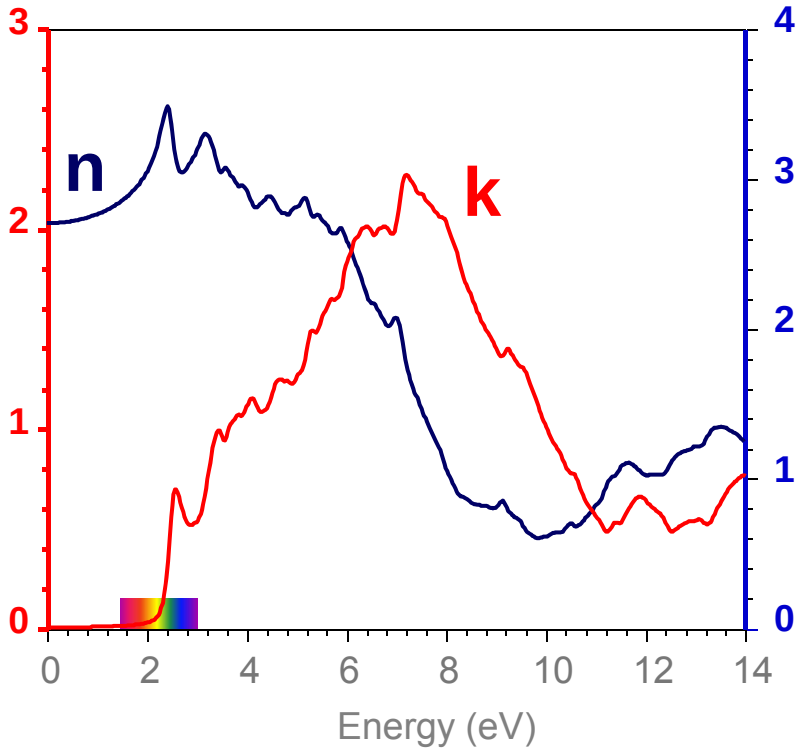
2 **Determination of ε_2**

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

Example of $BiVO_4$



3 **Determination of ε_1**

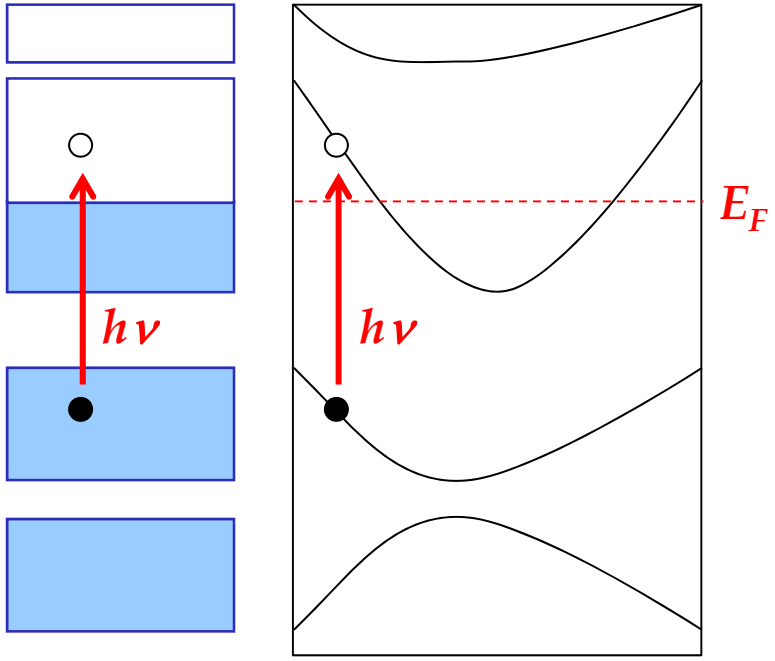


4 ***Determination of n = f(E) & k = f(E)***

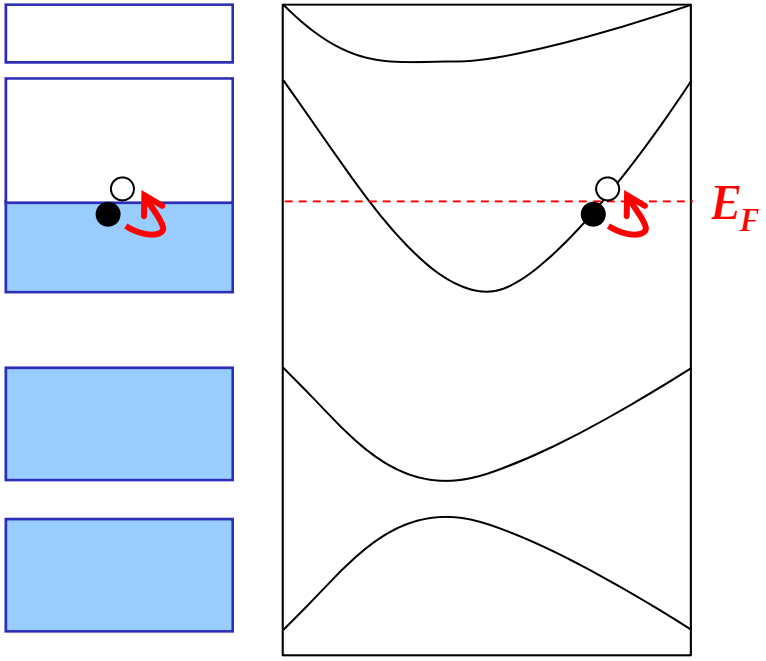
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

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)



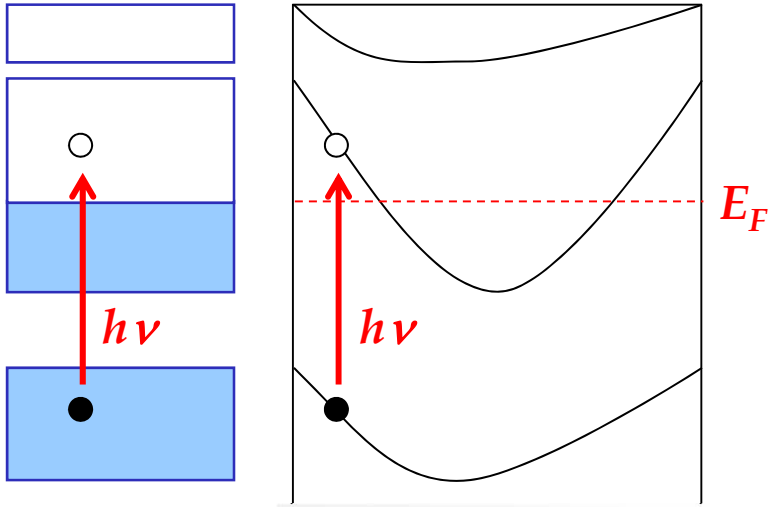
→ Dielectric tensor / Optical conductivity / Refractive index / Reflectivity / Absorption coefficient / Loss function (EELS)

**IPA: Independant Particle Approximation*

5 – 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*)*



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

joint density of states

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

transition probability

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

**IPA: Independant Particle Approximation*

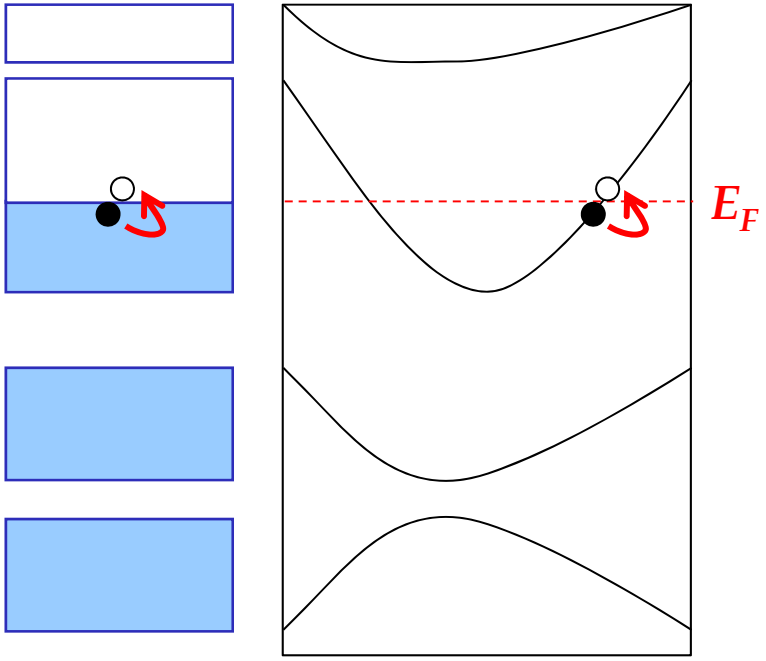
5 – INTERPRETATION: Intraband transitions (for metals)

intraband: Drude model,
(ω_p: plasma frequency)

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

Plasma frequency: (longitudinal oscillations of the electron gas)

Intraband contributions (using a Drude-like term)



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

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

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

- 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

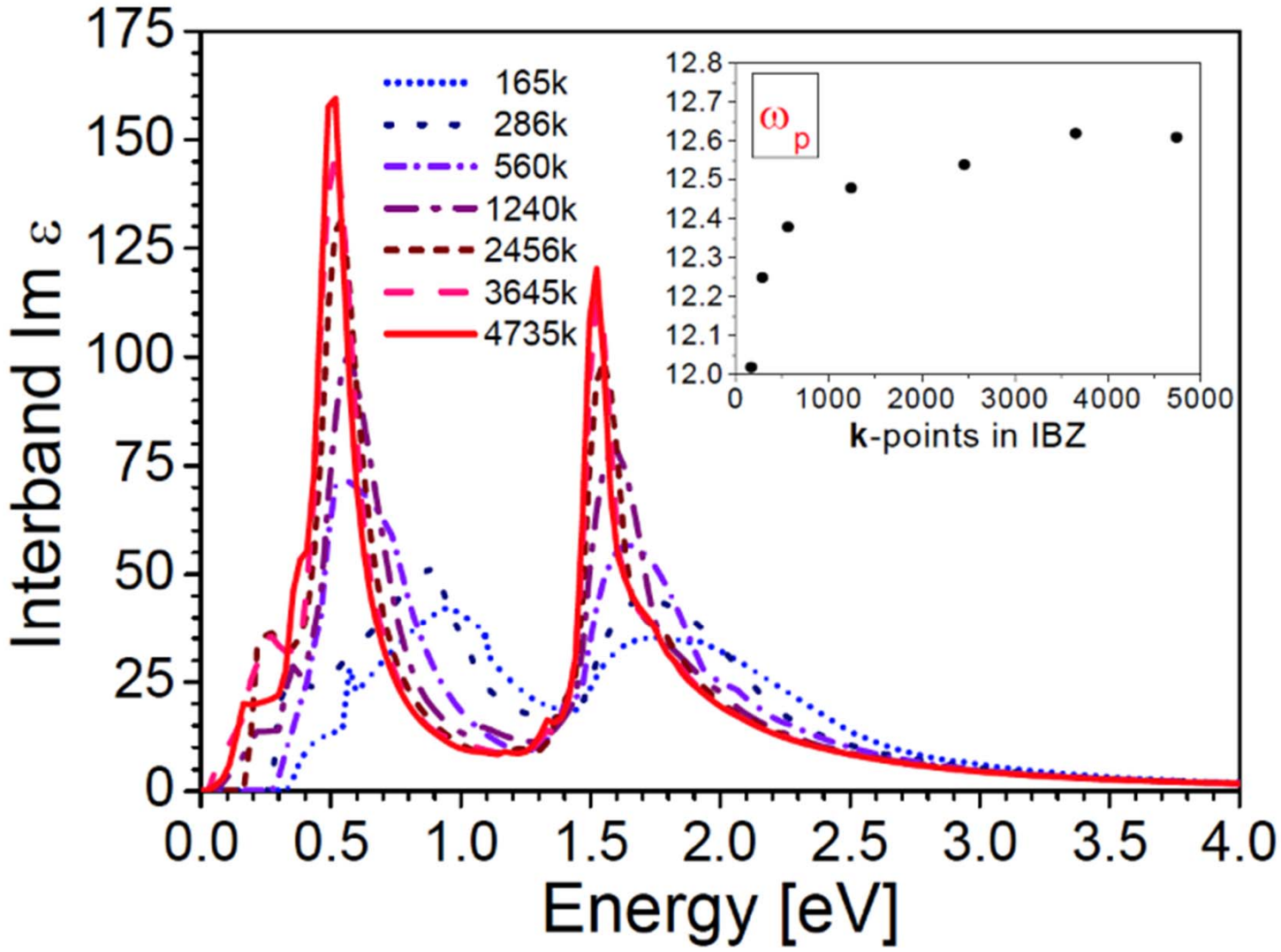
$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

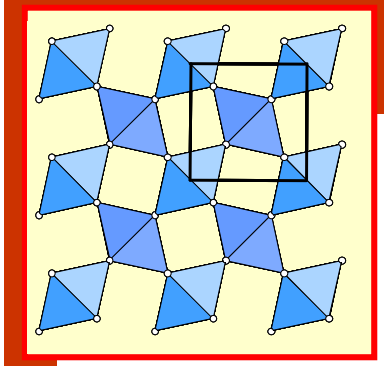
cubic

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

5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Convergence with k-mesh (expl.: Al)

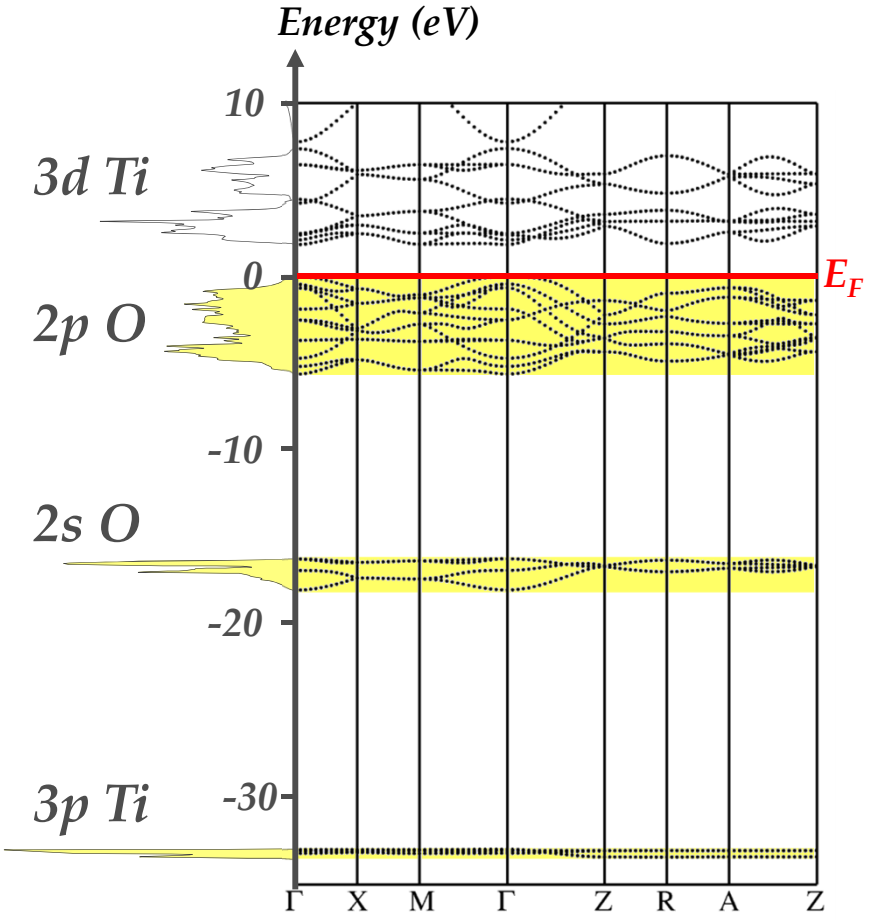


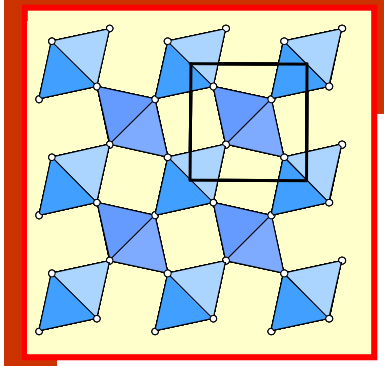


6 – ILLUSTRATIONS: TiO_2 series

Example of the rutile phase

Atomic structure ⇨ *Electronic structure* ⇨ *Dielectric function*

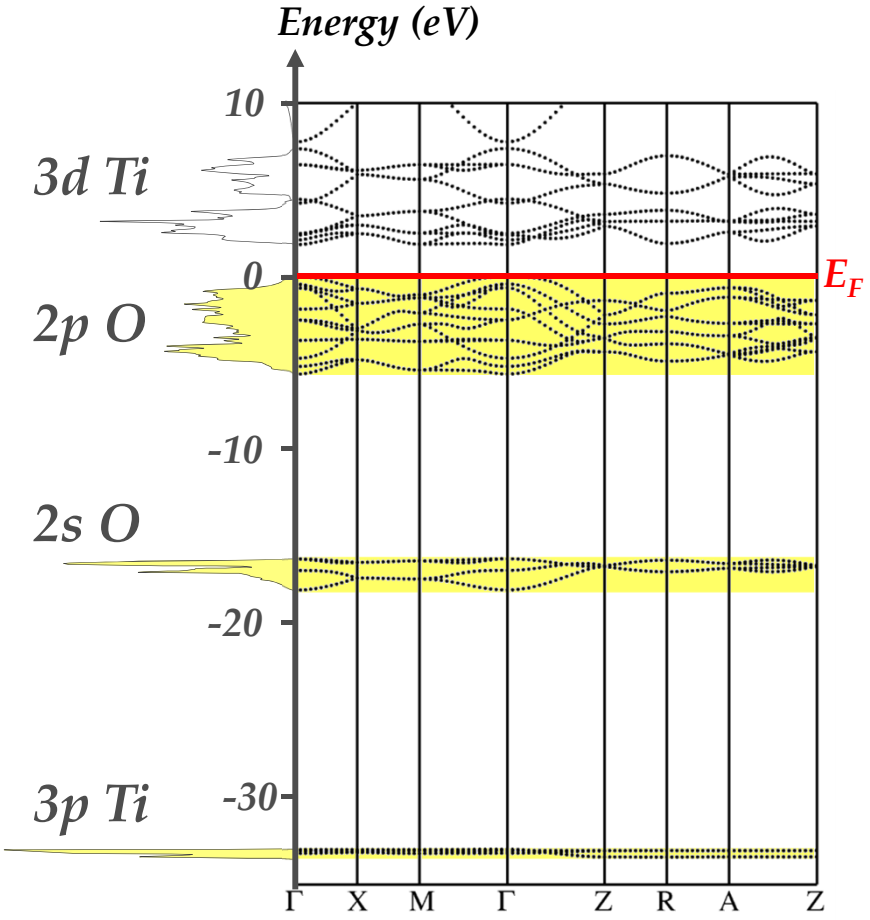


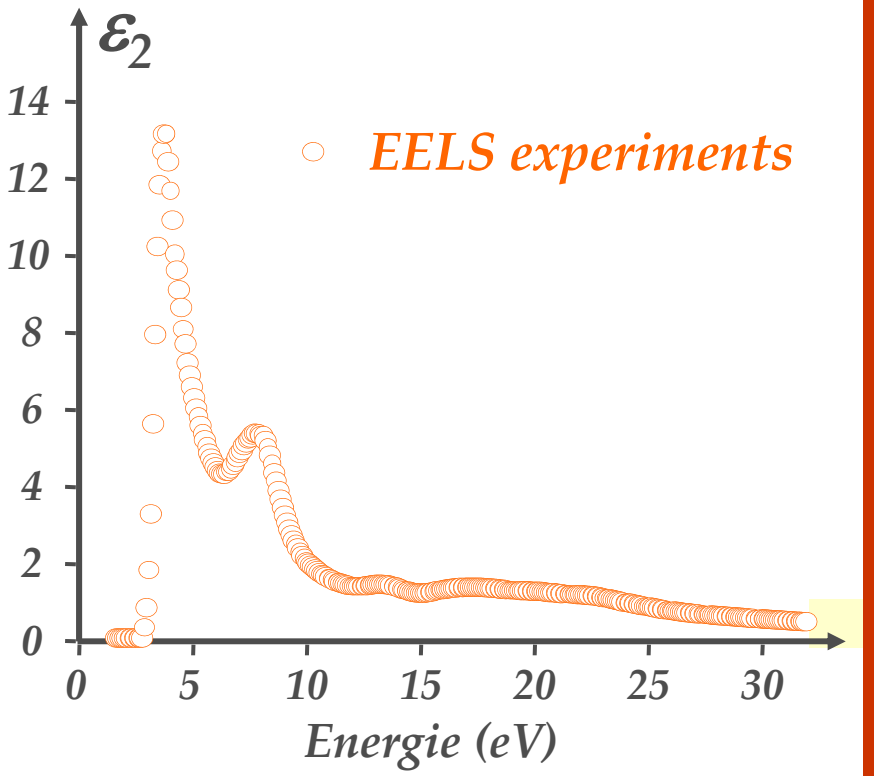


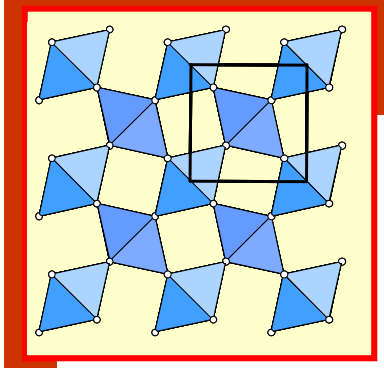
6 – ILLUSTRATIONS: TiO_2 series

Example of the rutile phase

Atomic structure ⇨ *Electronic structure* ⇨ *Dielectric function*



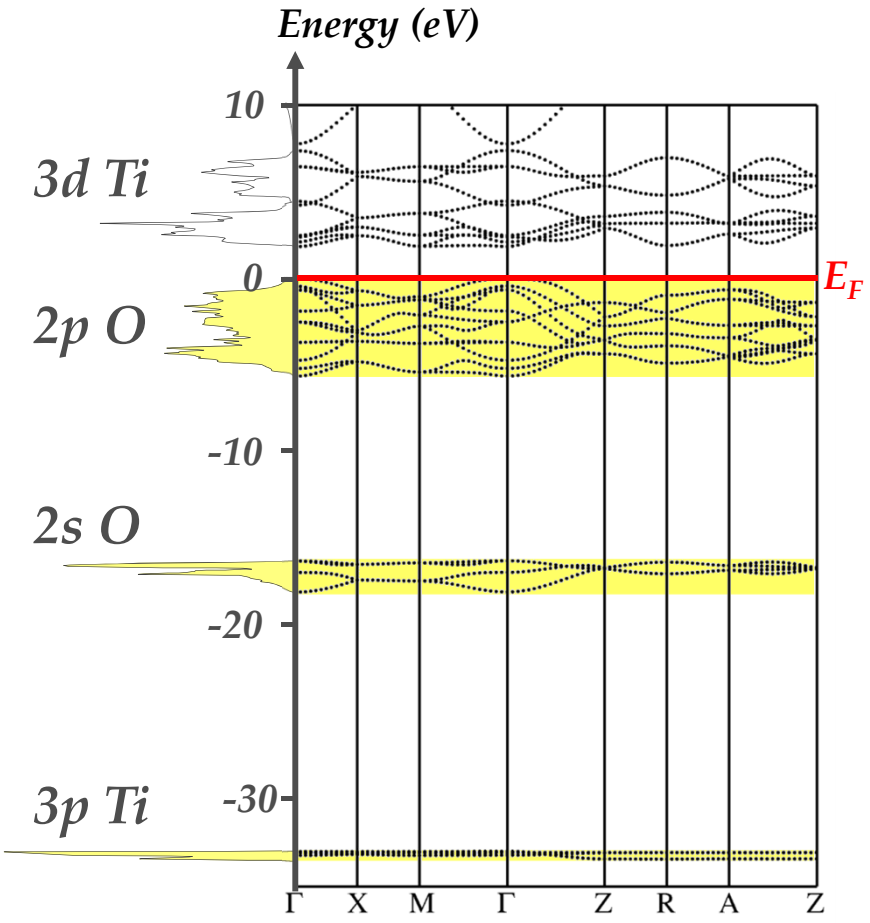


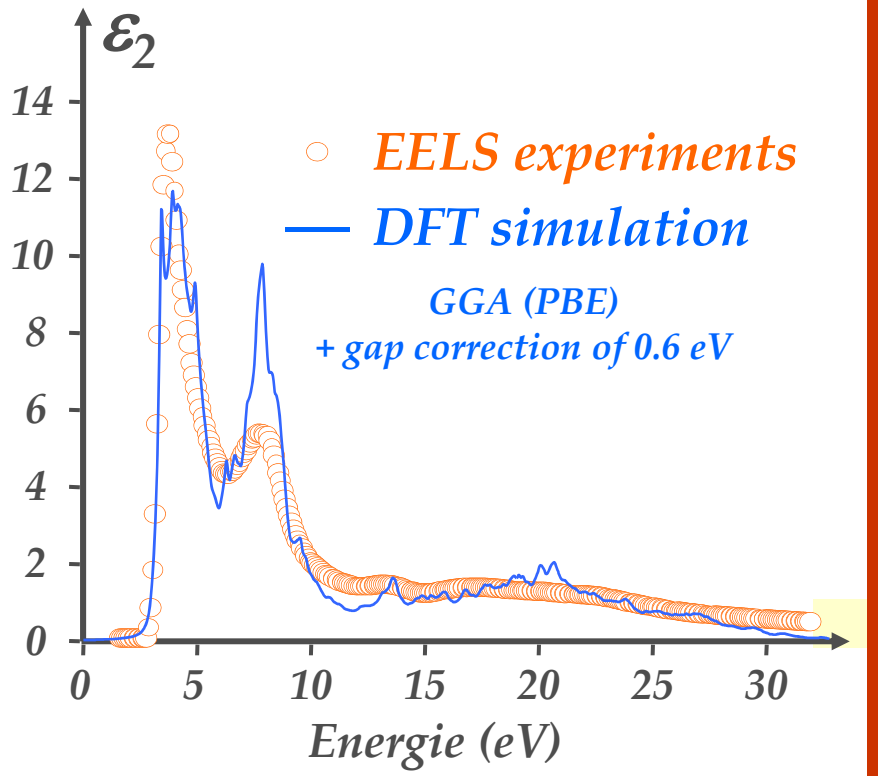


6 – ILLUSTRATIONS: TiO_2 series

Example of the rutile phase

Atomic structure ⇒ Electronic structure ⇒ Dielectric function





6 – OPTICS IN WIEN2k

0. normal SCF run ⟶ converged density

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

2. x lapw1 *-options* ⟶ eigenvectors on dense mesh and high E_{max}

3. x lapw2 -fermi *-options* ⟶ *case*.weight
   - metals: "TETRA 101.0" in *case*.in2

4. x optic *-options* ⟶ momentum matrix elements
   case.symmat: $\langle c\mathbf{k}|\hat{p}_i|v\mathbf{k}\rangle \langle v\mathbf{k}|\hat{p}_j|c\mathbf{k}\rangle$

5. **x joint → Im $\varepsilon_{ij}(\omega)$,(case.joint) (JDOS*symmat)**

6. **x kram → Re $\varepsilon_{ij}(\omega)$, other optical funct., broadening, scissor operator**

7. **opticplot**

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

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

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

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

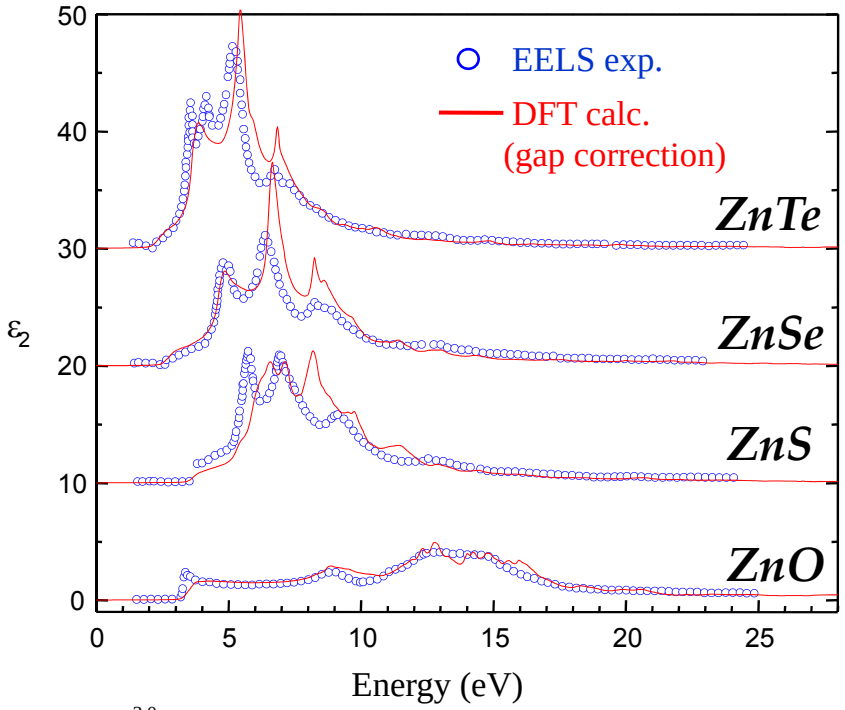
Files generated by:

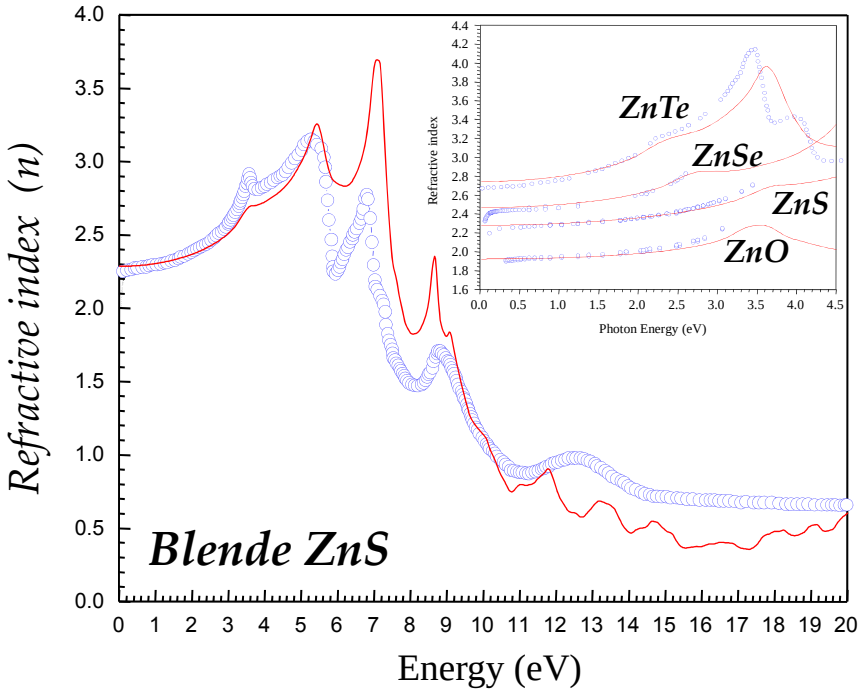
x optic → TiO2-RUT.symmat
→ TiO2-RUT.mommat

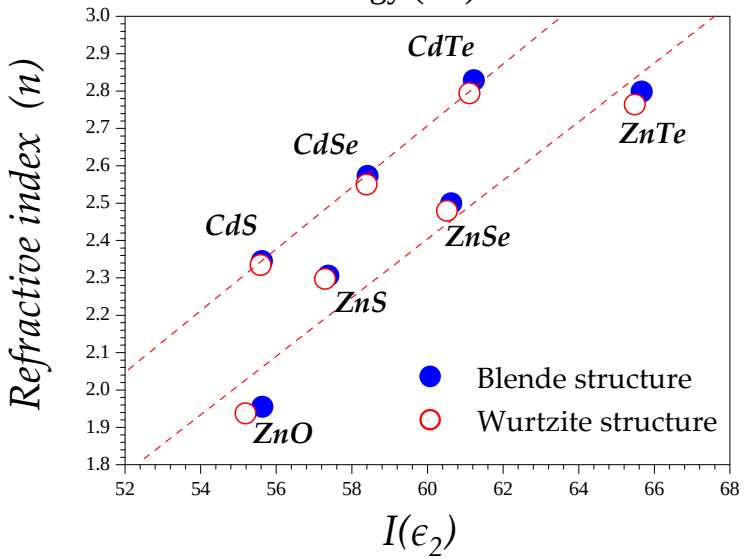
x joint → TiO2-RUT.joint

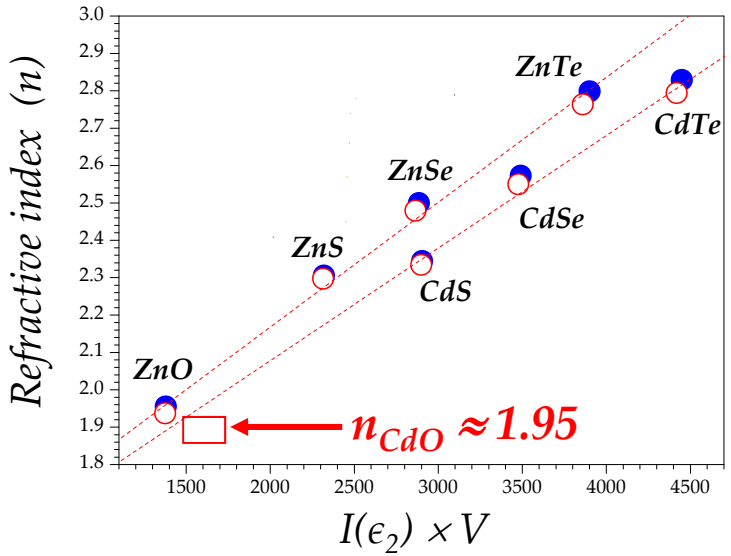
x kram → TiO2-RUT.epsilon
→ TiO2-RUT.sigmak
→ TiO2-RUT.refraction
→ TiO2-RUT.absorption
→ TiO2-RUT.eloss

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



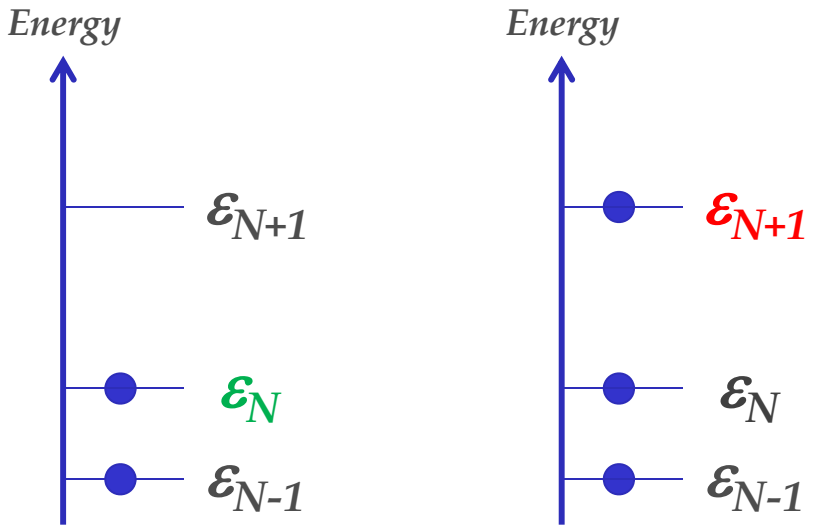




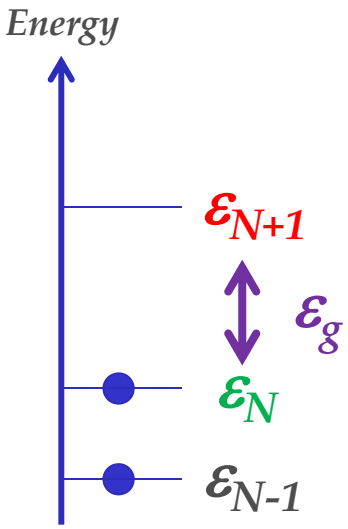


7 – Limitations:

The band gap problem → Necessity to go beyond DFT



$$E_g = \varepsilon_{N+1}(N+1) - \varepsilon_N(N) = I - A$$



$$E_g = \varepsilon_{N+1}(N) - \varepsilon_N(N)$$

$$E_g = \underline{\varepsilon_{N+1}(2N) - \varepsilon_N(2N)} + \underline{\varepsilon_{N+1}(2N+1) - \varepsilon_{N+1}(2N)}$$

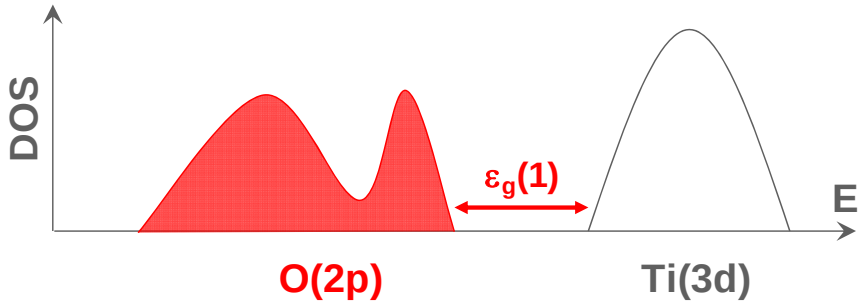
$$E_g = \varepsilon_g + \Delta_{xc} \quad \text{with } \Delta_{xc}: \text{Scissor Operator/mBJ/hybrid/GW…}$$

Ionization energy: $\varepsilon_N(N) = -I$ *Electro-affinity:* $\varepsilon_{N+1}(N+1) = -A$

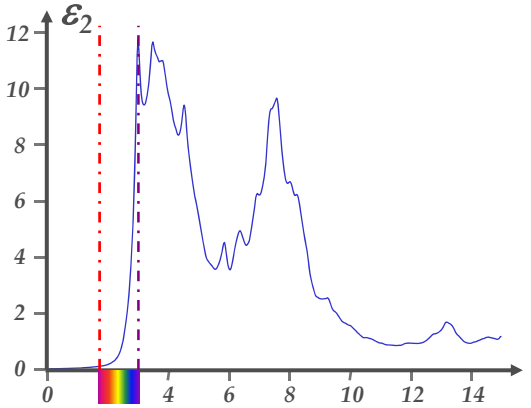
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Fundamental gap: electronic gap ≠ optical gap

Deduced from the band structure



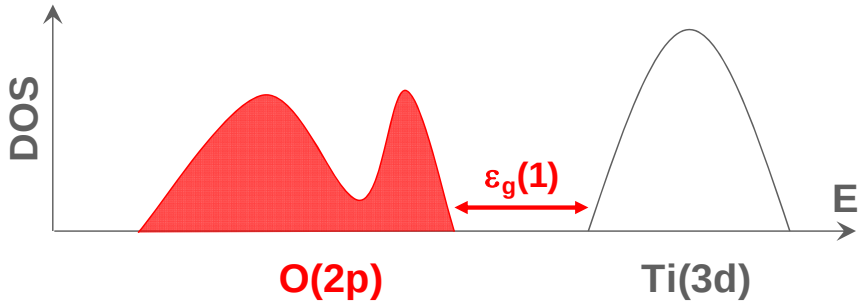
Dipolar transitions



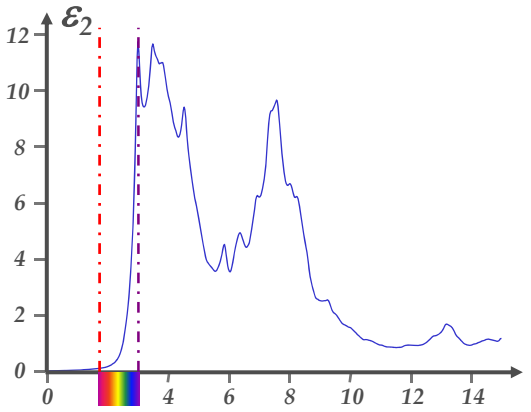
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

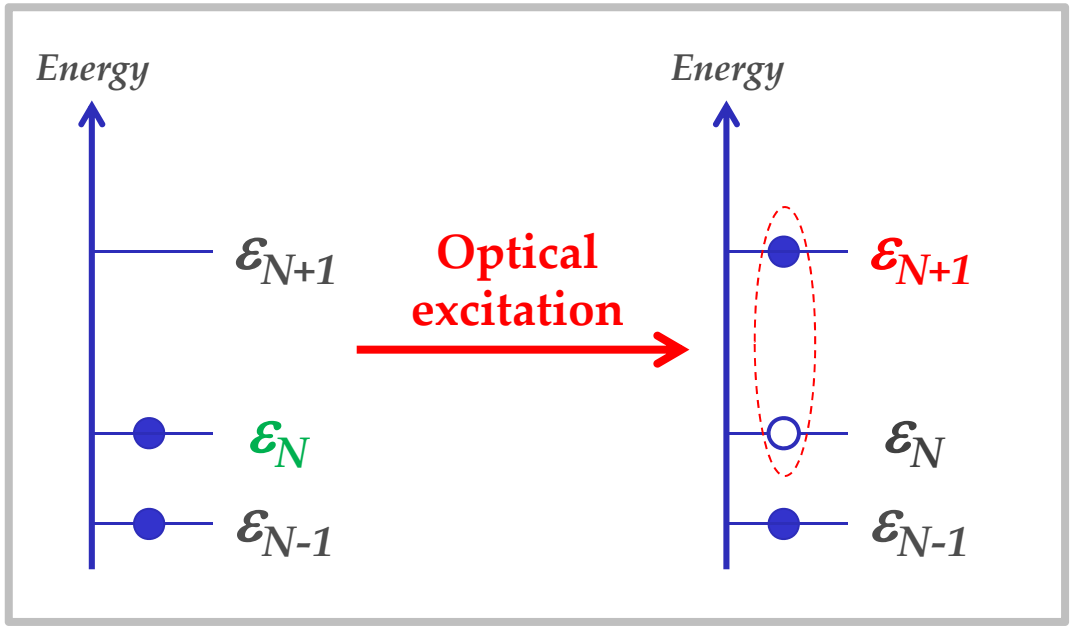
Fundamental gap: electronic gap ≠ optical gap

Deduced from the band structure



Dipolar transitions





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

7 – Some limitations of DFT simulation of optical properties

- Kohn-Sham eigenstates interpreted as excited states

- 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…