TECHNISCHE UNIVERSITÄT WIEN

Optical properties, Core-level spectroscopy, GW and BSE

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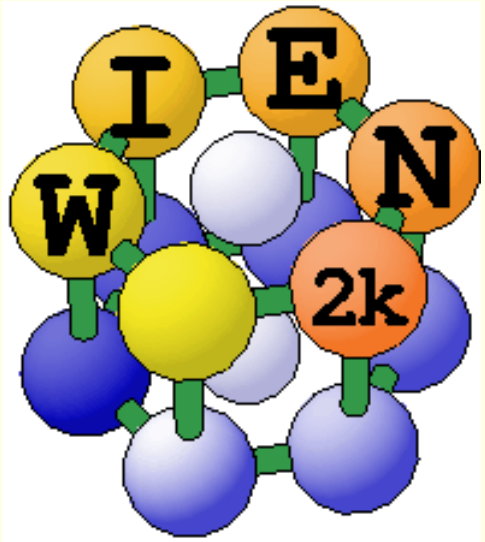
TU Wien

Xavier Rocquefelte

University of Rennes



Modelling the Optical Properties of Inorganic Materials

1 – MULTIPLE FACETS OF COLOURED MATTER

2 – ELECTRONIC STRUCTURE OF A SOLID

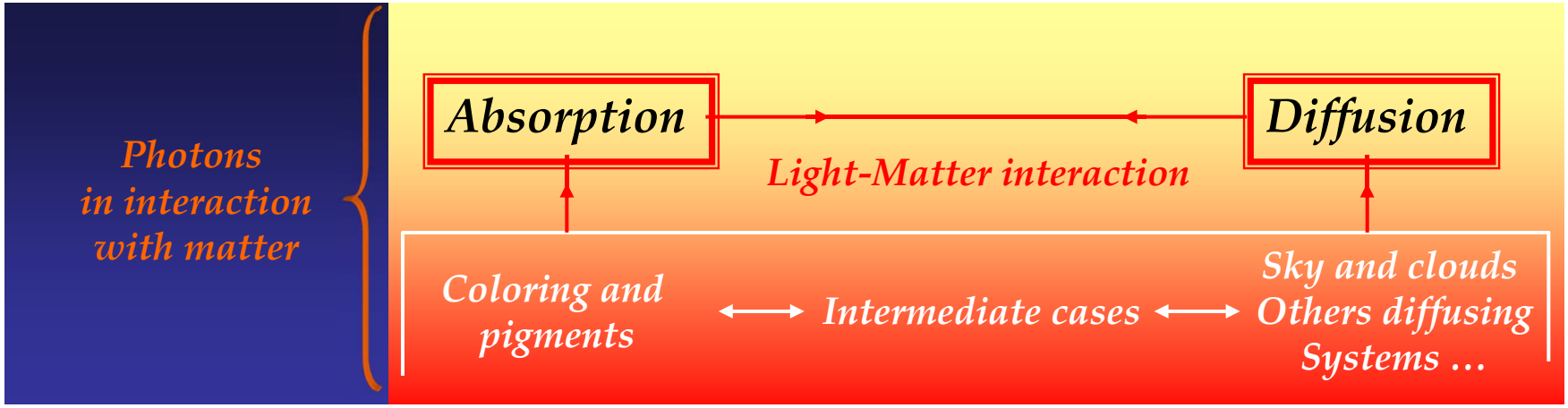
3 – UNDERSTANDING OF COLORS FROM BANDS

4 – LIGHT-MATTER INTERACTION

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

6 – ILLUSTRATIONS

1 – MULTIPLE FACETS OF COLOURED MATTER



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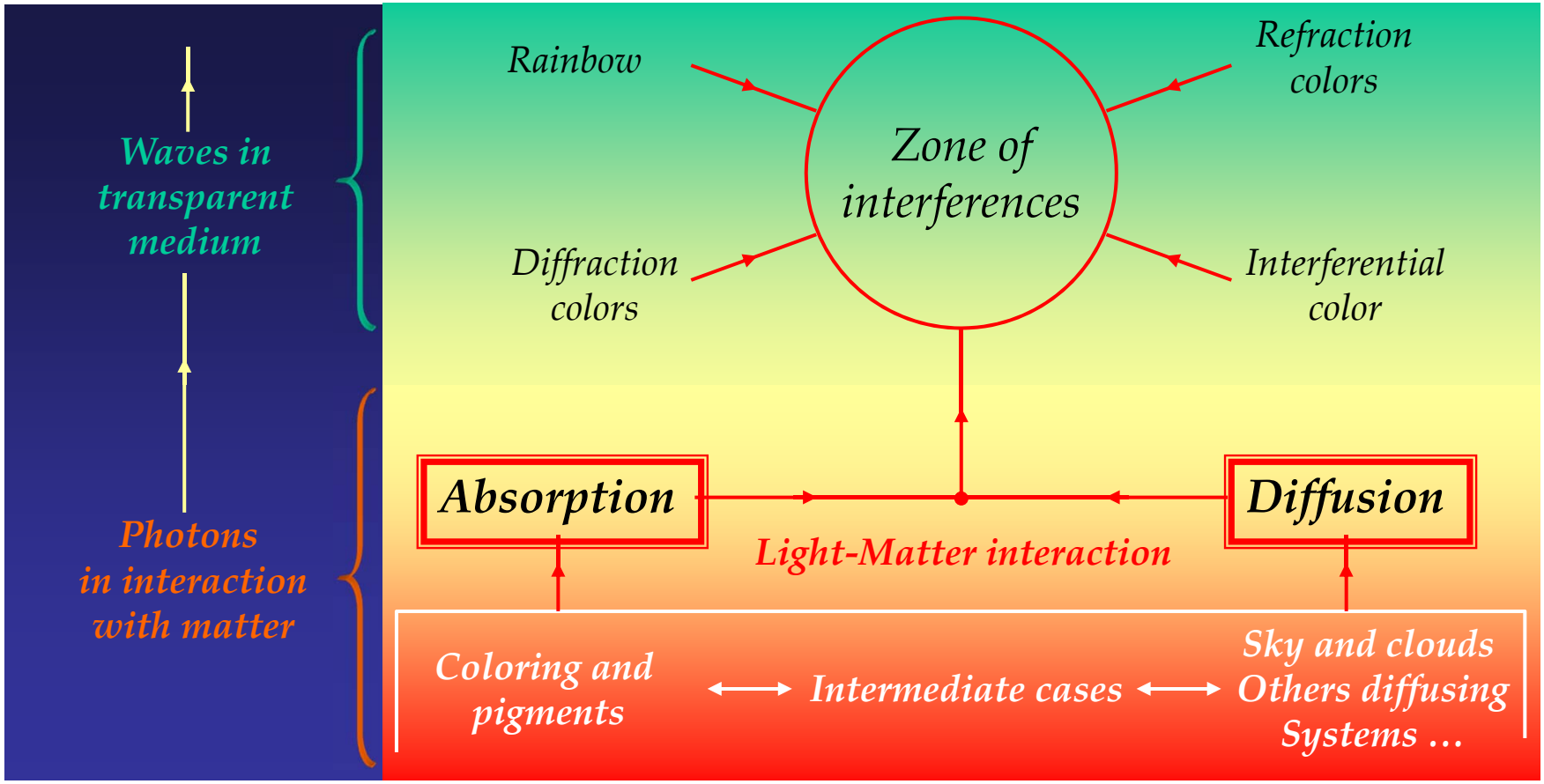

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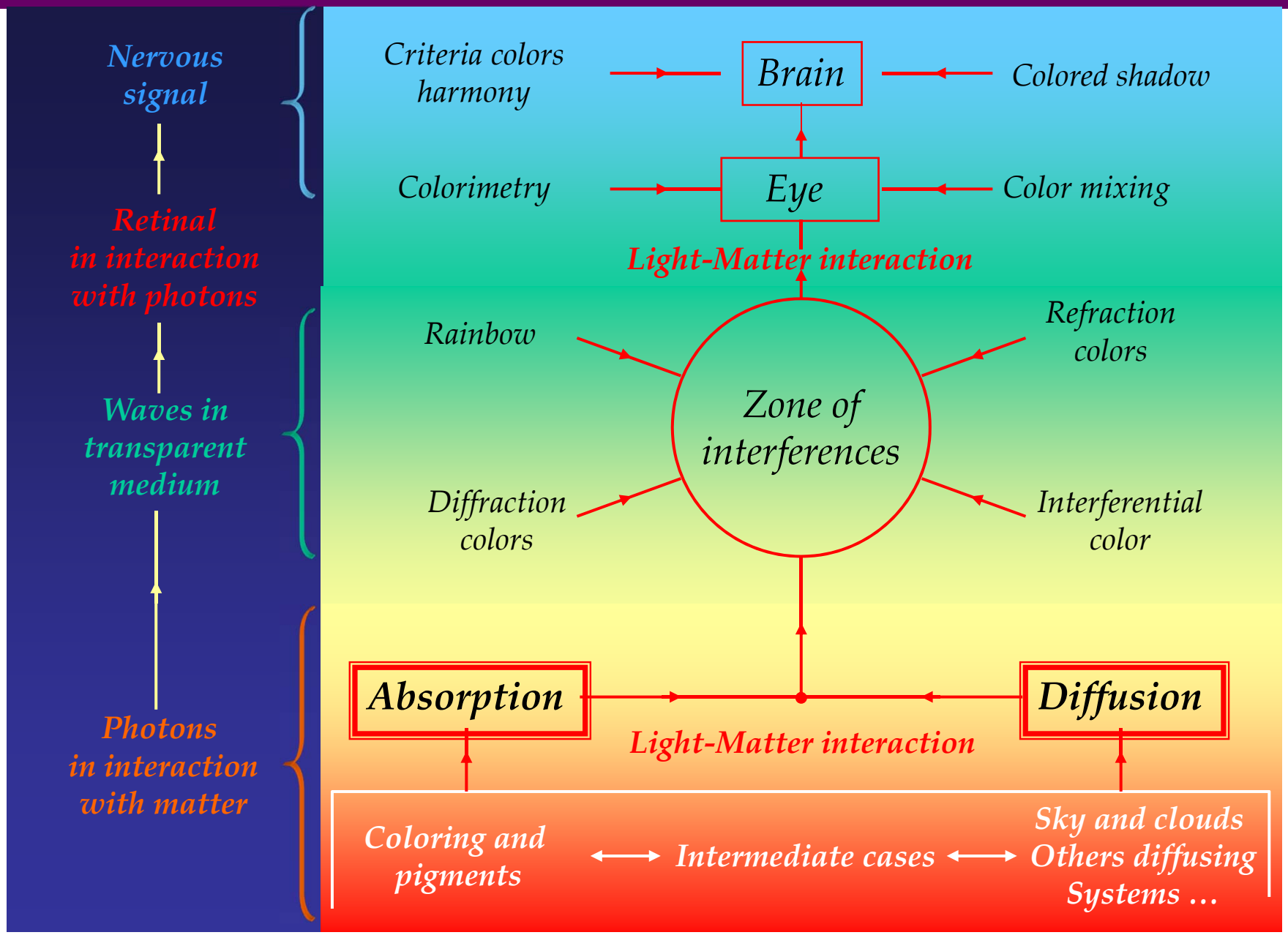

1 – MULTIPLE FACETS OF COLOURED MATTER

Interaction between the electromagnetic field and matter

Physical color

Diffusion et interferences
Dispersion / Reflection et Refraction / Scattering

Transparent matter

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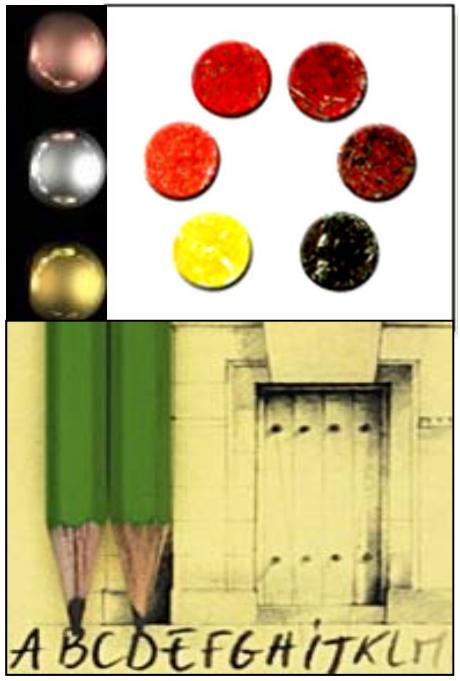
Chemical color



Absorption
Energy dissipation

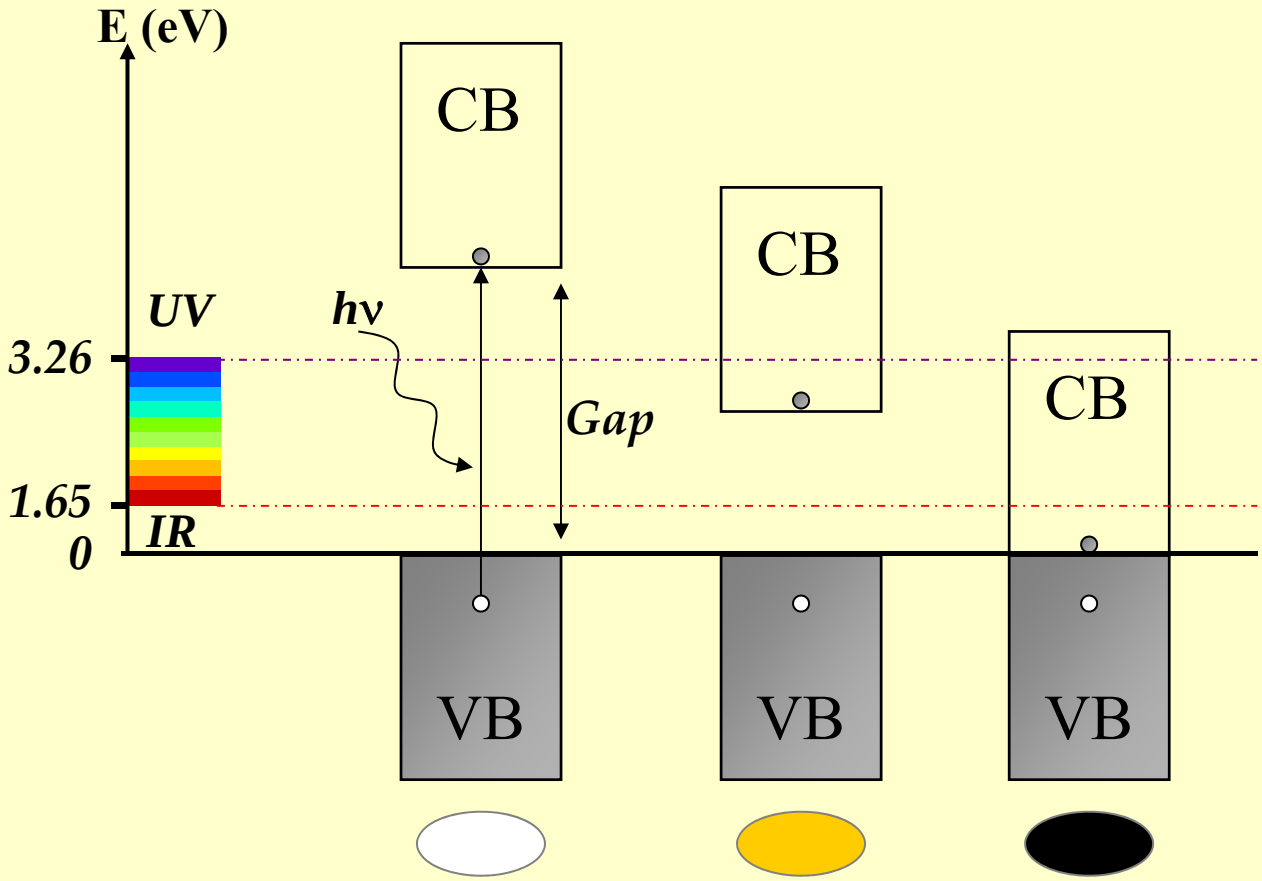
Opaque matter

1 – MULTIPLE FACETS OF COLOURED MATTER

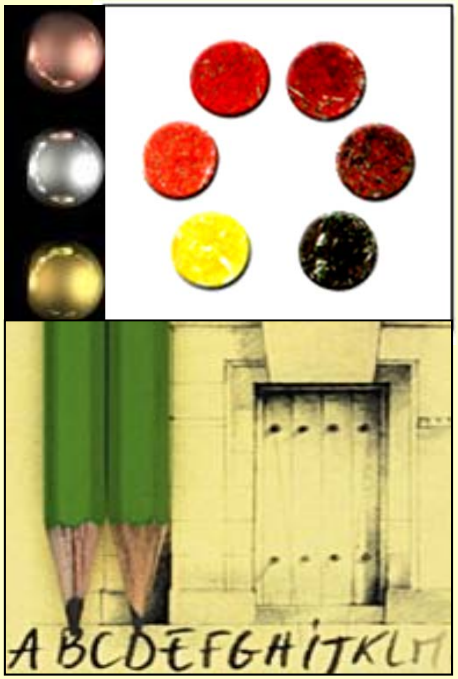
Chemical color → « Inelastic diffusion »

Acceptor electron levels ⇒ Dissipative absorption

From insulator to semiconductor to metal systems



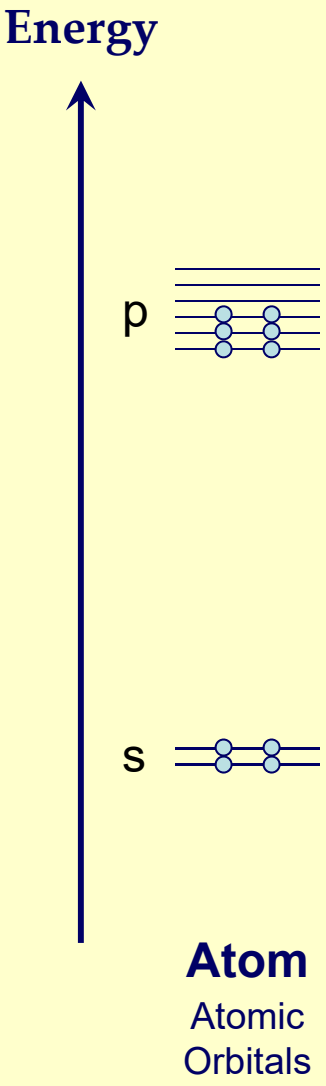
Chemical colors



Absorption
Energy dissipation

Opaque Matter

From the atom to the molecule and to the solid



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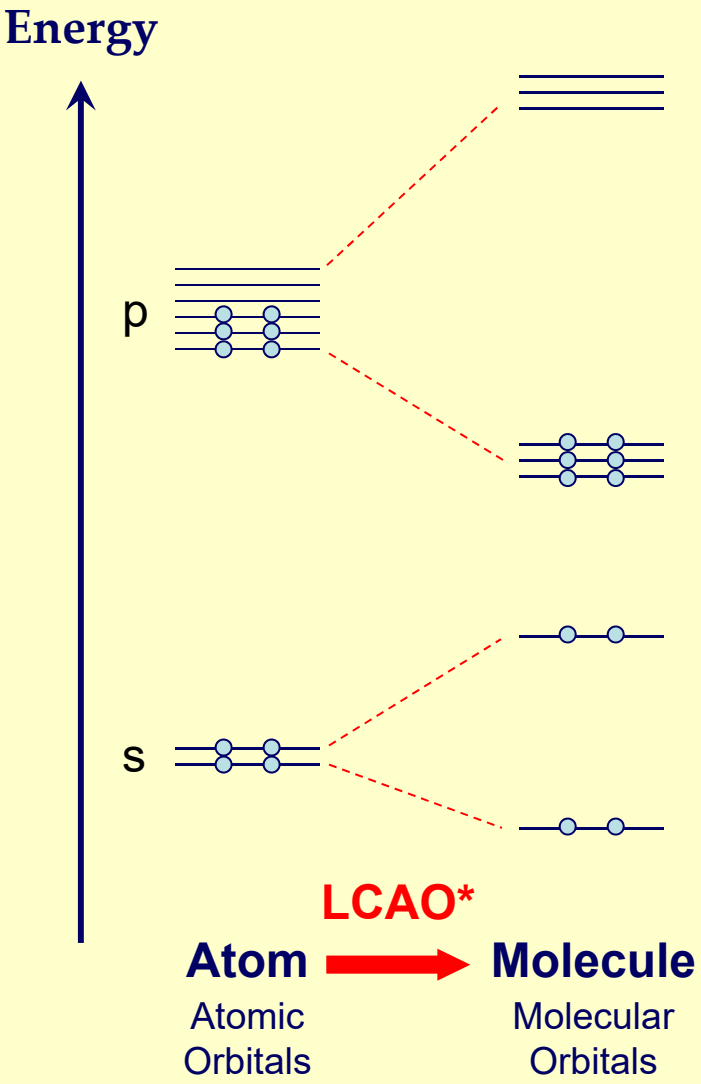
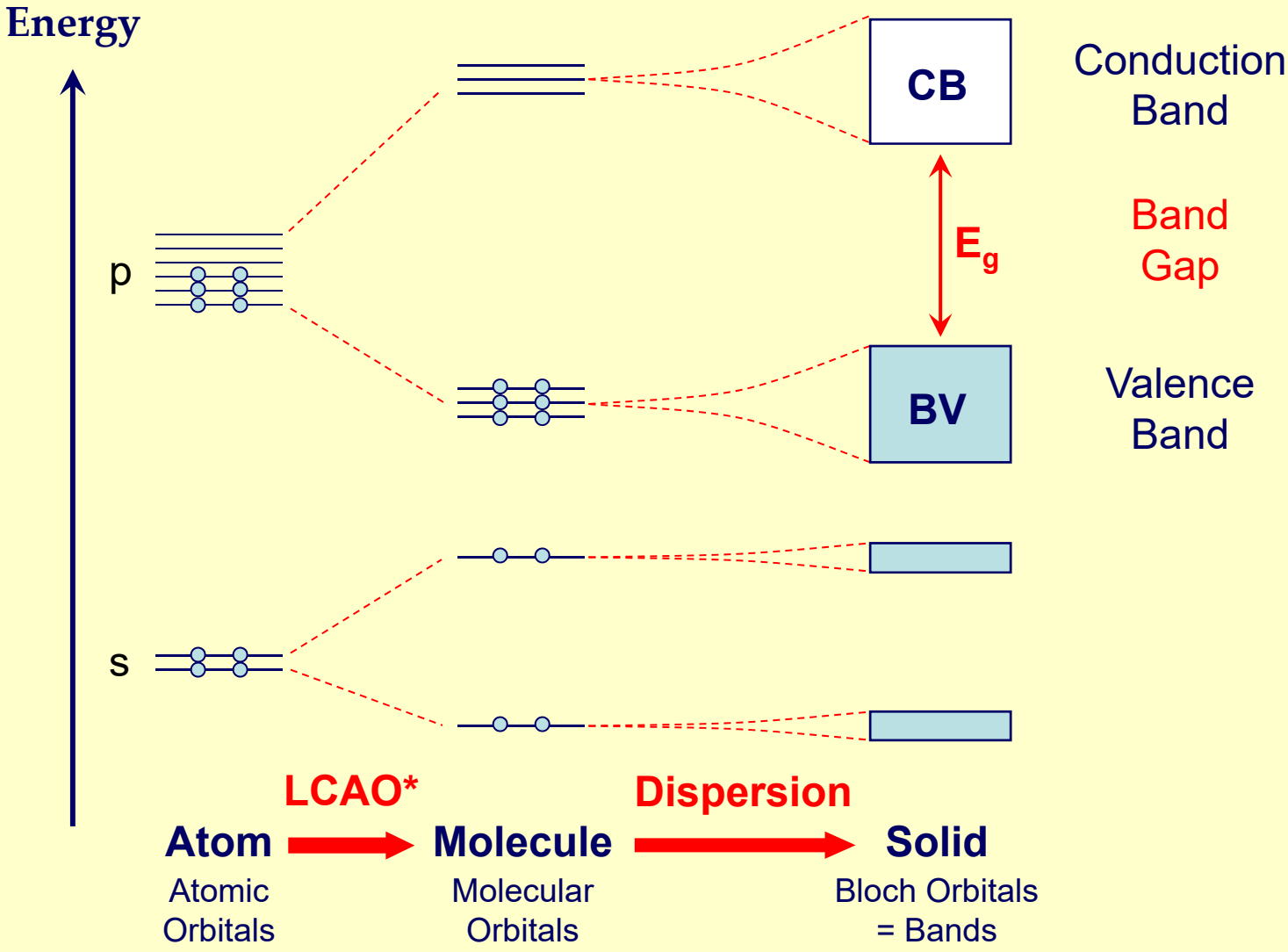


*LCAO : Linear Combination of Atomic Orbitals

2 – ELECTRONIC STRUCTURE OF A SOLID

From the atom to the molecule and to the solid



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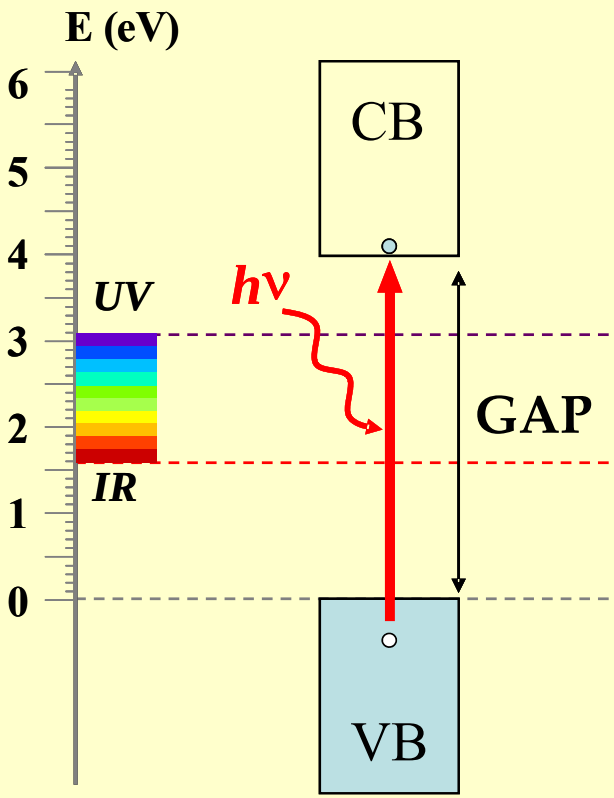
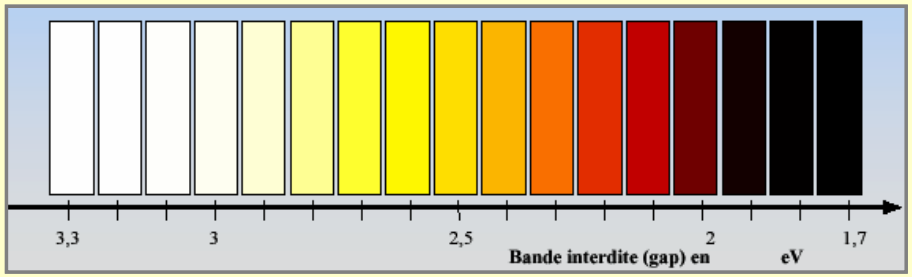
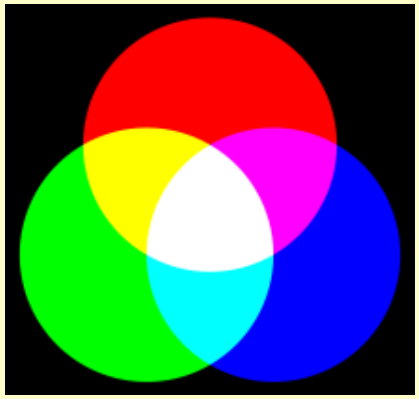
3 – UNDERSTANDING OF COLORS FROM BANDS



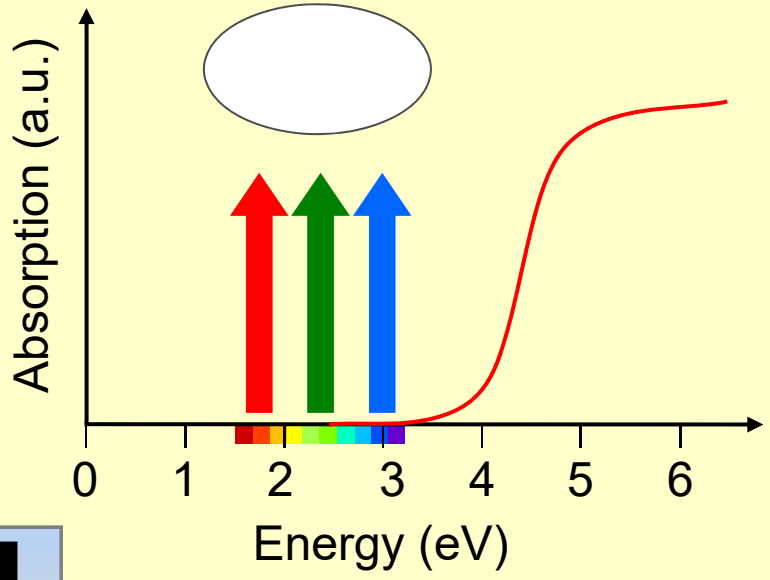
Color of the compound





Color of a SC* with 1 gap

Transmitted light



*SC : Semiconductor

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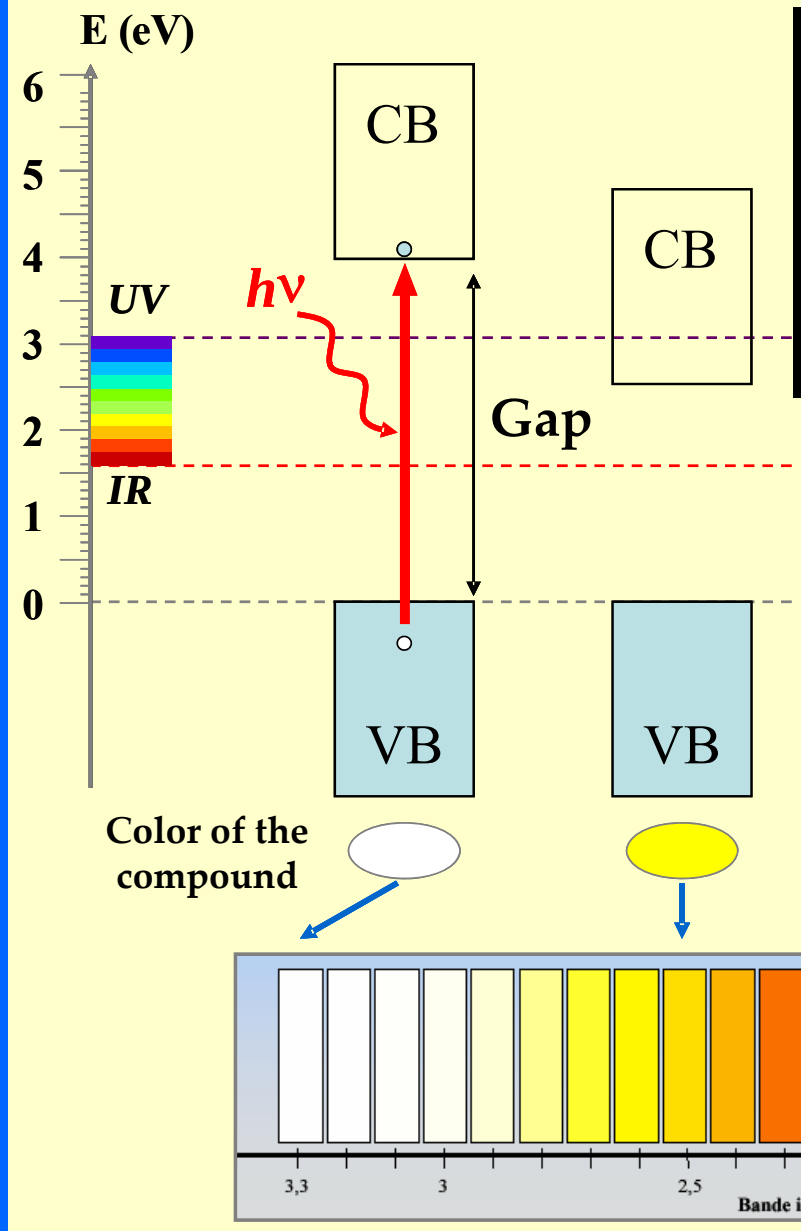

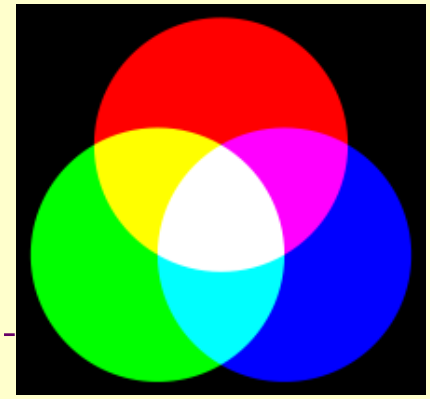

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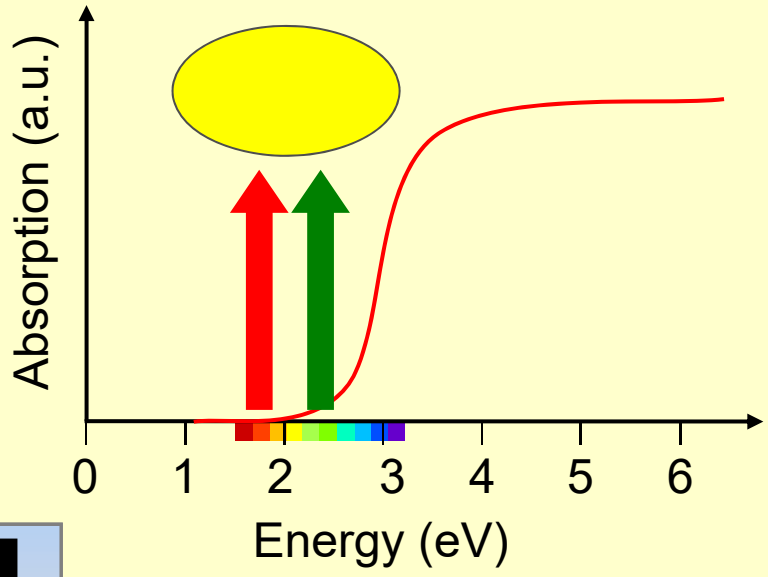

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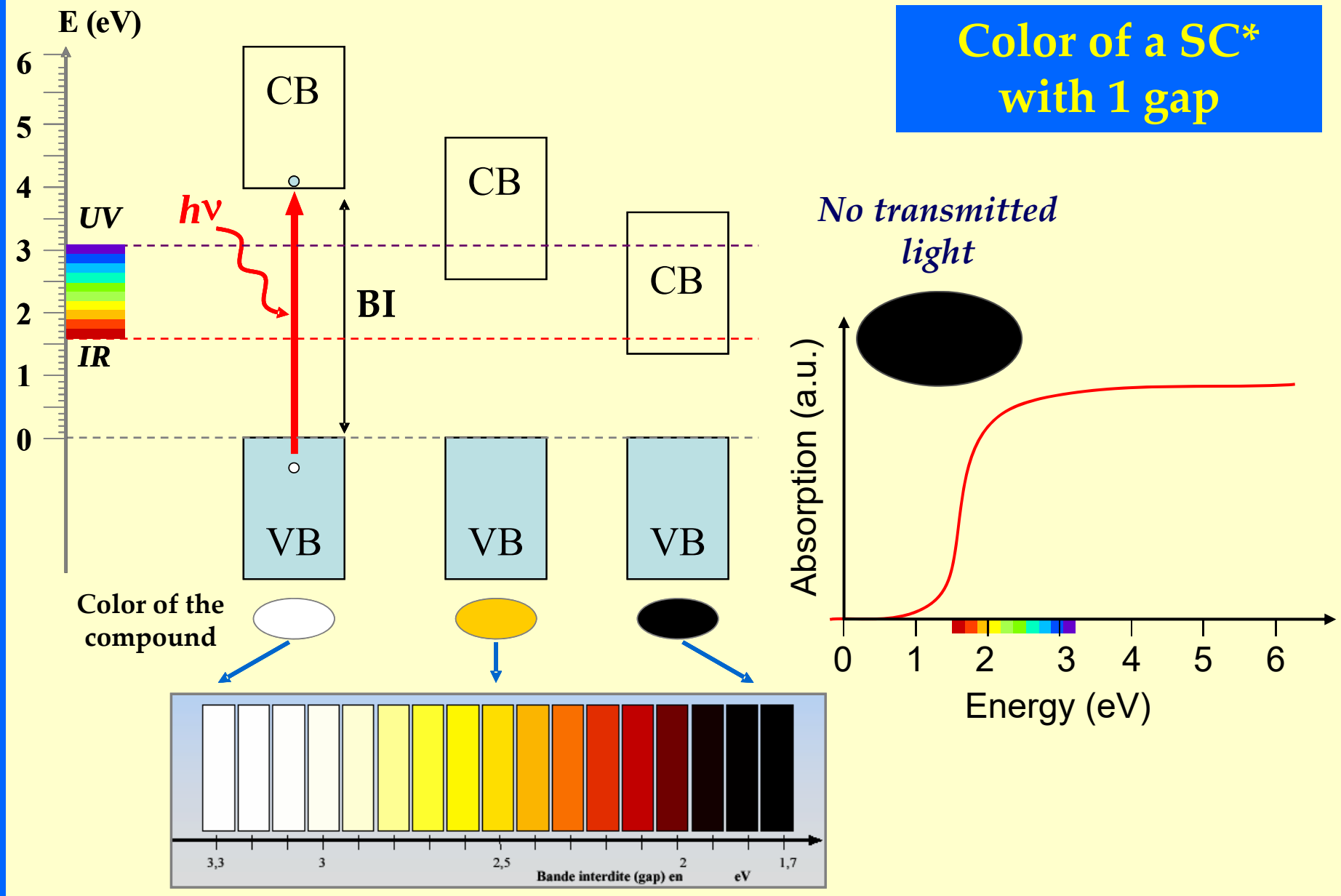


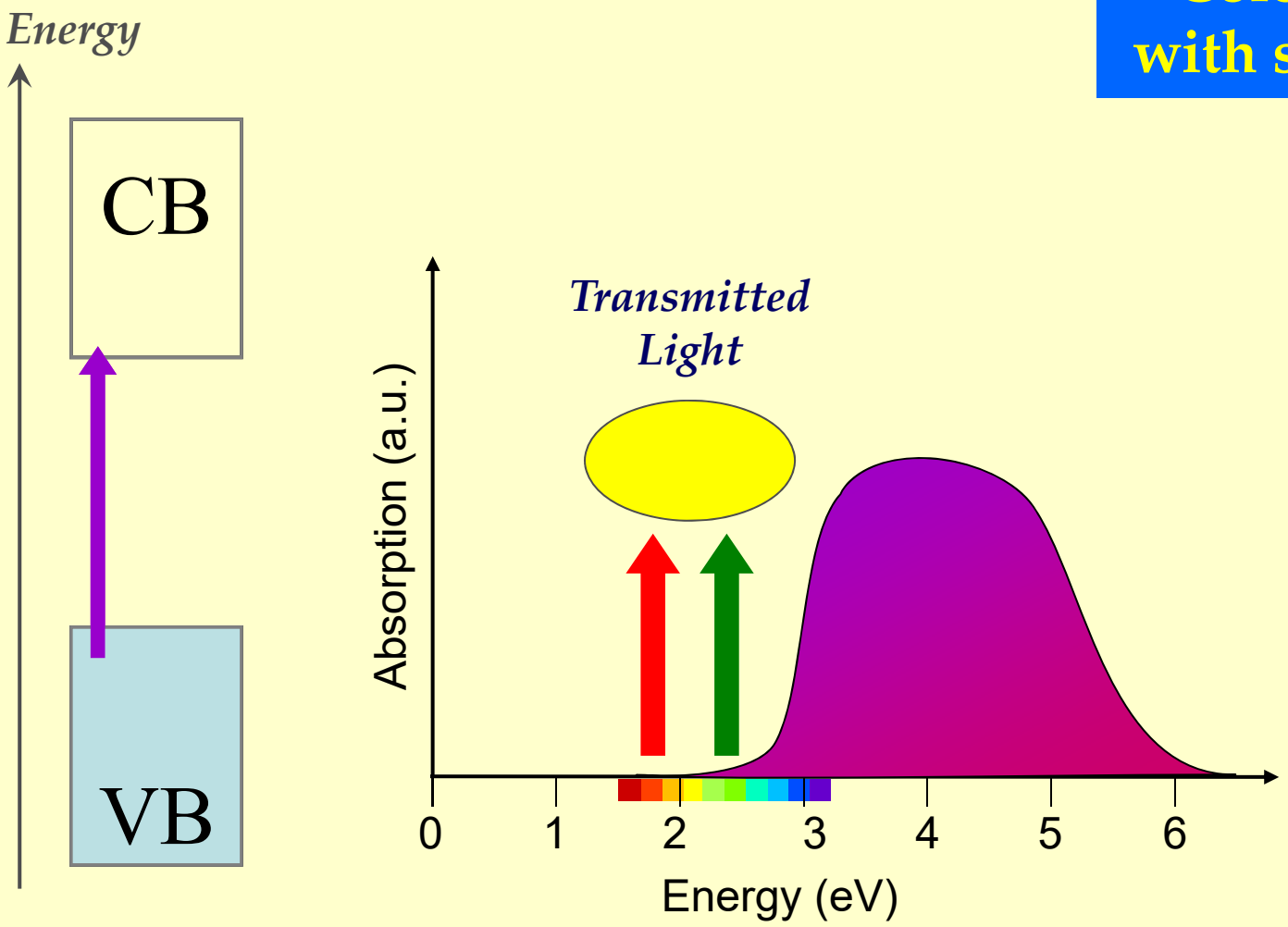
Color of a SC* with 1 gap

No transmitted light

*SC : Semiconductor

3 – UNDERSTANDING OF COLORS FROM BANDS

Color of a SC* with several gaps



*SC : Semiconductor

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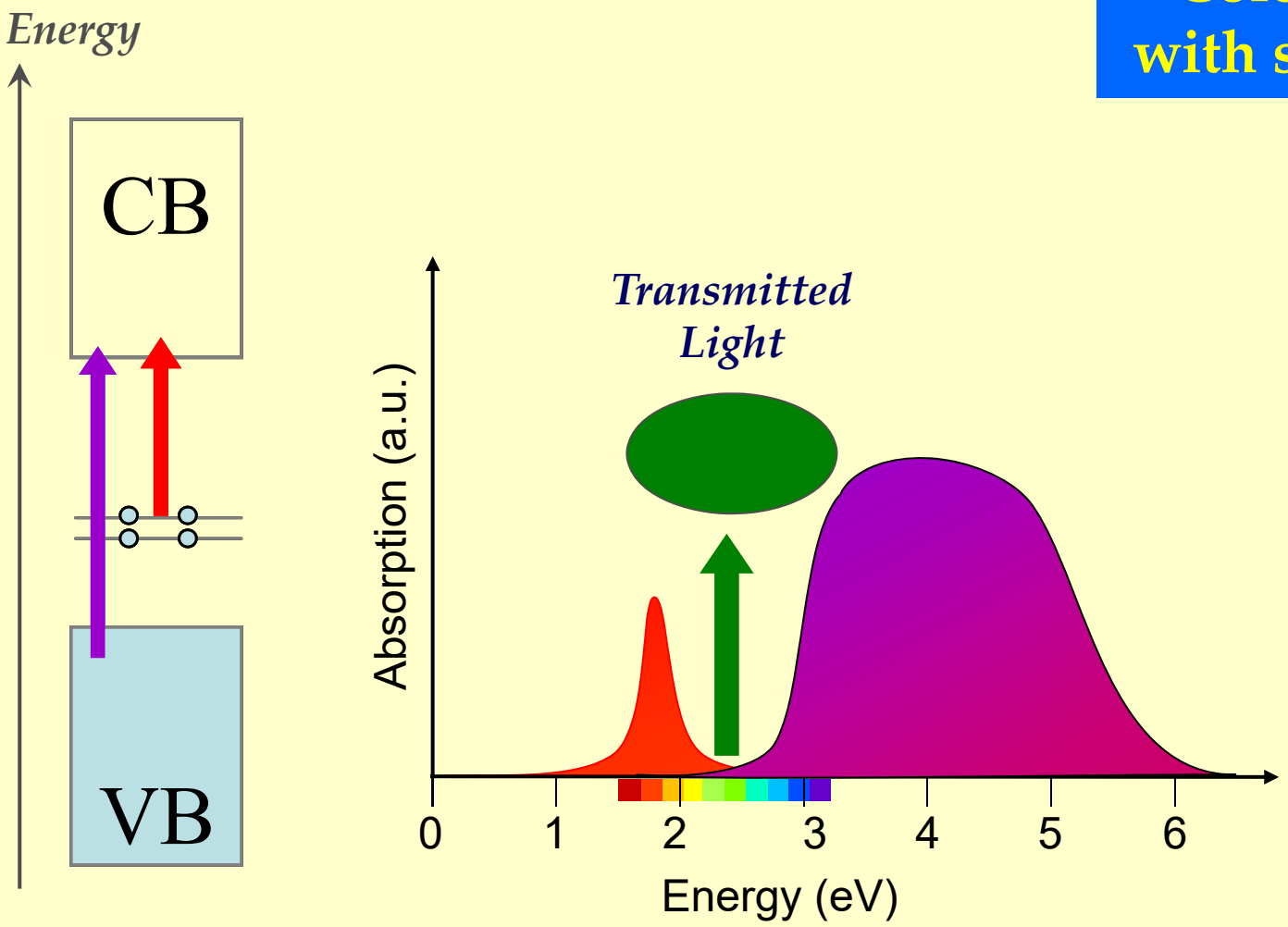
Color of a SC* with several gaps



*SC : Semi-conducteur – BI : Bande interdite

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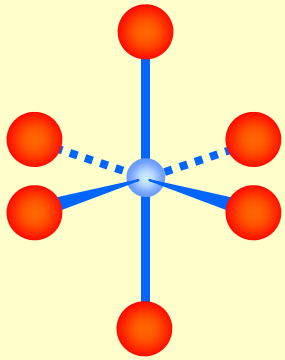
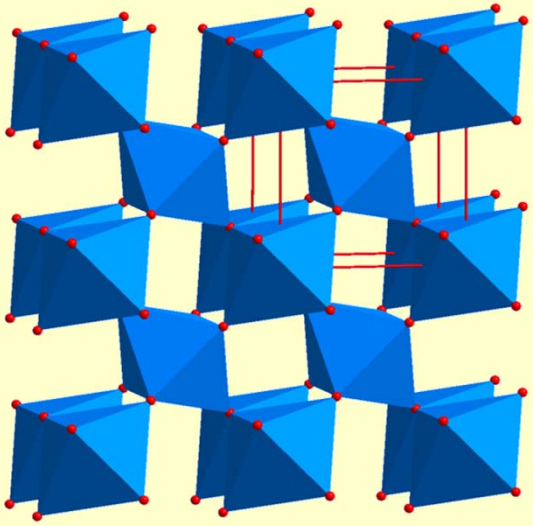


TiO_2



Powder sample of TiO_2 (rutile)

Charge transfer→ color

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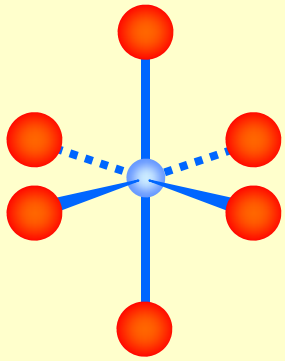

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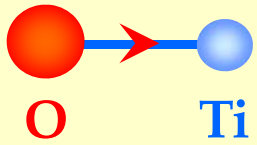

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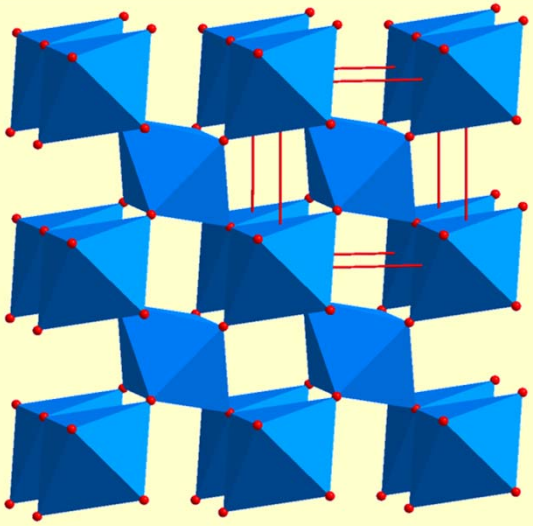

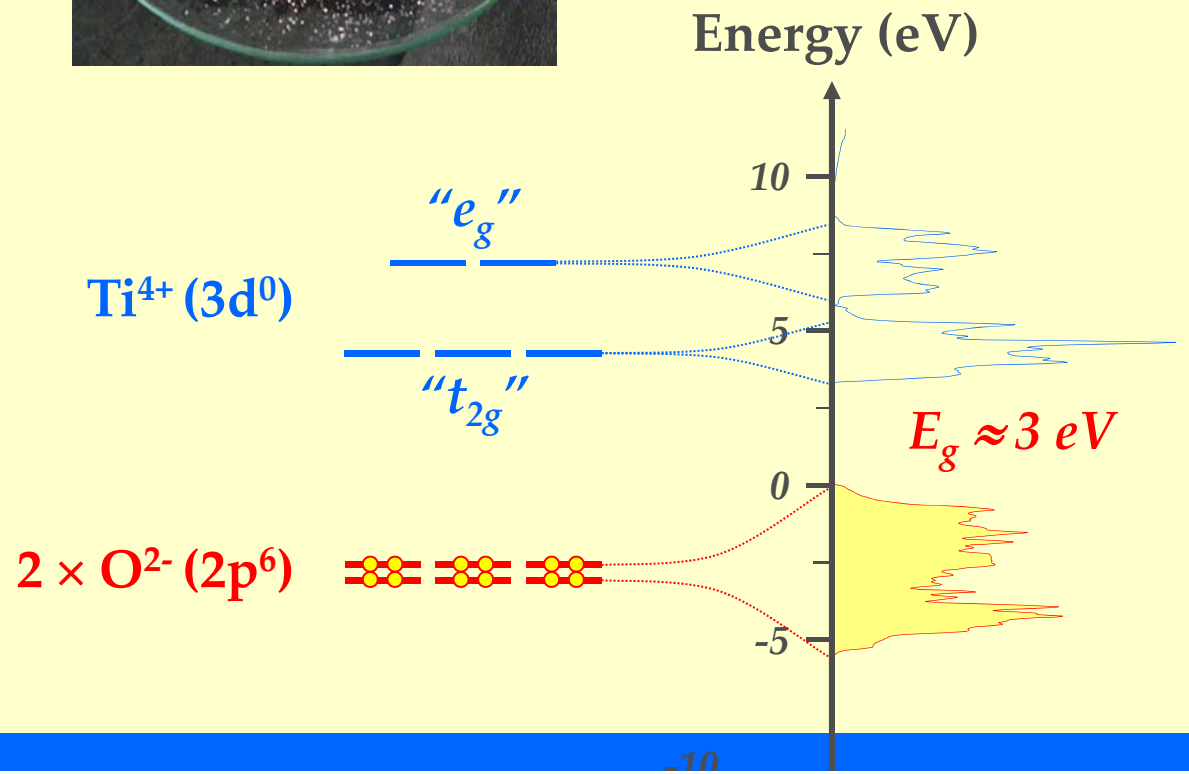

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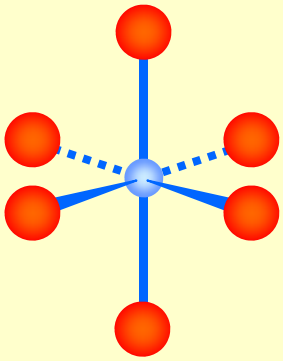

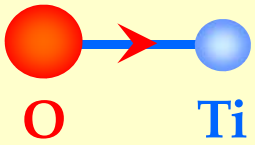

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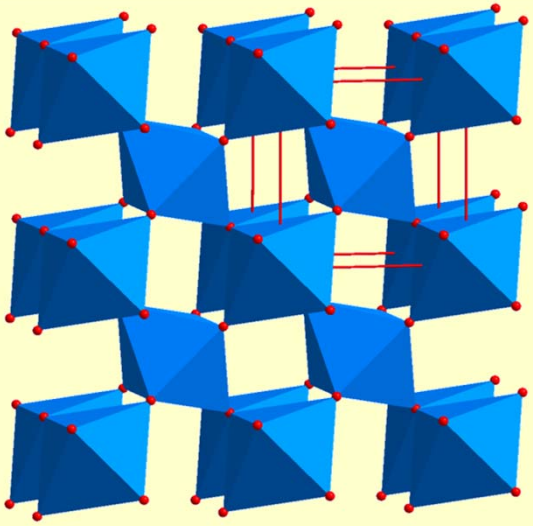
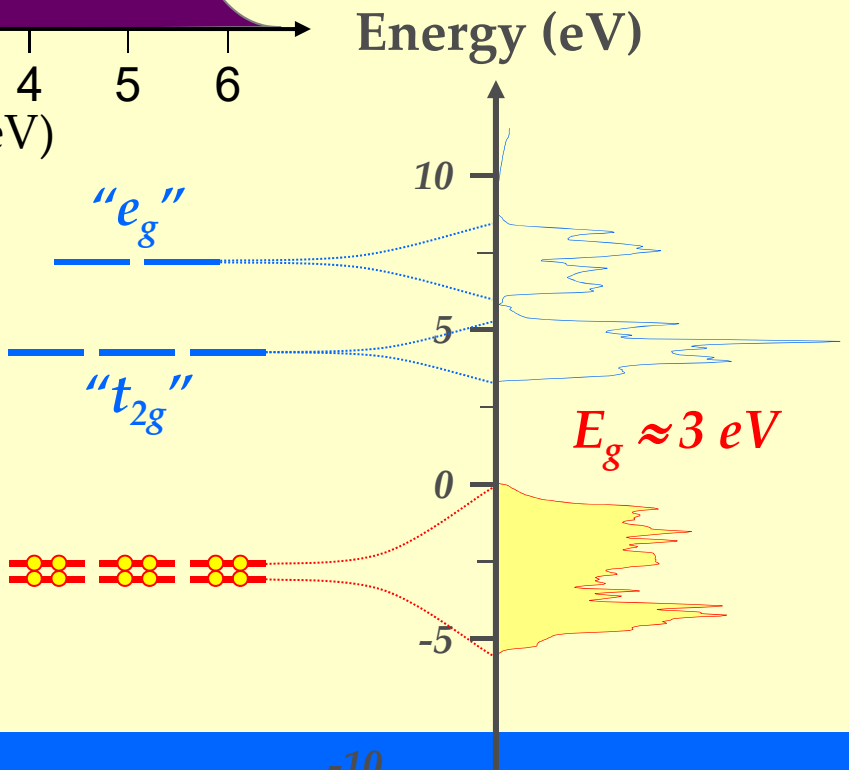


Ti^{4+} ($3d^0$)

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



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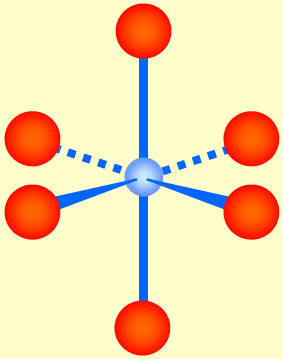

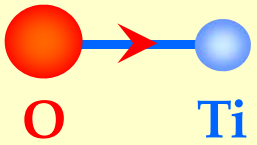

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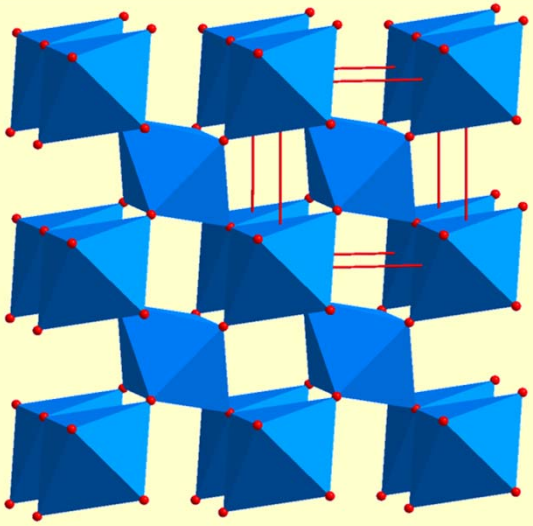

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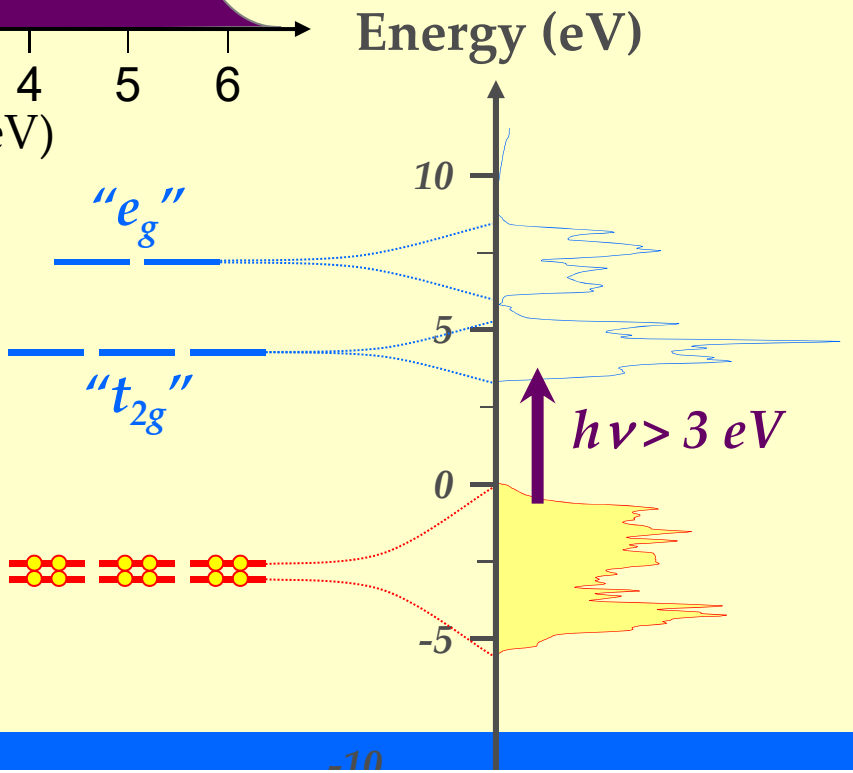

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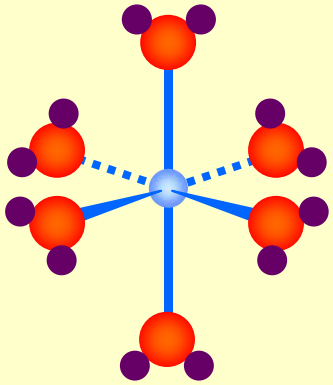
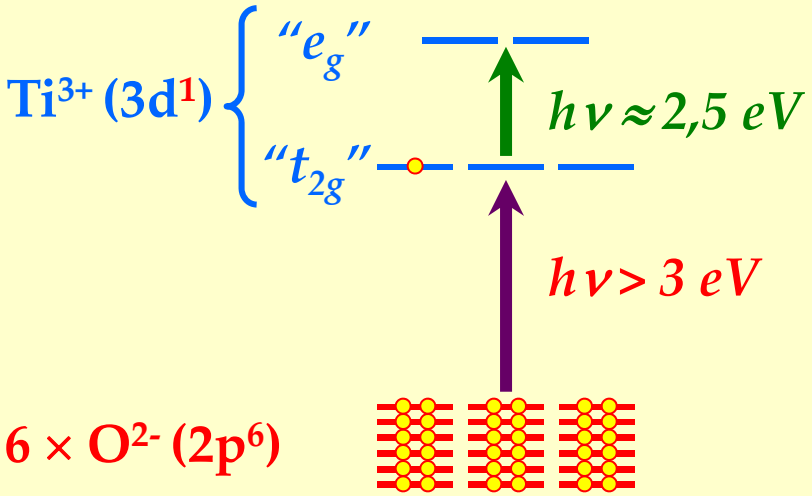


$Ti[H_2O]^{3+}$

$TiCl_3$
in solution

d-d transition → color



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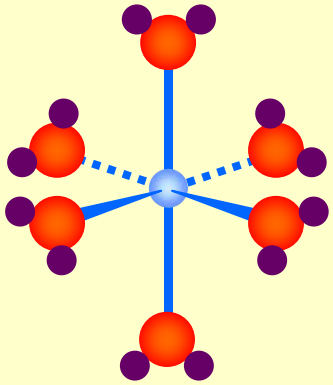

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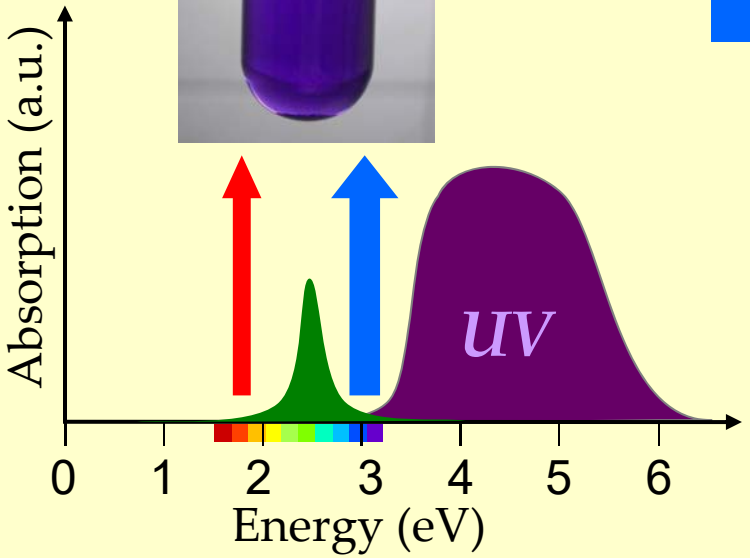
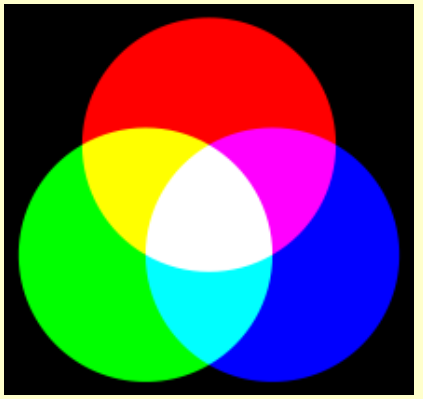
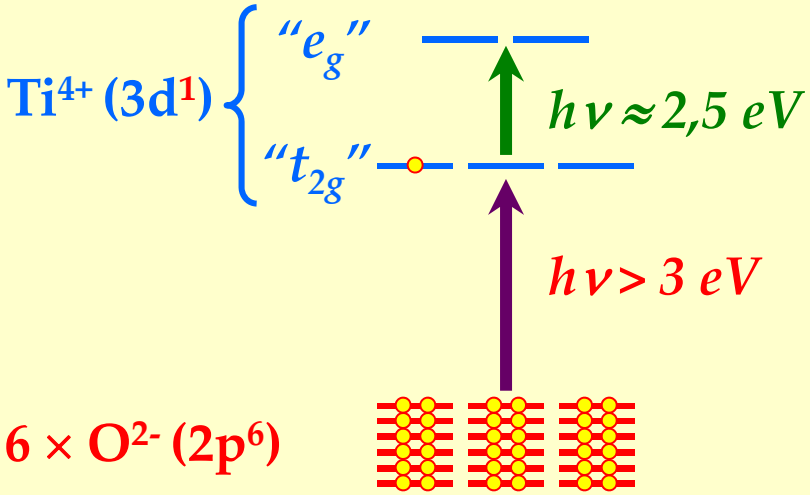


d-d transition → color



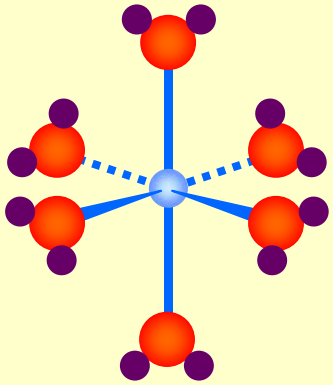


Rq. : For d^n with n > 1

→ Interelectronic correlations must be taken into account

→Tanabe-Sugano diagrams (spectroscopic terms)

3 – UNDERSTANDING OF COLORS FROM BANDS



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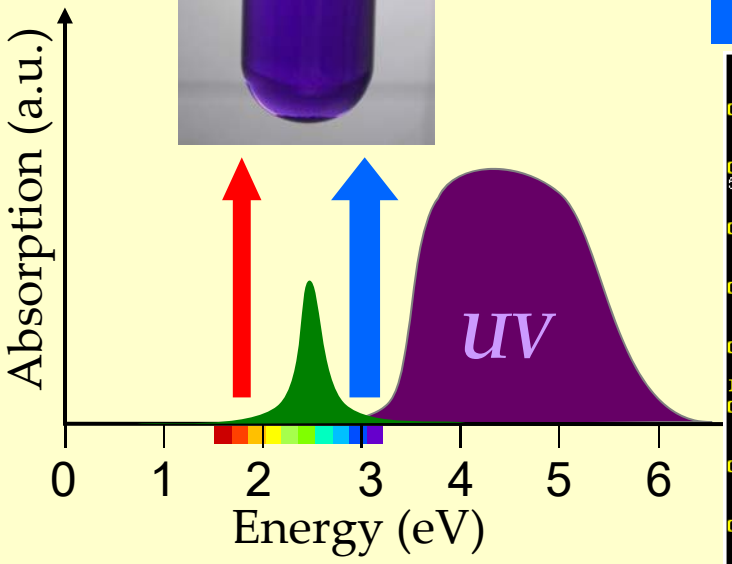

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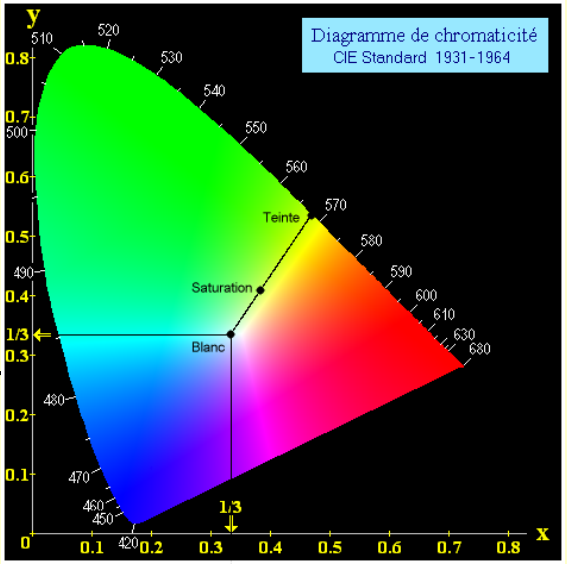

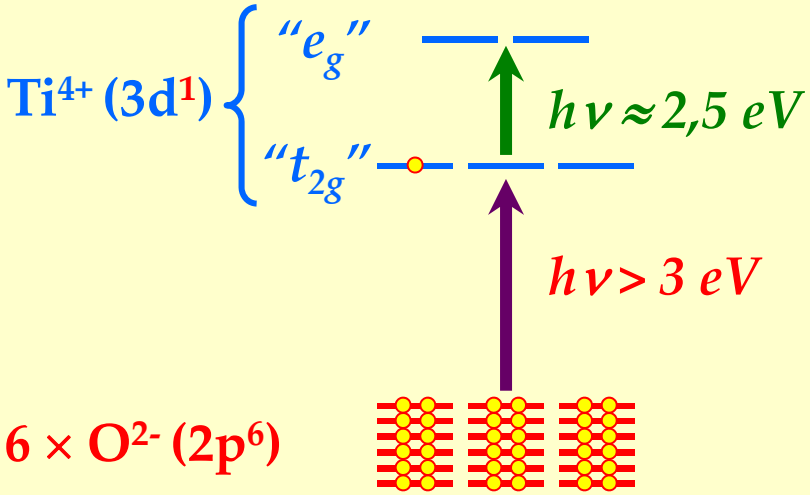

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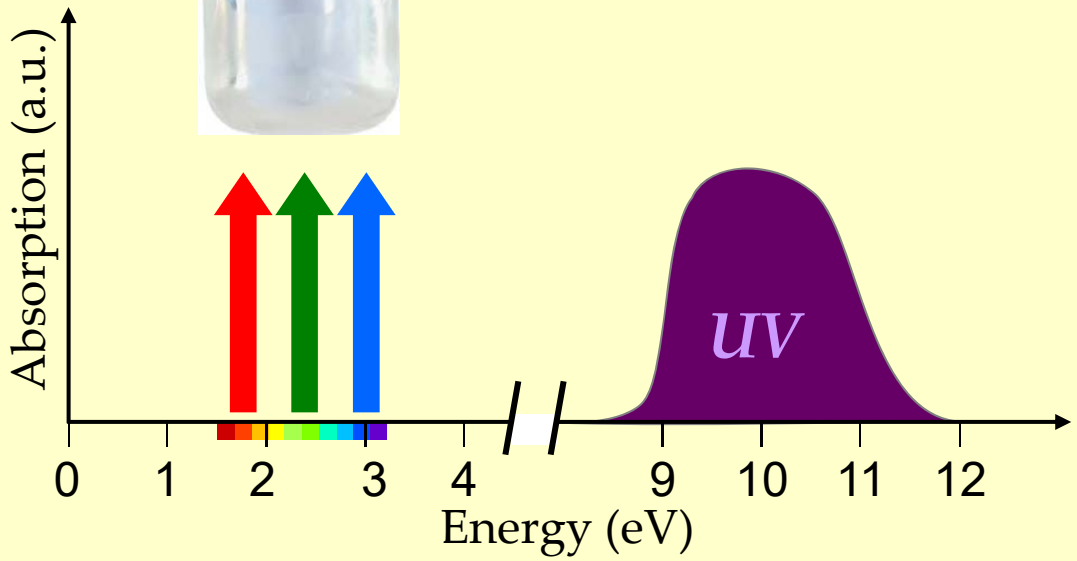
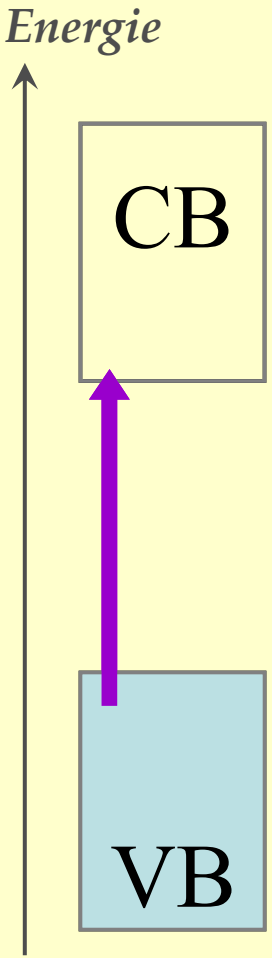
3 – UNDERSTANDING OF COLORS FROM BANDS

Alumine corindon (Al_2O_3)



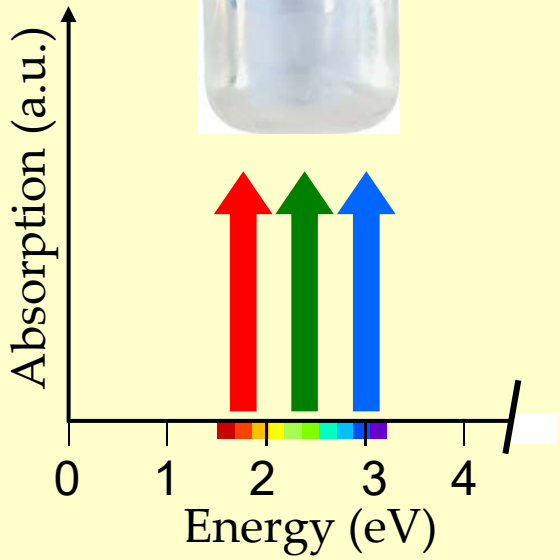


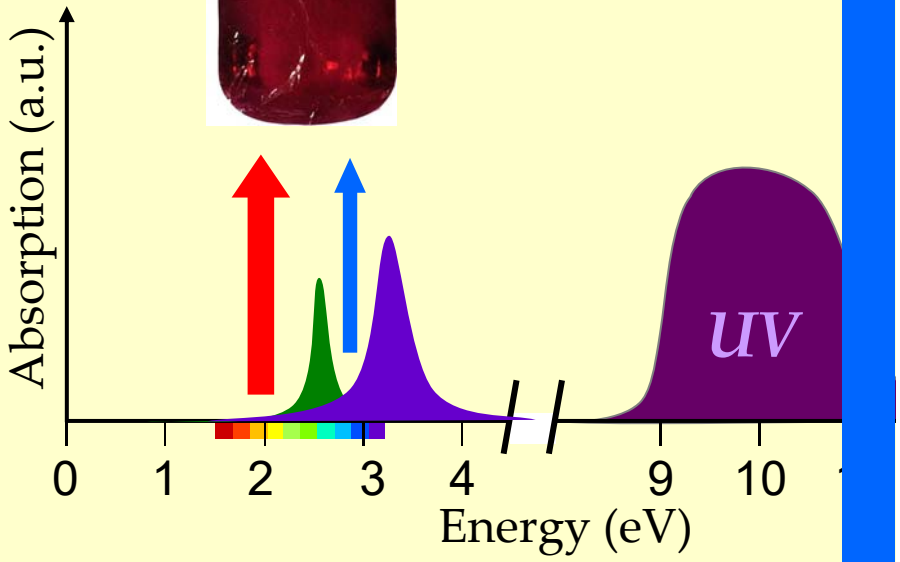
3 – UNDERSTANDING OF COLORS FROM BANDS

Alumine corindon (Al_2O_3)

+ 1% Cr^{3+}

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





3 – UNDERSTANDING OF COLORS FROM BANDS

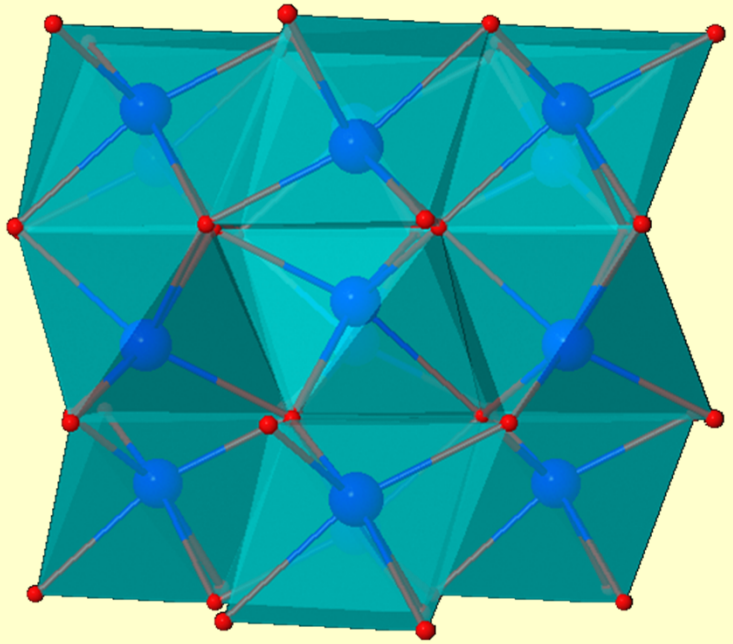
Rubis
(Al_2O_3:1%Cr^{3+})

Impurity (d-d)
→ color

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

→ Interelectronic correlations must be taken into account

→Tanabe-Sugano diagrams (spectroscopic terms)



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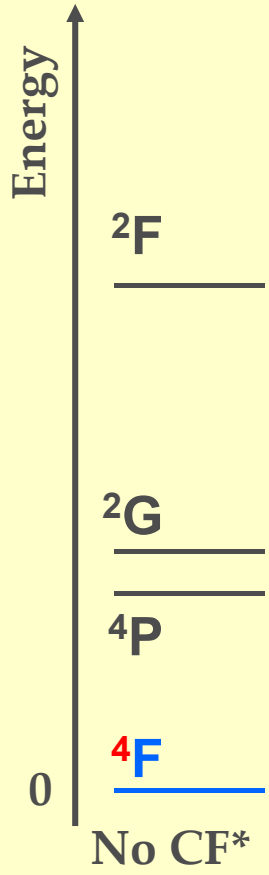
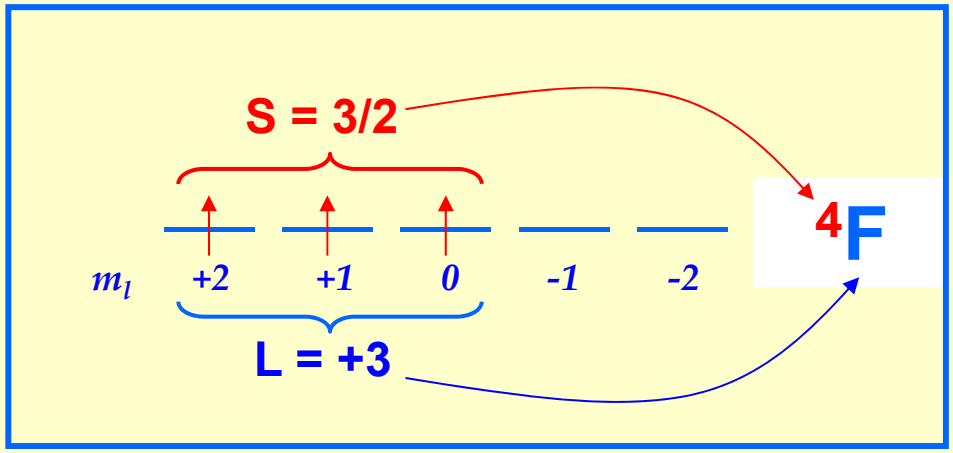


Free ion: we define the spectroscopic terms :

Multiplicity of spin → 2S+1X



*CF : Cristal Field

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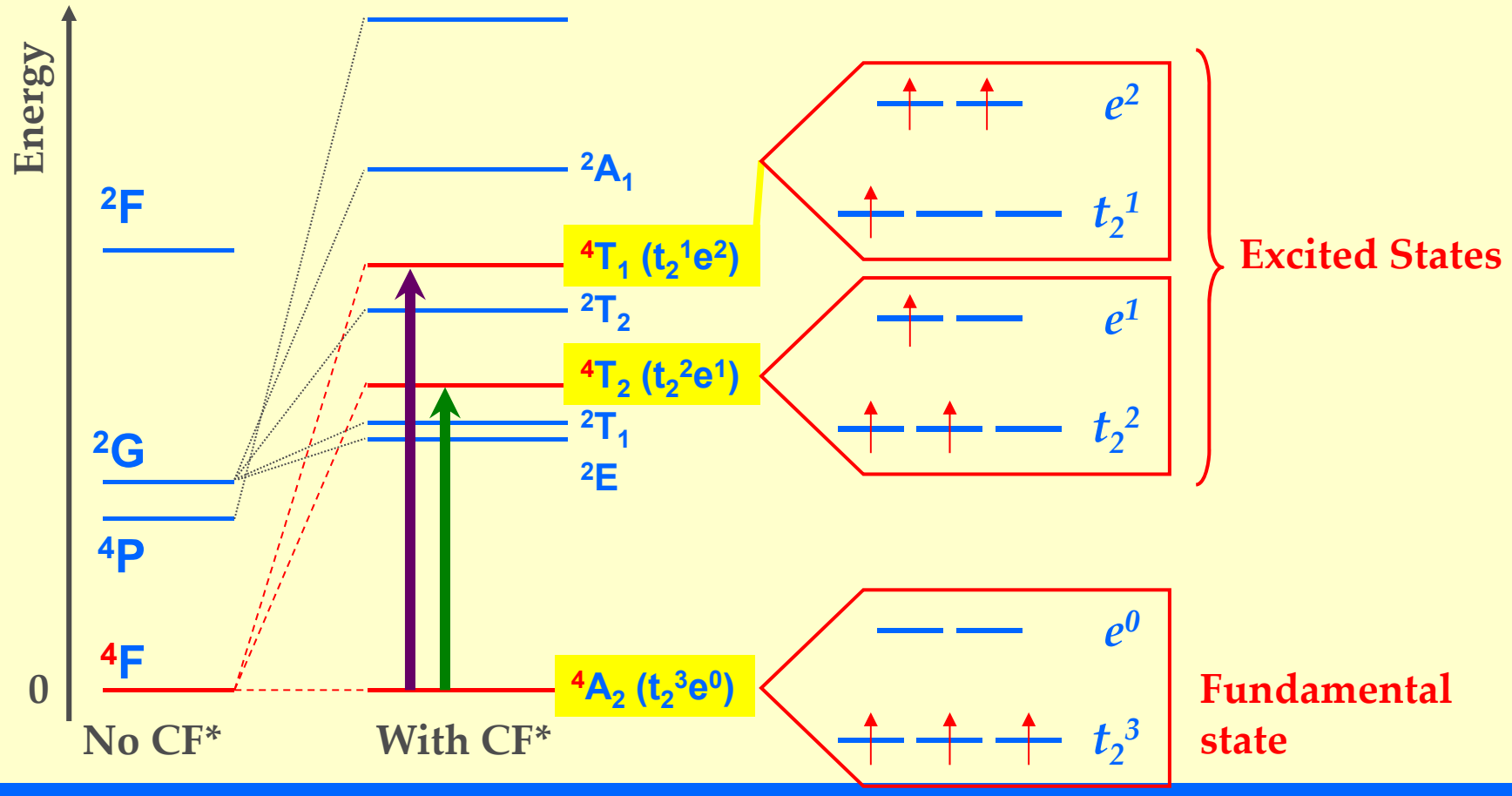
Rubis
(Al_2O_3:1%Cr^{3+})

Impurity (d-d) → color

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

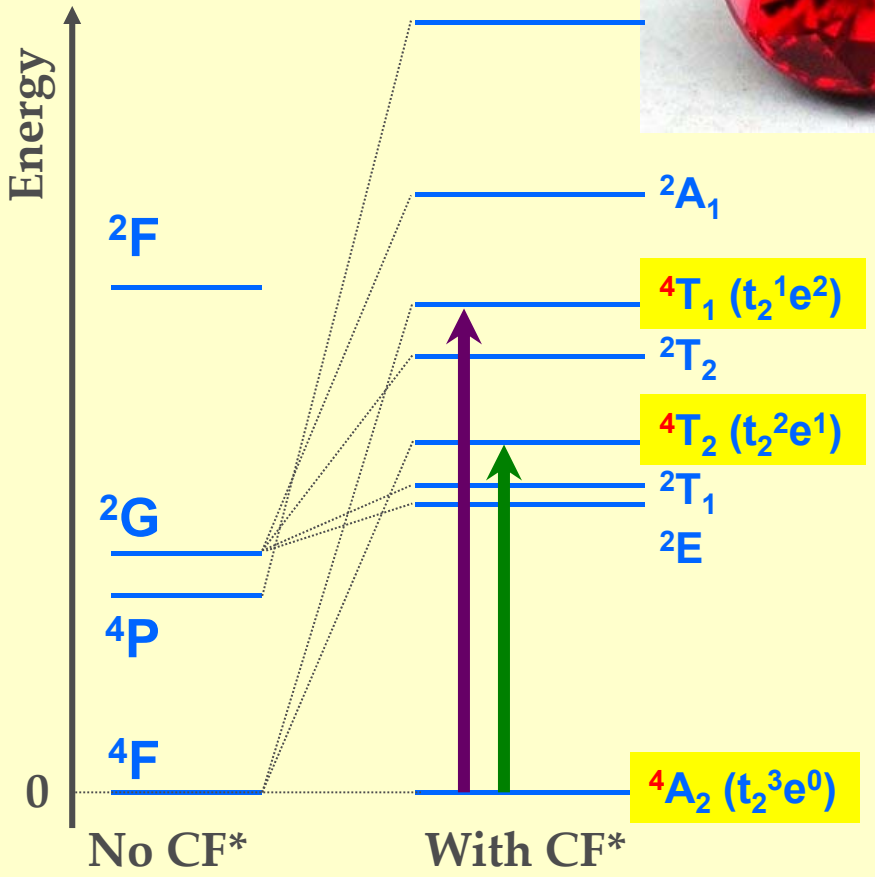
→ Degeneracy lifting due to the octahedral crystal field effect created by the ligands



*CF : Cristal Field

3 – UNDERSTANDING OF COLORS FROM BANDS

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

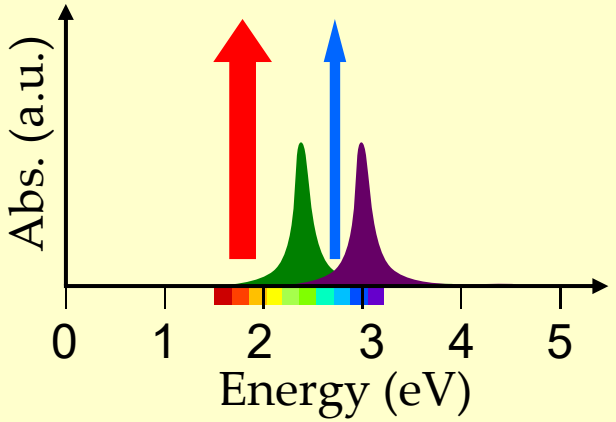


Impurity (d-d) → color

Red color

+

Slightly blue



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

→ Interelectronic correlations must be taken into account

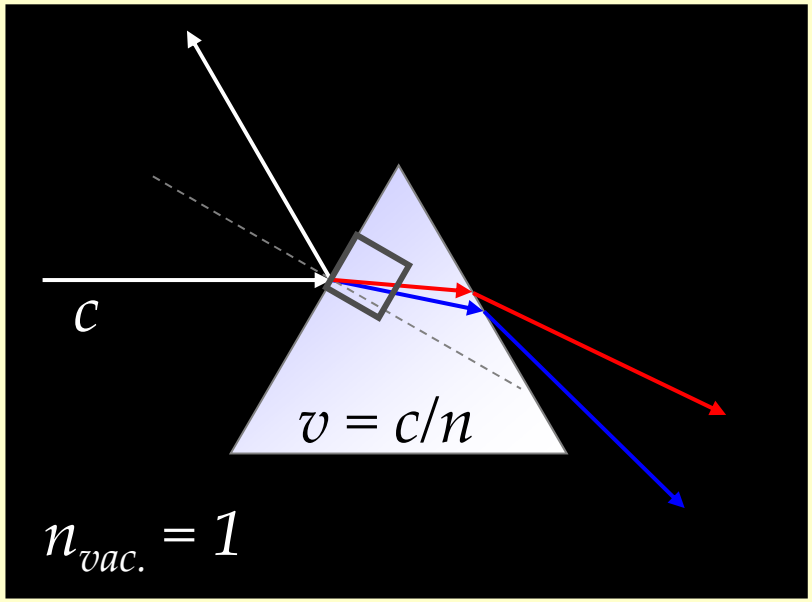
→Tanabe-Sugano diagrams (spectroscopic terms)

*CC : Champ Cristallin

4 – LIGHT-MATTER INTERACTION

Physical color → « Elastic diffusion »

Example of a prism



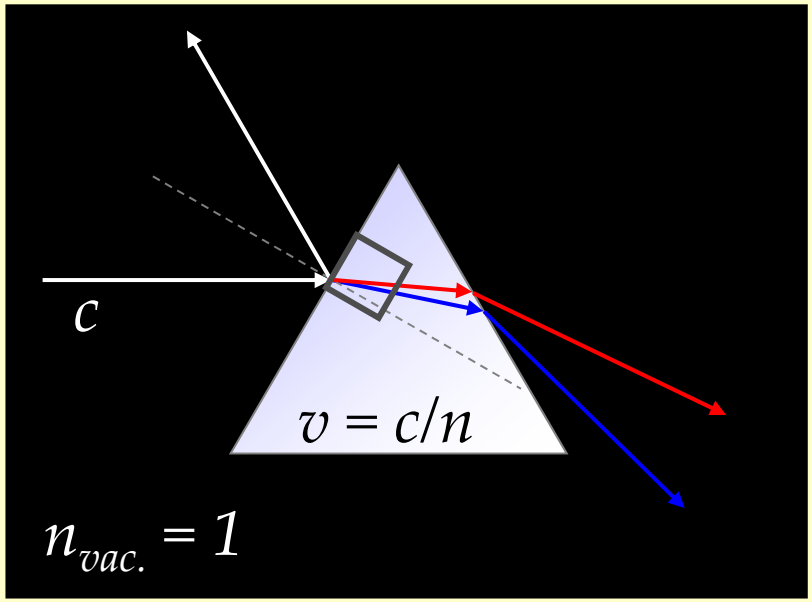
n : index of refraction

Propagation speed is changed

4 – LIGHT-MATTER INTERACTION

Physical color → « Elastic diffusion »

Example of a prism

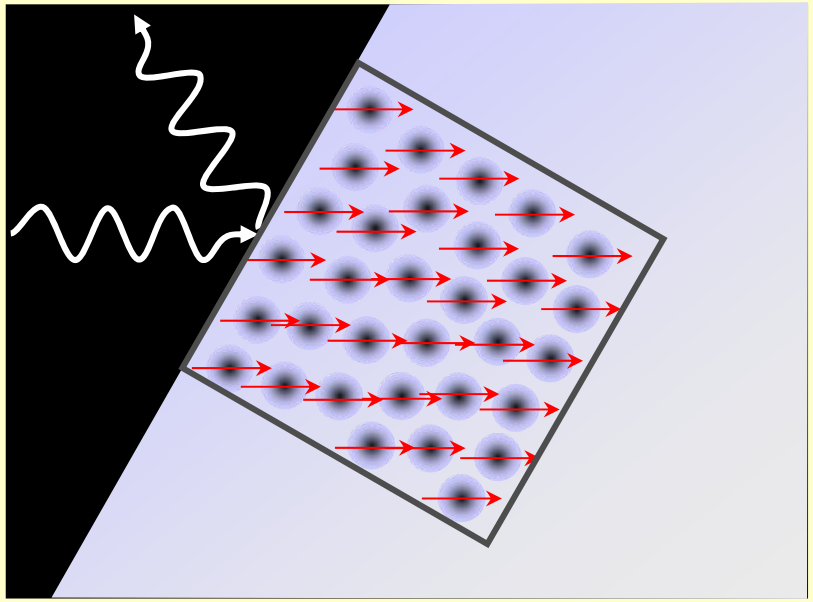


n : index of refraction

Propagation speed is changed

Elastic diffusion mechanism

at the atomic level



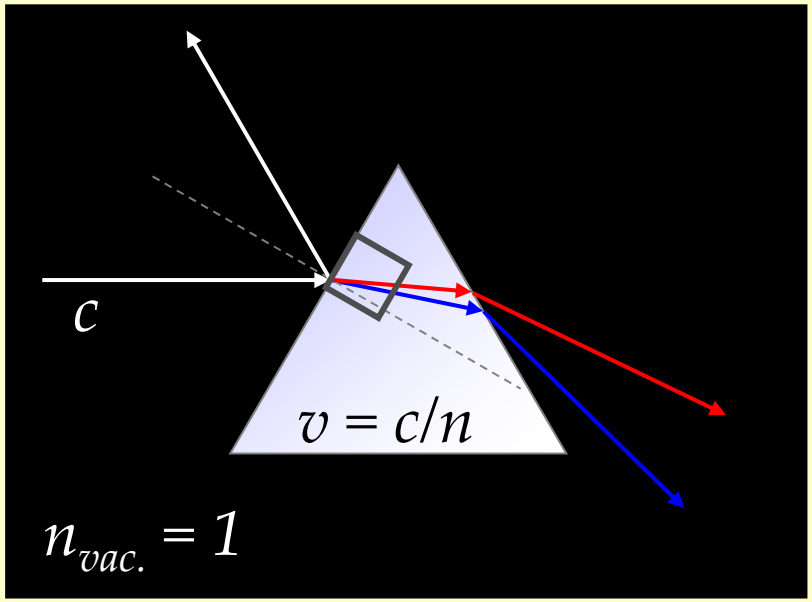
→ *: Inductive dipole moment ⇔*
Receiver-transmitter ***antenna***

Succession of absorption and emission

4 – LIGHT-MATTER INTERACTION

Physical color → « Elastic diffusion »

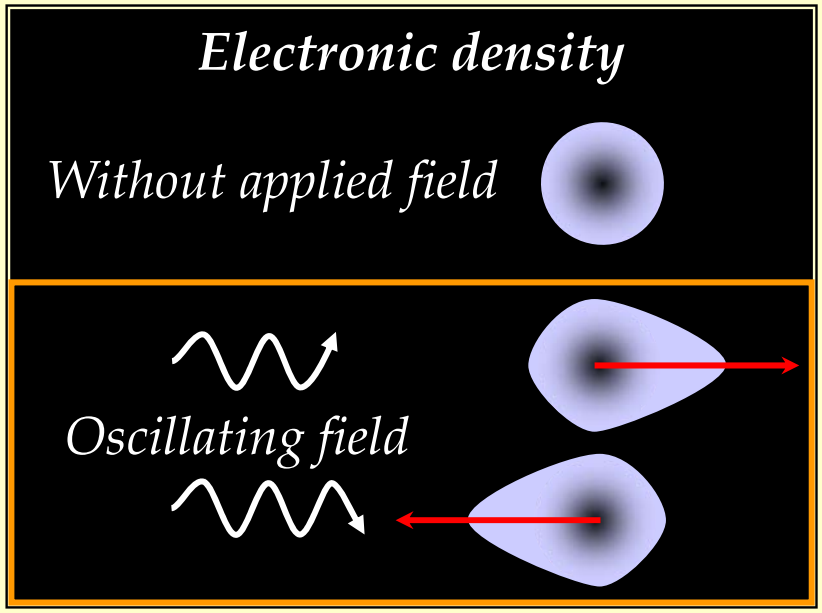
Example of a prism



Dipole moment

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

Elastic diffusion mechanism at the electronic level



***Oscillating Electric Field** polarize ρ*

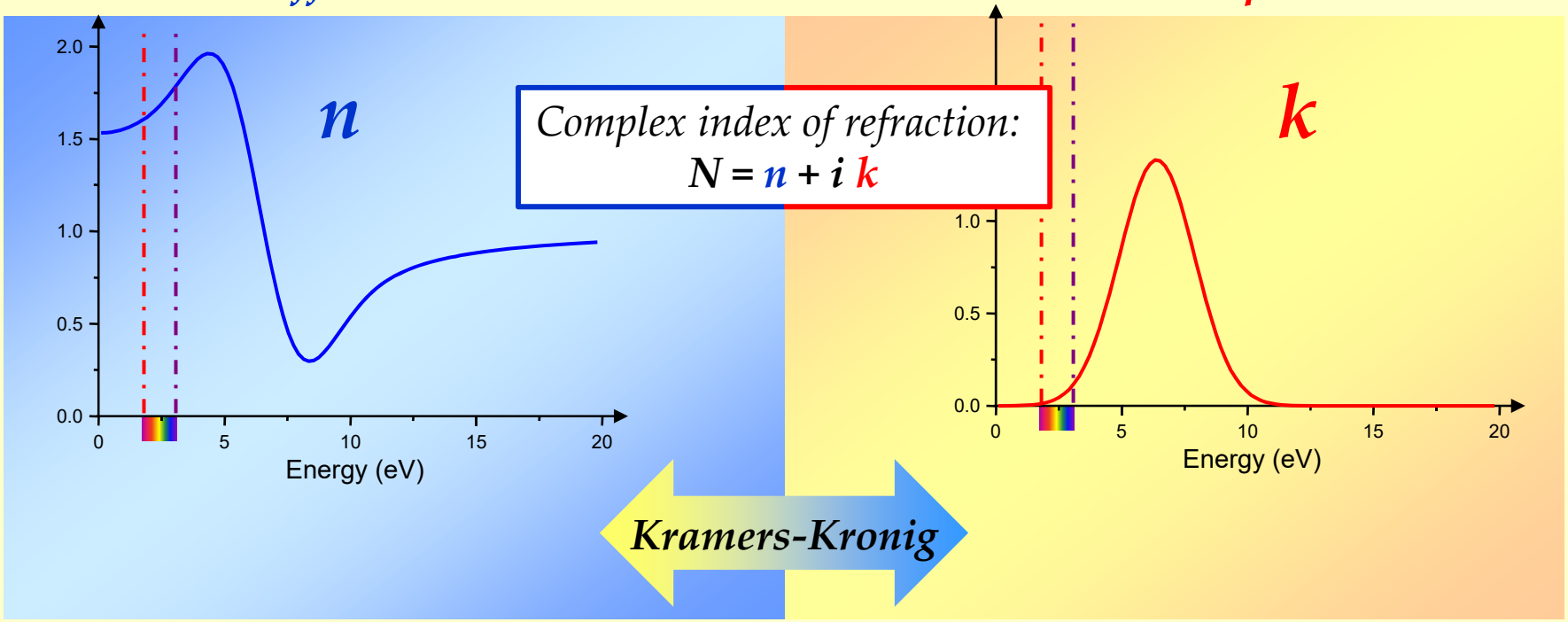
→ *: Inductive dipole moment ⇔ Receiver-transmitter **antenna***

Succession of absorption and emission

4 – LIGHT-MATTER INTERACTION

Diffusion

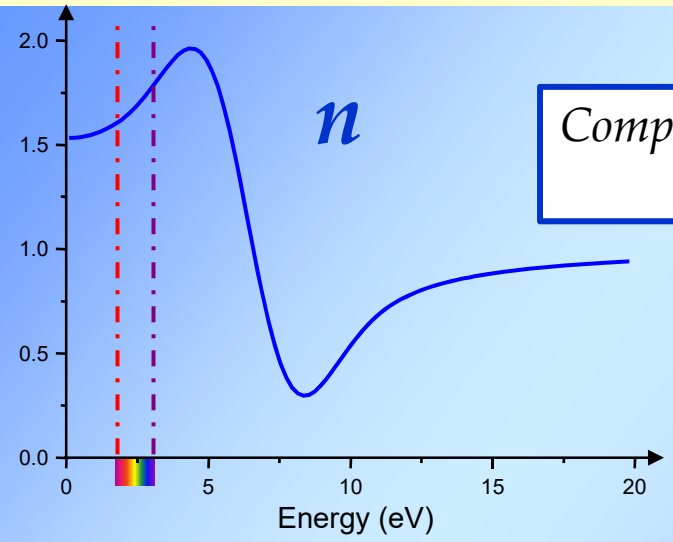
Absorption

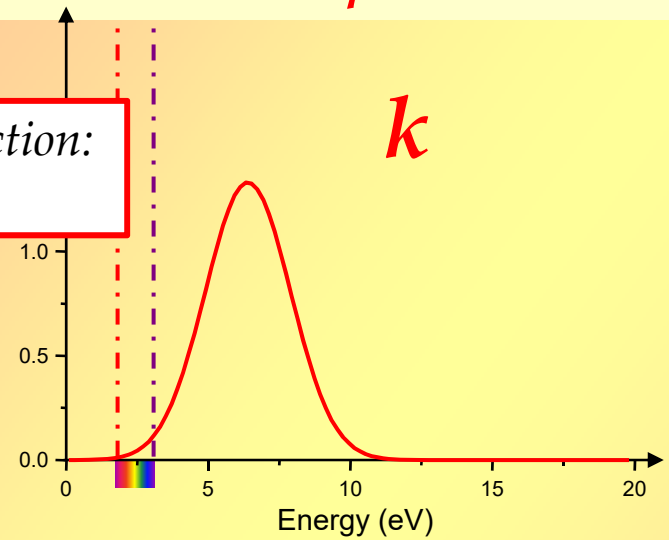


4 – LIGHT-MATTER INTERACTION

Diffusion

Absorption

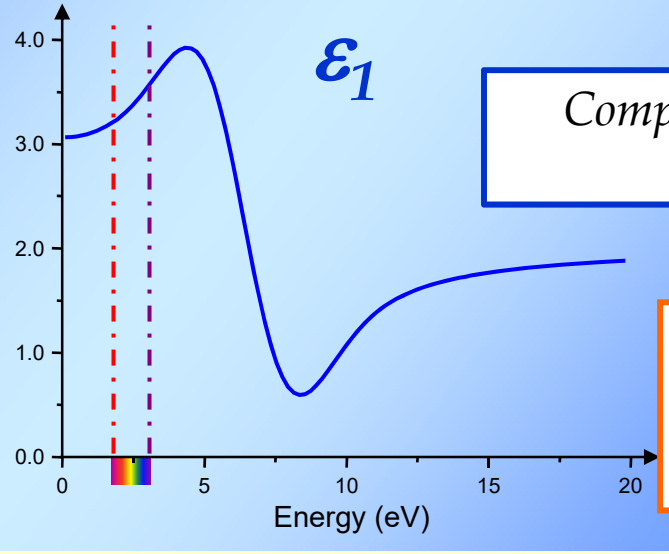


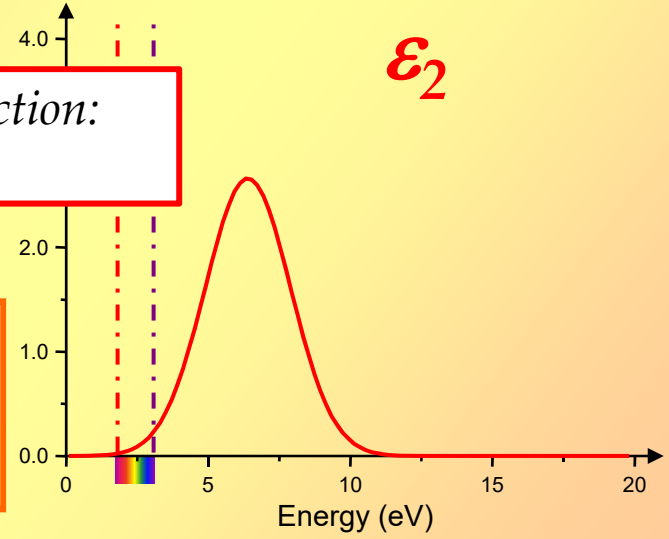


Complex index of refraction:

$N = n + i\,k$

Kramers-Kronig





Complex dielectric function:

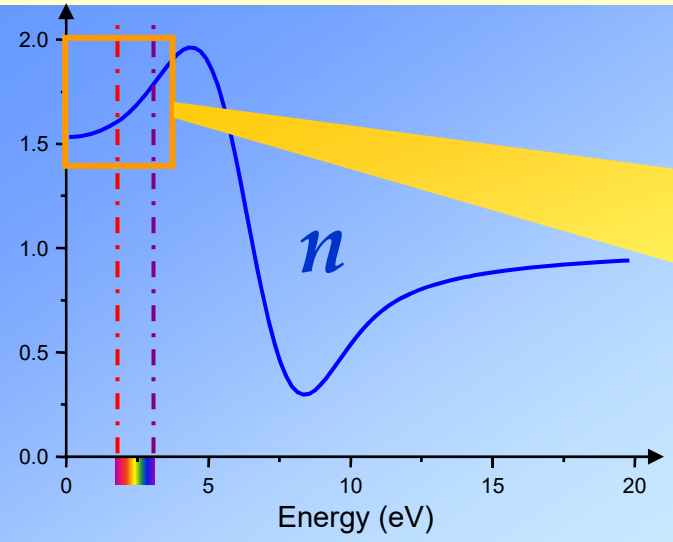
$\varepsilon = \varepsilon_1 + i\,\varepsilon_2$

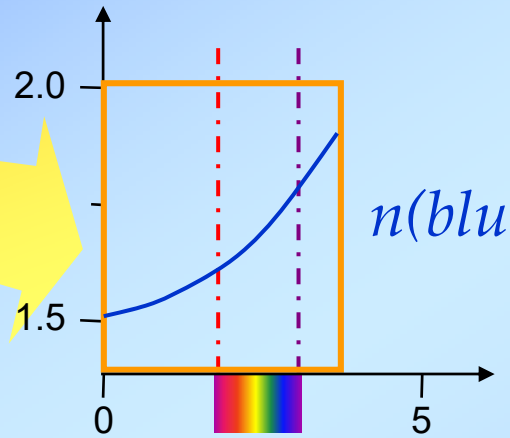
$\varepsilon_1 = n^2 - k^2$

$\varepsilon_2 = 2nk$

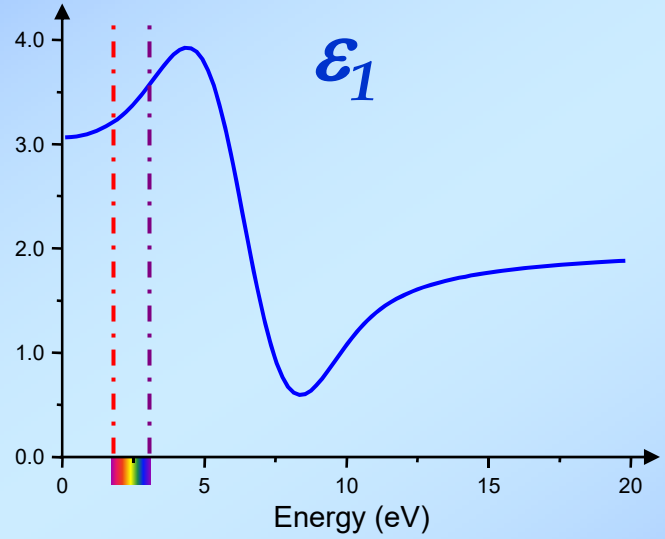
4 – LIGHT-MATTER INTERACTION

Diffusion in the case of a prism



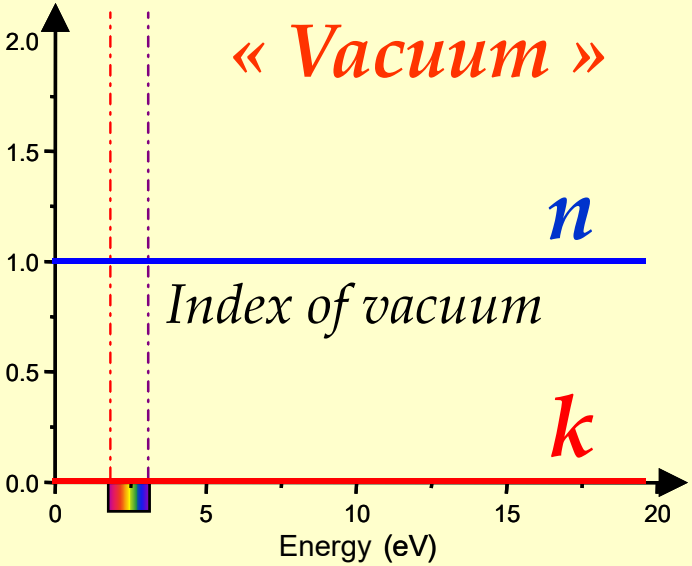


$n(blue) > n(red)$



4 – LIGHT-MATTER INTERACTION

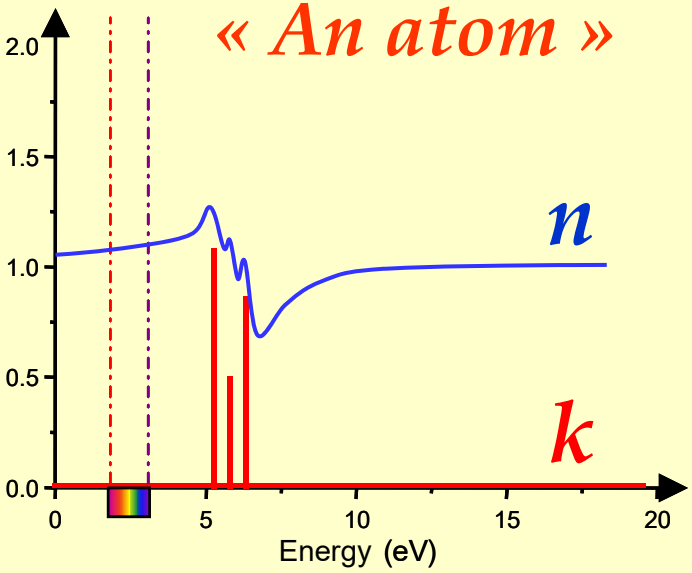
« Vacuum »



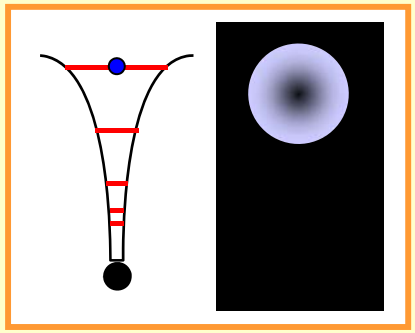
Index of refraction :
n = 1

No Absorption

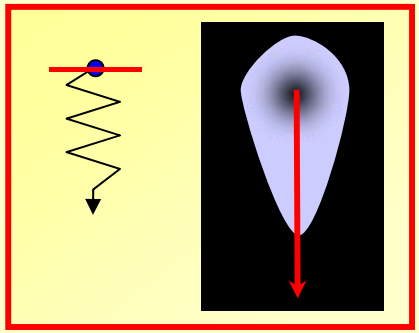
« An atom »



Without applied electric field

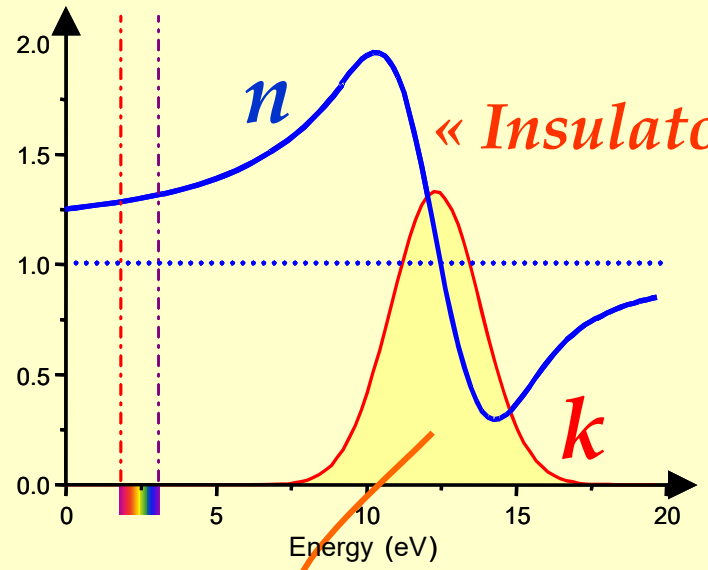


Answer to an applied electric fied

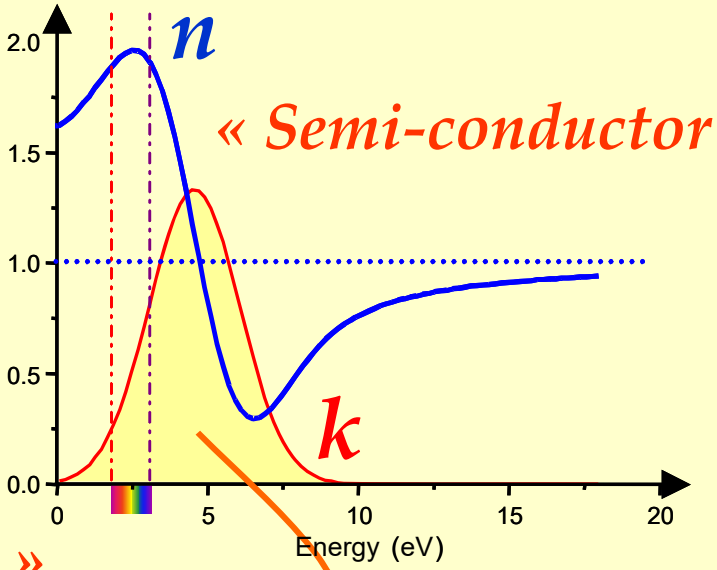


« Spring »

4 – LIGHT-MATTER INTERACTION



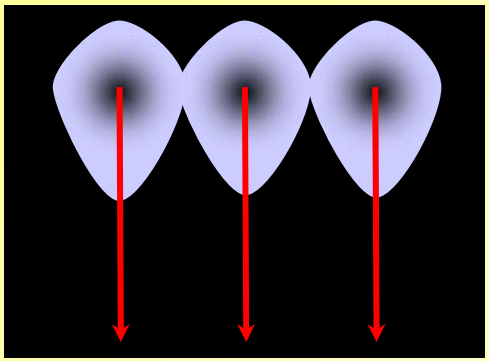
« Insulator »



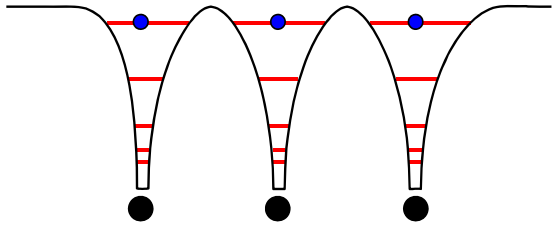
« Semi-conductor »

« Insulator »

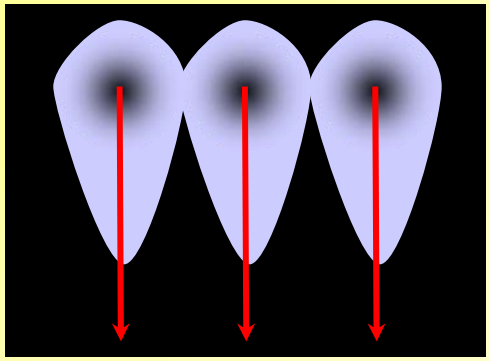
« Semi-conductor »



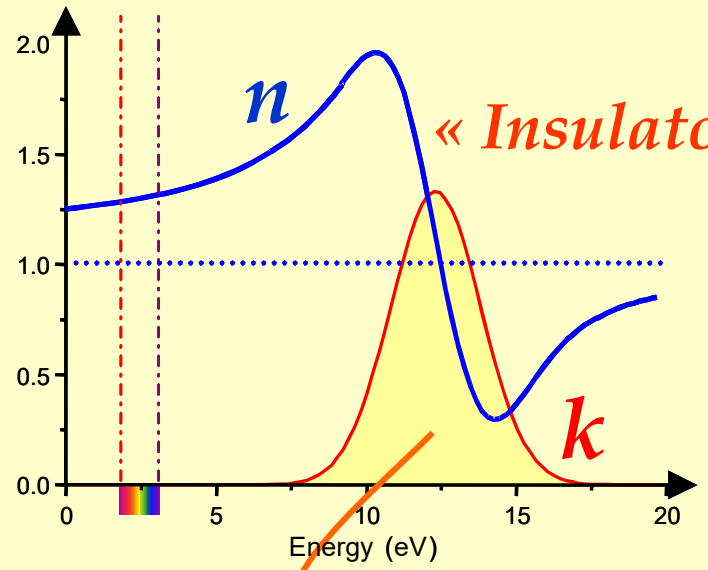
Bounded electrons



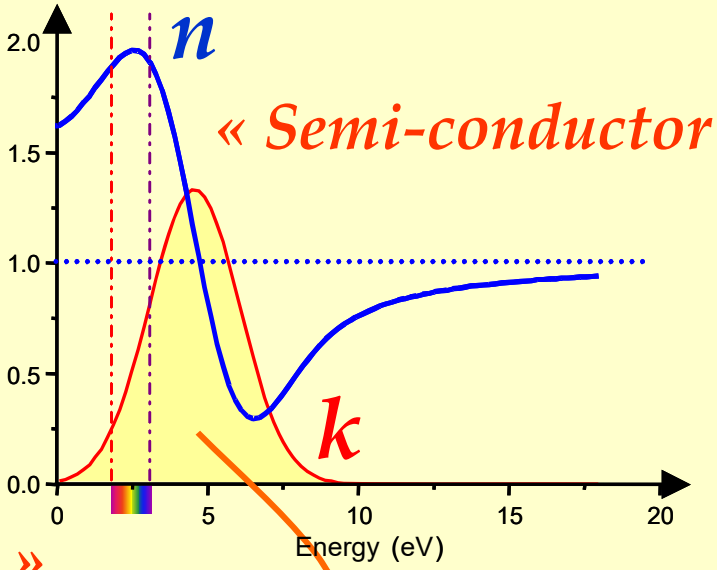
Electrostatic Potential of the nuclei



4 – LIGHT-MATTER INTERACTION



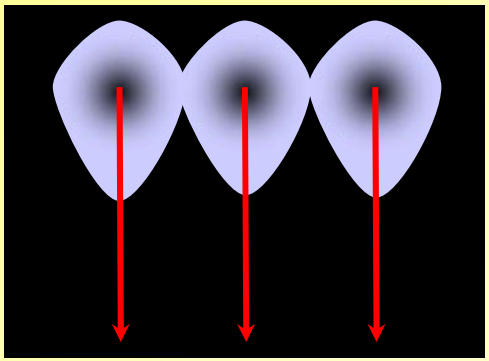
« Insulator »

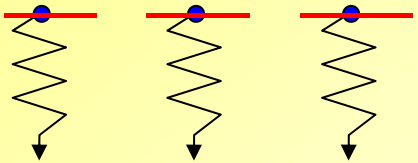


« Semi-conductor »

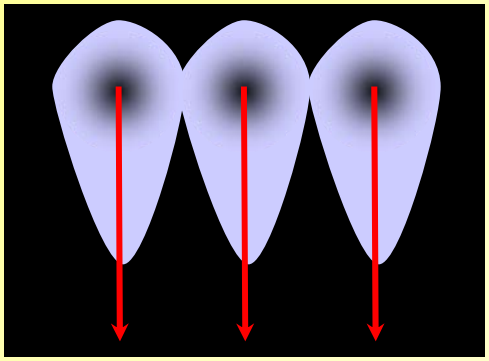
« Insulator »

« Semi-conductor »

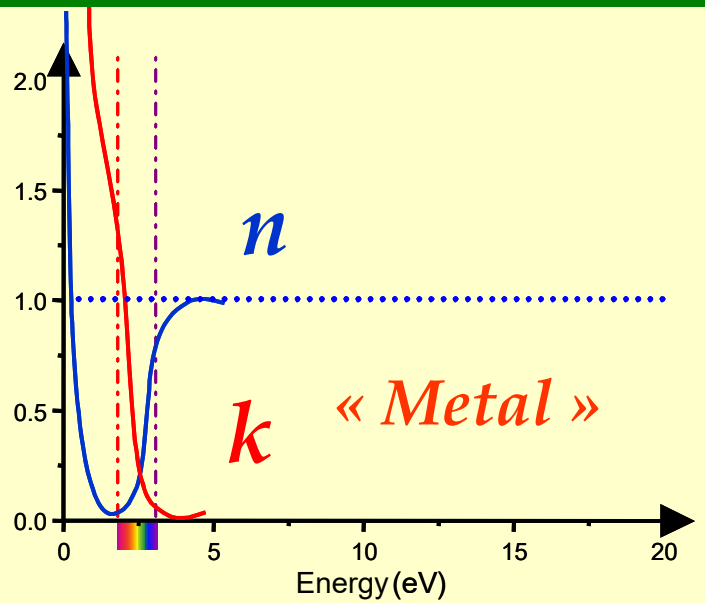


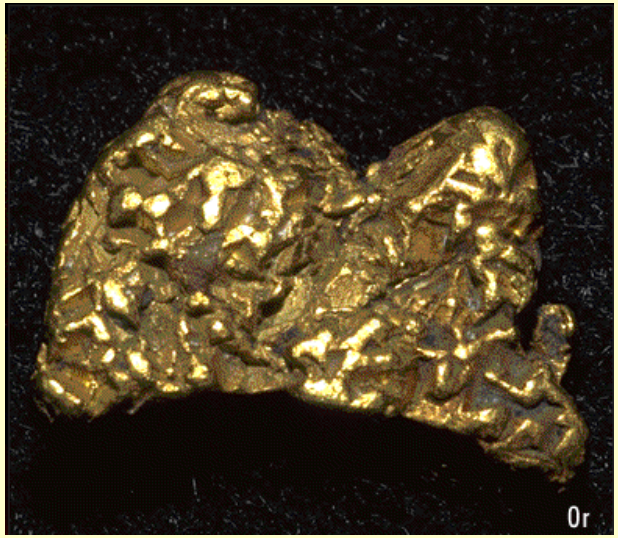


« Interior-sprung Mattress »



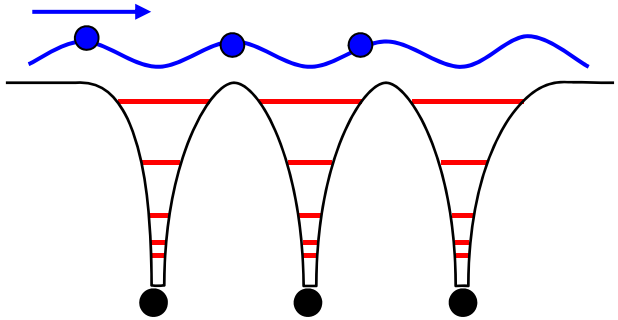
4 – LIGHT-MATTER INTERACTION



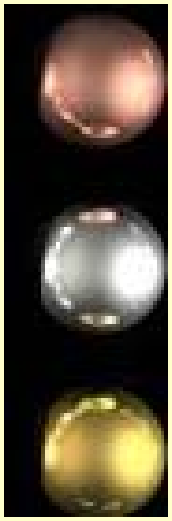


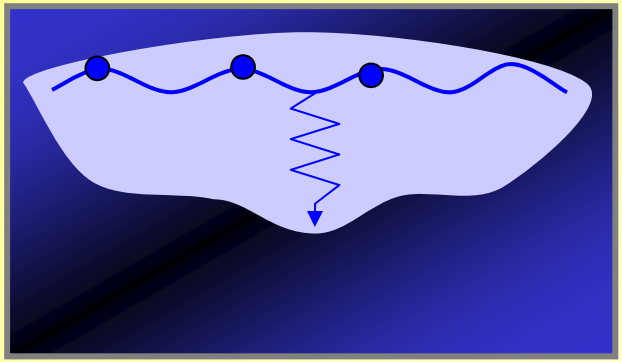
Collective answer of an optical excitation

Conduction electron



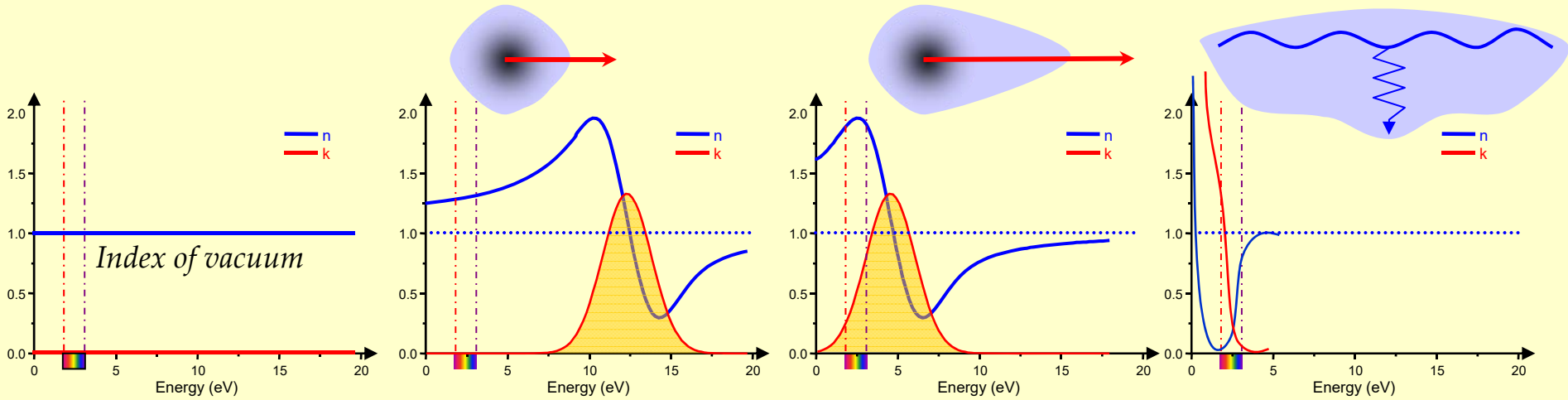
Electrostatic Potential of the nuclei





« *Springboard* »

4 – LIGHT-MATTER INTERACTION



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

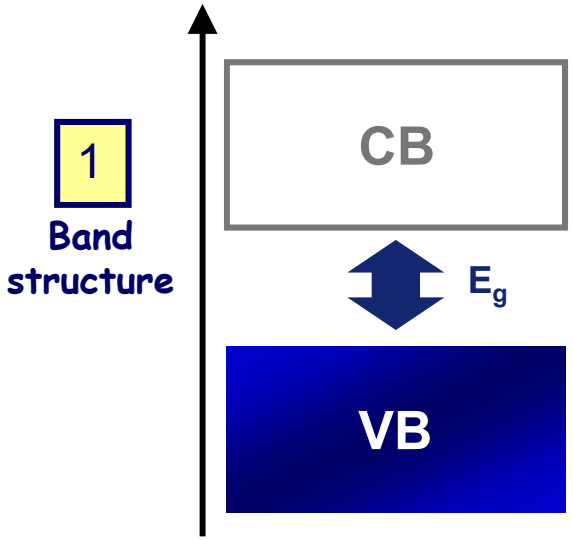
Electron more and more free

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?

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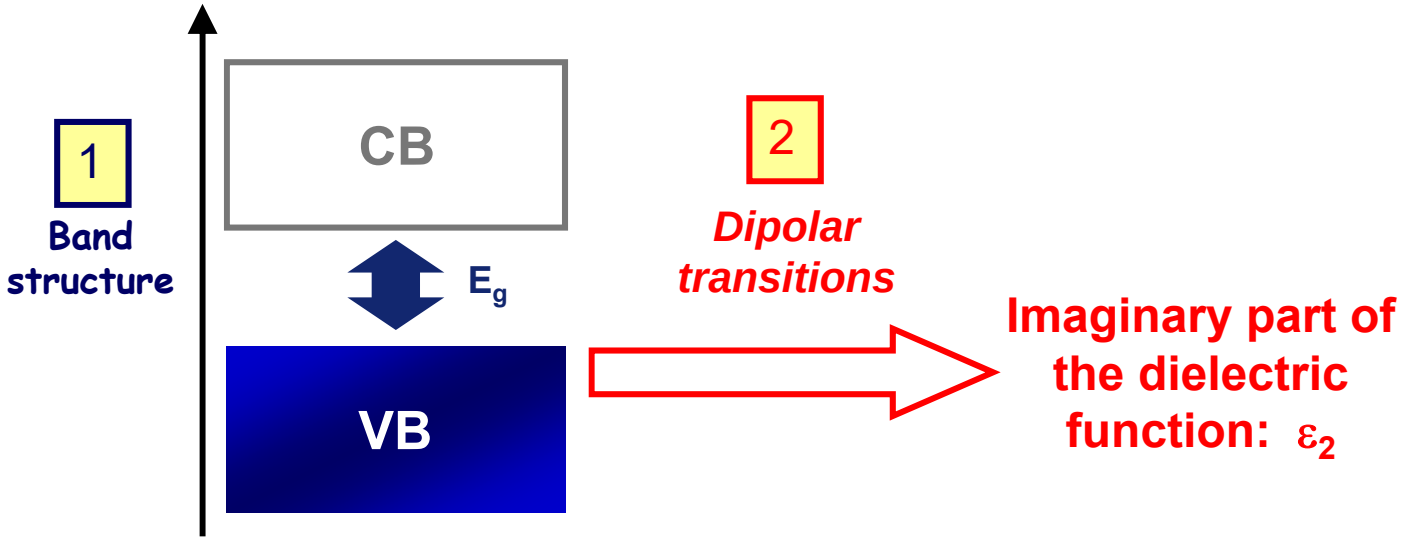

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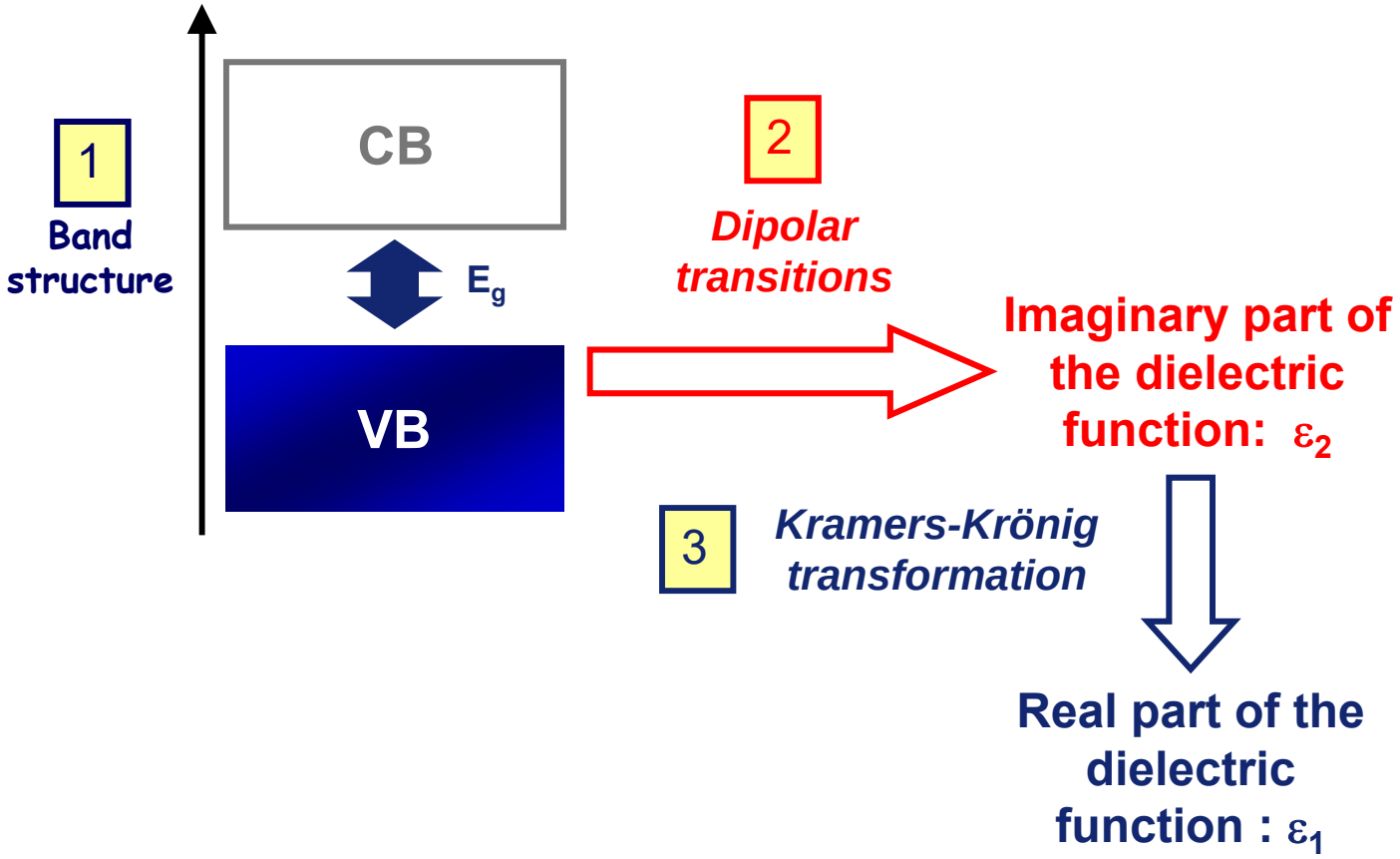
The different steps to calculate the optical properties:



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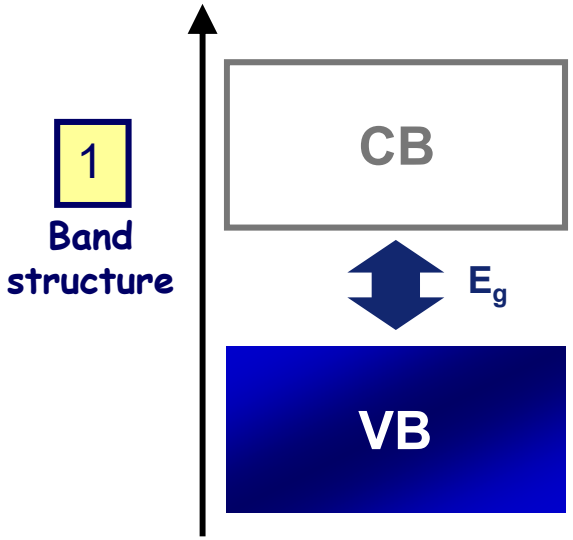


2

Dipolar transitions

Imaginary part of the dielectric function: ε_2

3 *Kramers-Krönig transformation*

Real part of the dielectric function : ε_1

4

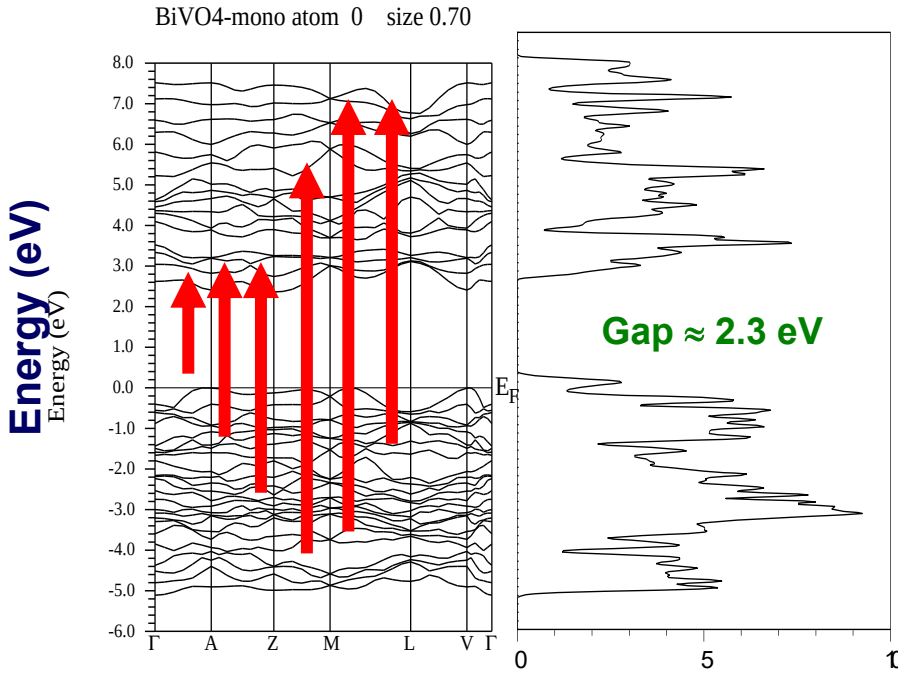
Determination pf n = f(E) & k = f(E)

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

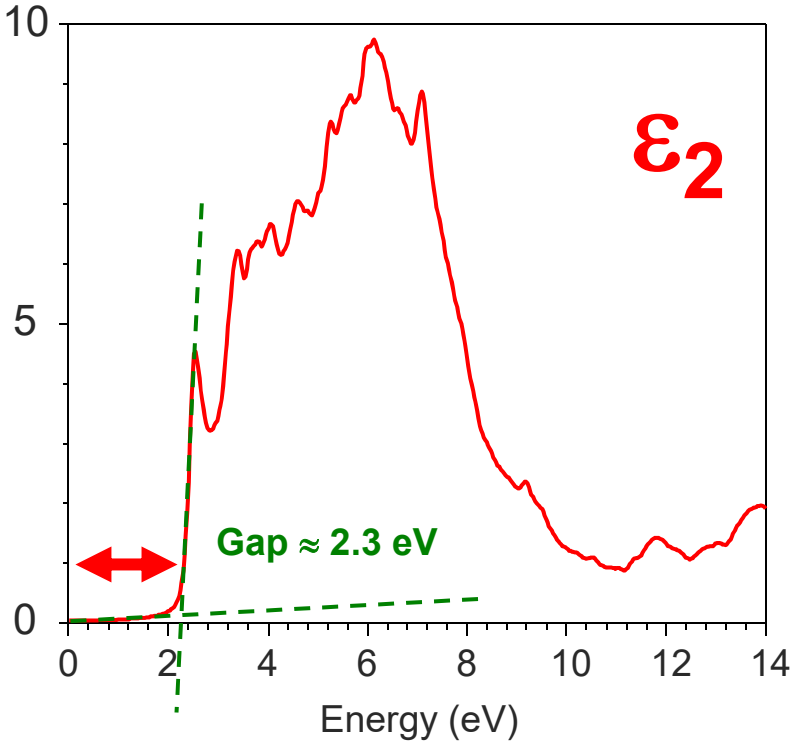
$$\varepsilon_2 = 2nk$$

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

Example of $BiVO_4$



Band structure **DOS**

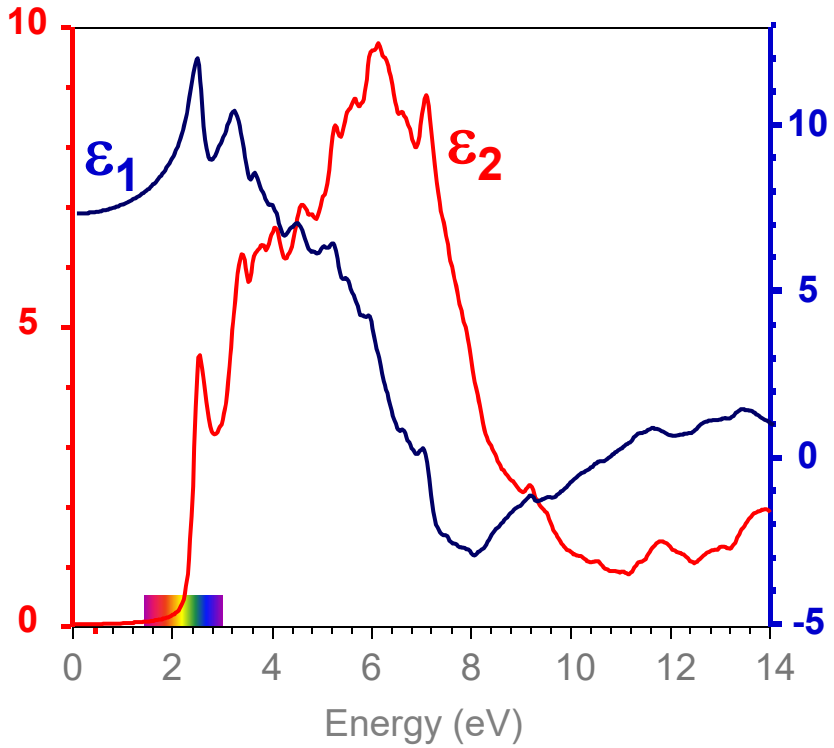


1 **Band structure calculation**

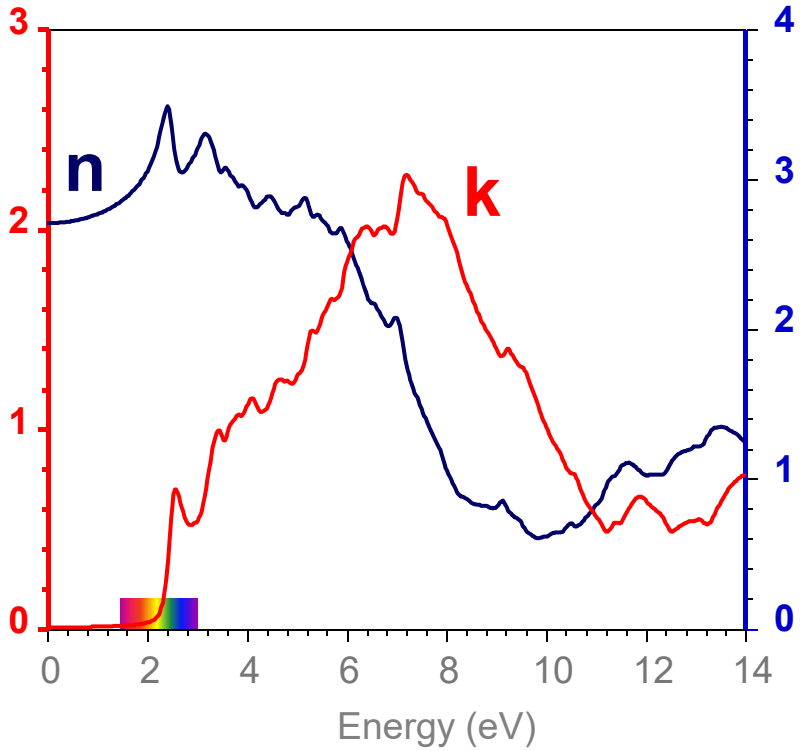
2 **Determination of ε_2**

5 – OPTICAL PROPERTIES: WHICH TREATMENT?

Example of $BiVO_4$



3 **Determination of ε_1**

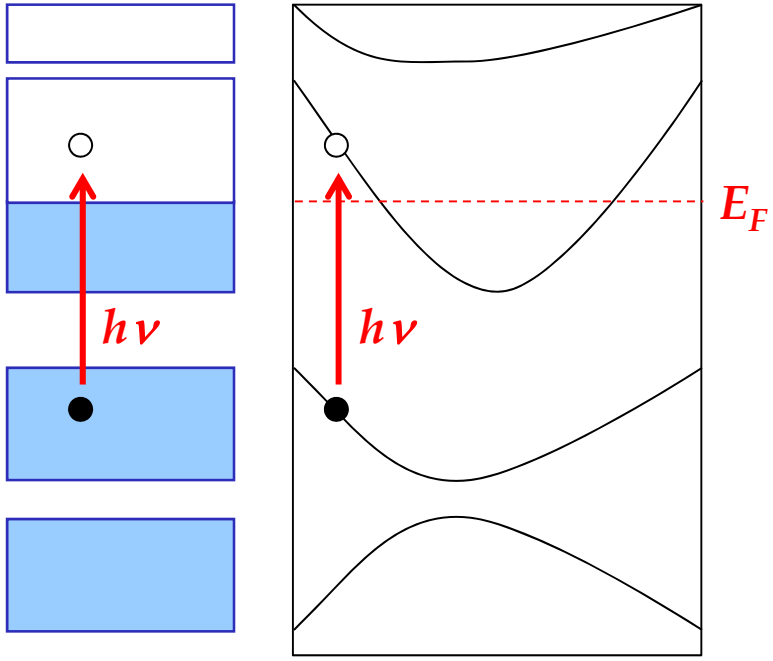


4 ***Determination of n = f(E) & k = f(E)***

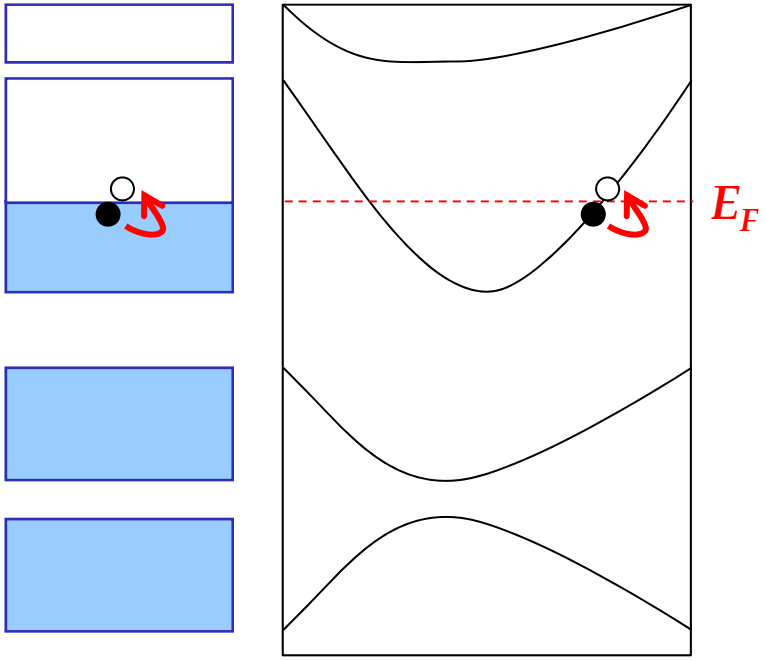
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

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)



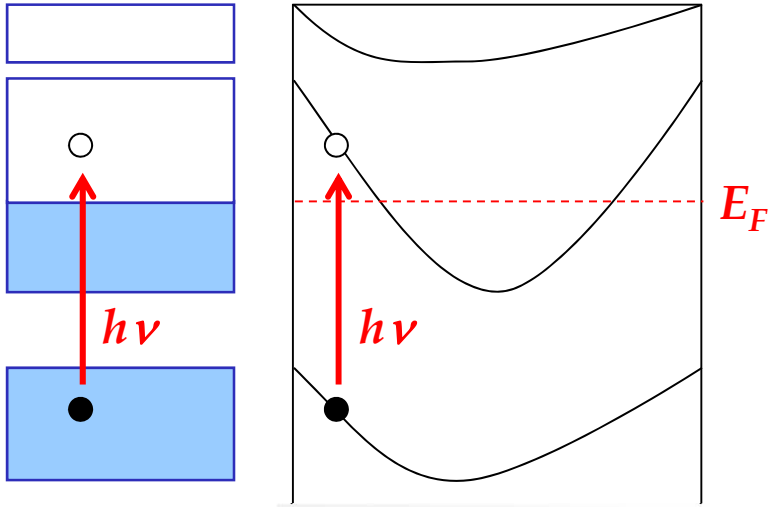
→ Dielectric tensor / Optical conductivity / Refractive index / Reflectivity / Absorption coefficient / Loss function (EELS)

**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)

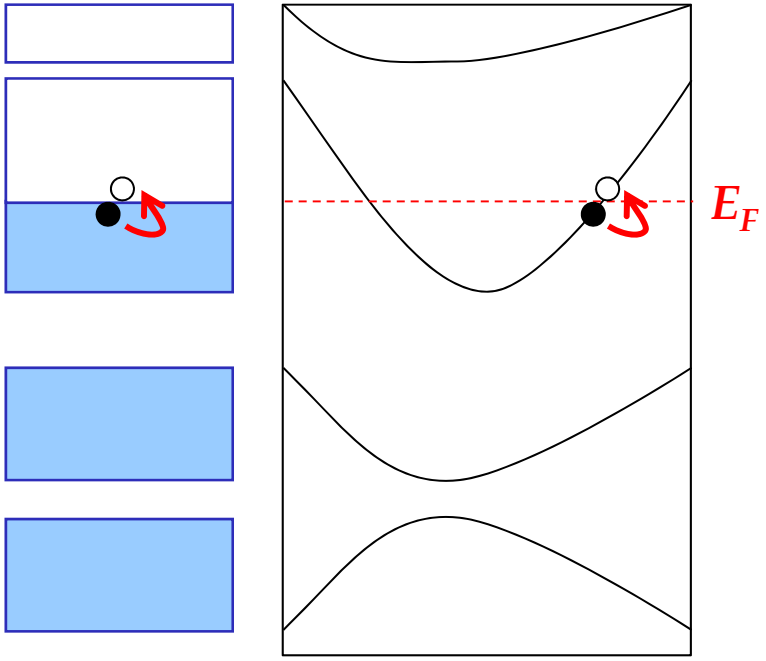
In WIEN2k, two types of contributions to the dielectric function ($\varepsilon = \varepsilon_1 + i.\varepsilon_2$) could be estimated:

intraband: Drude model,
(ω_p: plasma frequency)

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

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

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

- 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

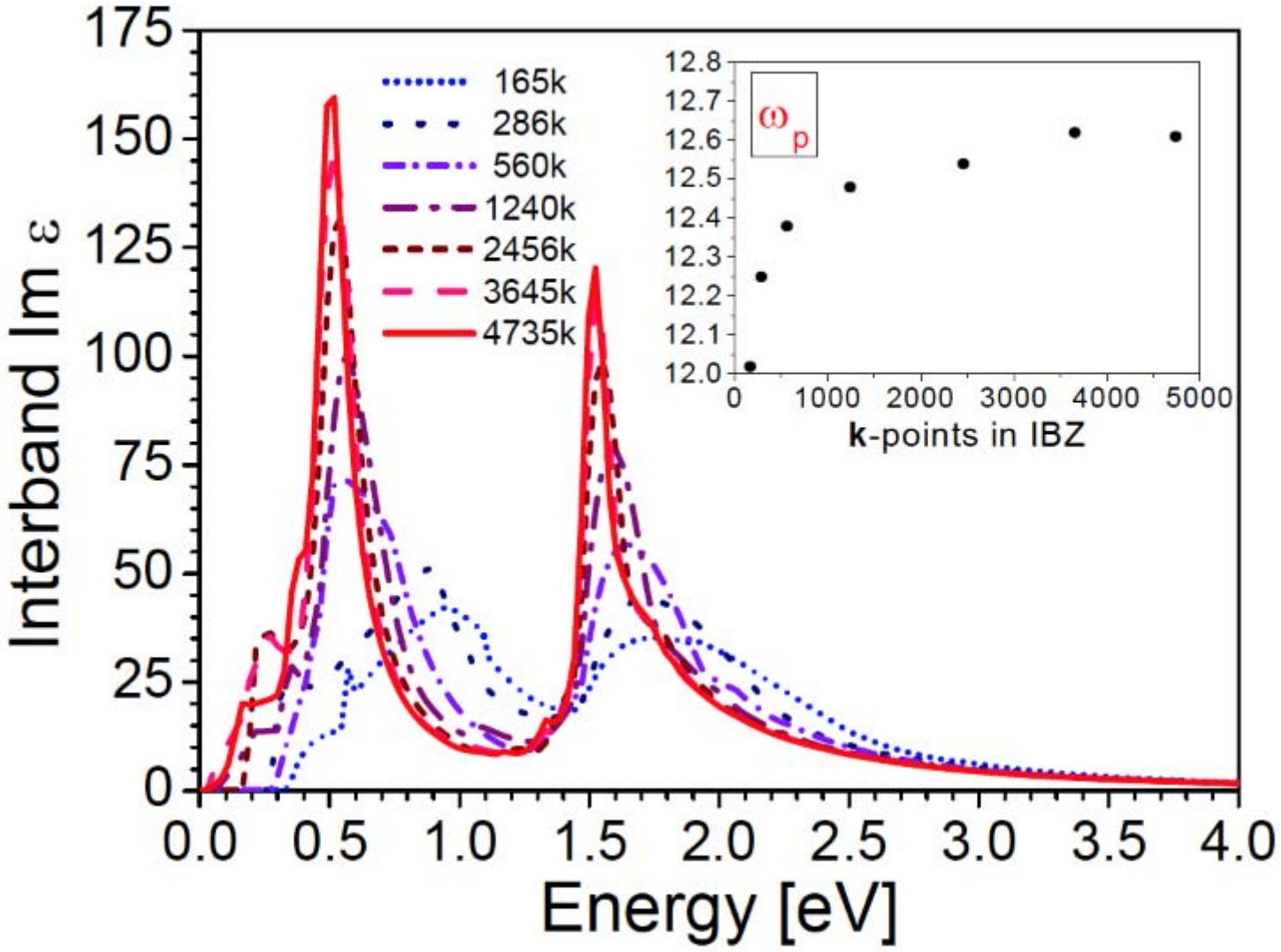
$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

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

0. normal SCF run ⟶ converged density

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

2. x lapw1 *-options* ⟶ eigenvectors on dense mesh

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)**

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

7. **opticplot**

5 – SOME ADDITIONAL DETAILS

spin-polarized calculations

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

procedure for metals

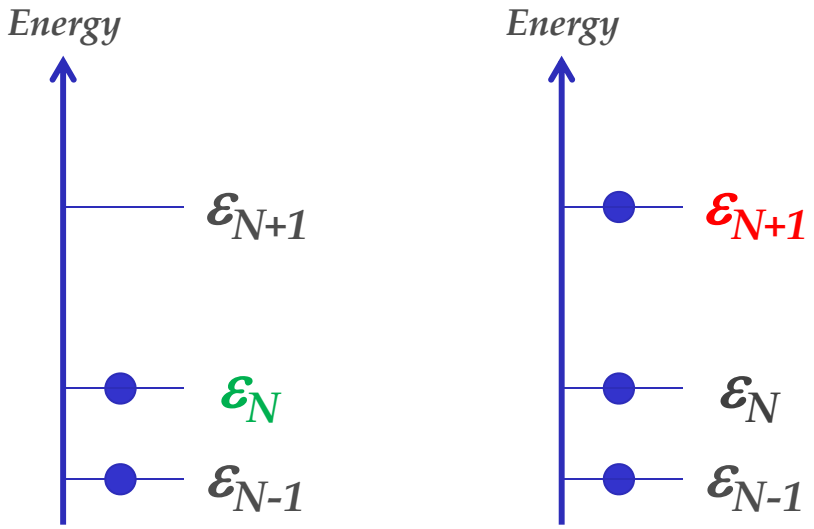
1. `x joint (mode=6)` $\longrightarrow$ plasma frequencies $\omega_{\mathrm{p}ij}$
2. `x joint (mode=4)` $\longrightarrow$ interband $\mathrm{Im}\,\varepsilon$
3. `x kram (intra=1,` insert ω_{p}`)`

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

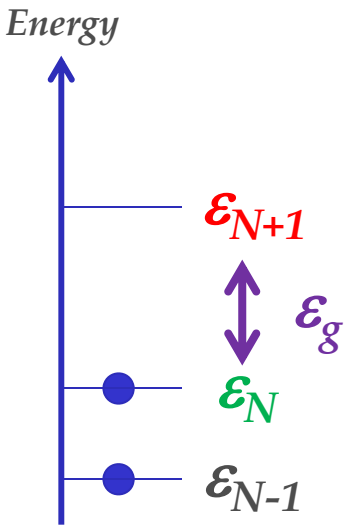
$$\mathrm{Re}\,\varepsilon_{ij} = \delta_{ij} + \frac{2}{\pi}\mathcal{P}\int_0^\infty \mathrm{d}\Omega\,\frac{\Omega}{\Omega^2-\omega^2}\,\mathrm{Im}\,\varepsilon_{ij}$$

5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

The band gap problem → Necessity to go beyond DFT



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



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

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

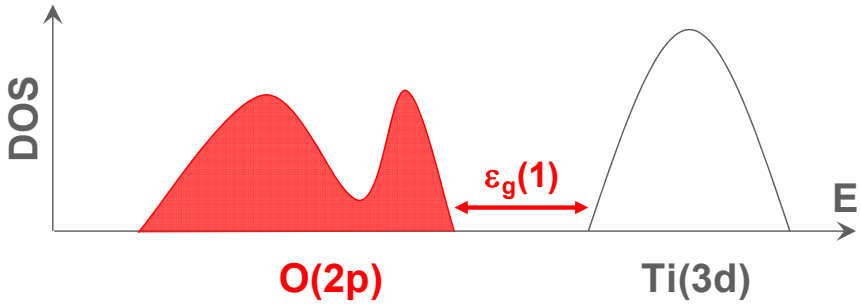
$$E_g = \varepsilon_g + \Delta_{xc} \quad \textit{with } \Delta_{xc} \textit{ : Scissor Operator / GW / hybrid…}$$

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

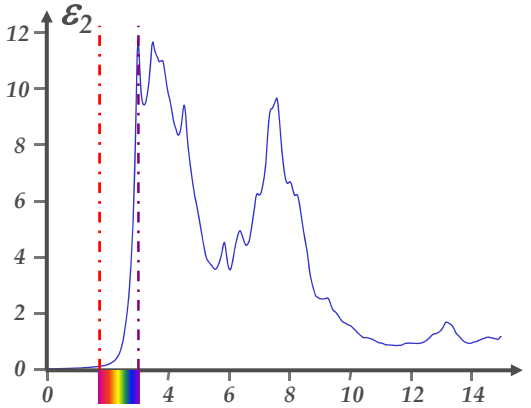
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

Fundamental gap: electronic gap ≠ optical gap

Deduced from the band structure



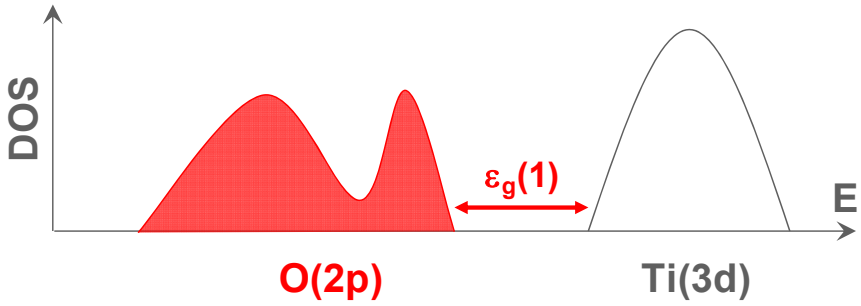
Dipolar transitions



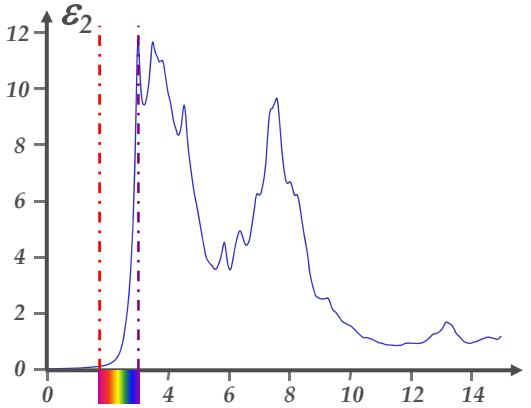
5 – OPTICAL PROPERTIES SIMULATION IN WIEN2k

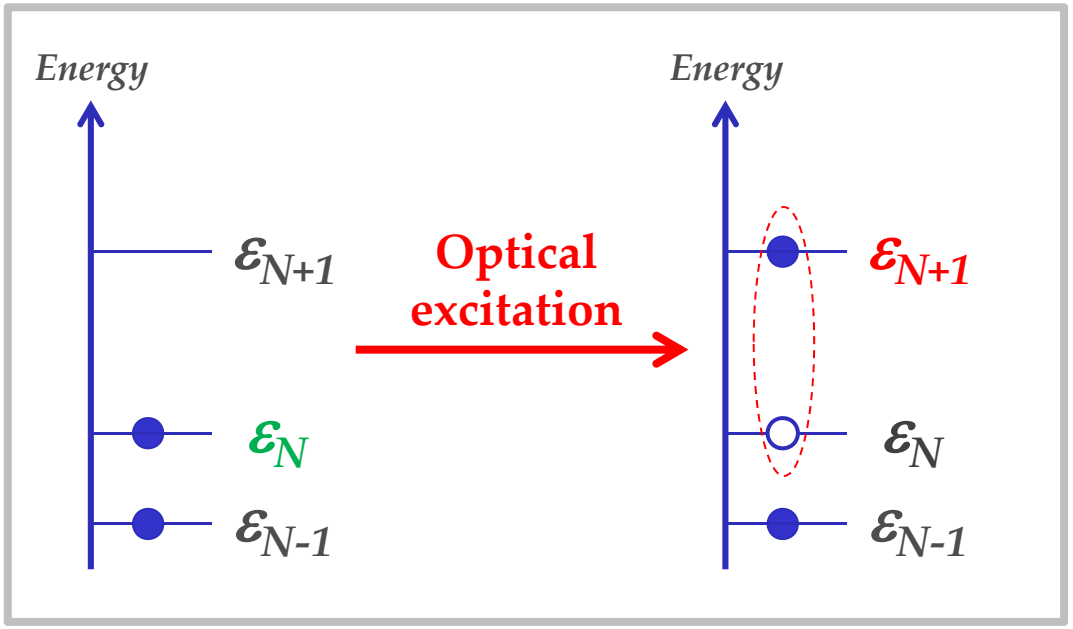
Fundamental gap: electronic gap ≠ optical gap

Deduced from the band structure

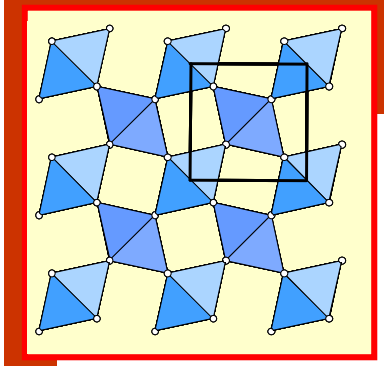


Dipolar transitions





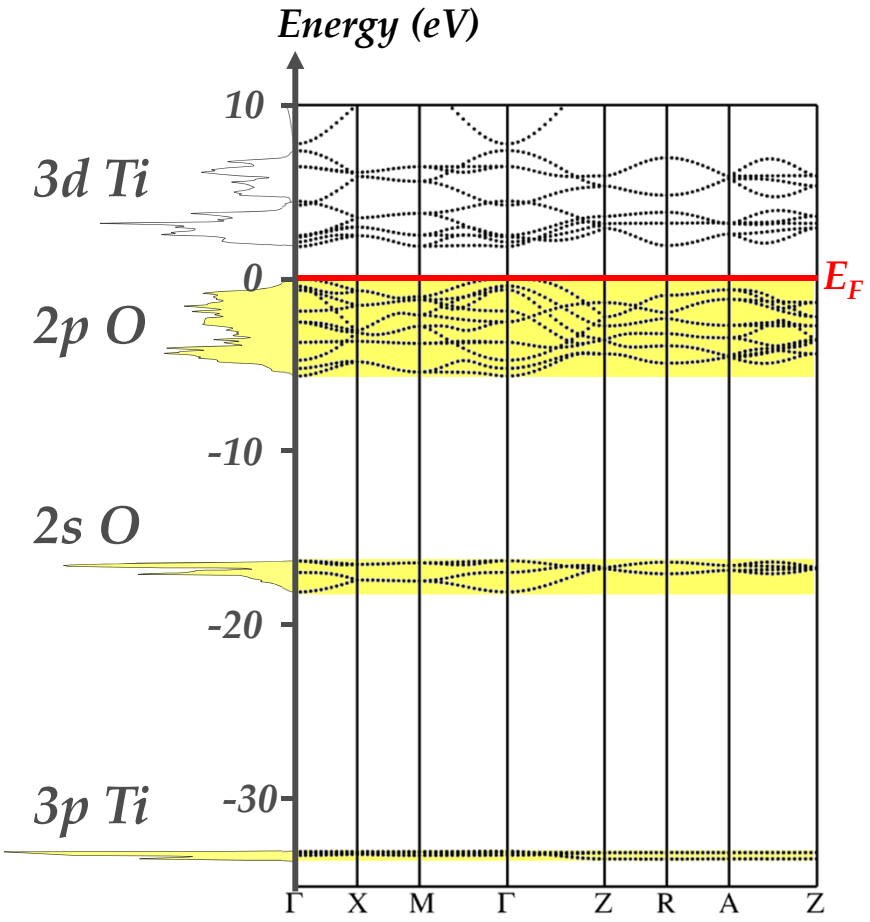
If excitonic effects:
we should go beyond
(TDDFT / BSE)

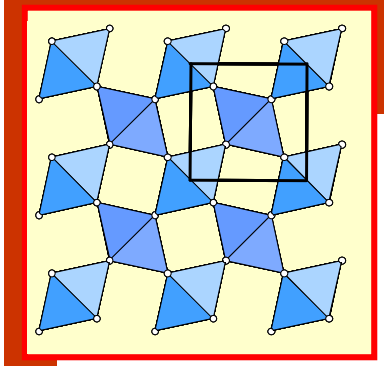


6 – ILLUSTRATIONS: TiO_2 series

Example of the rutile phase

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





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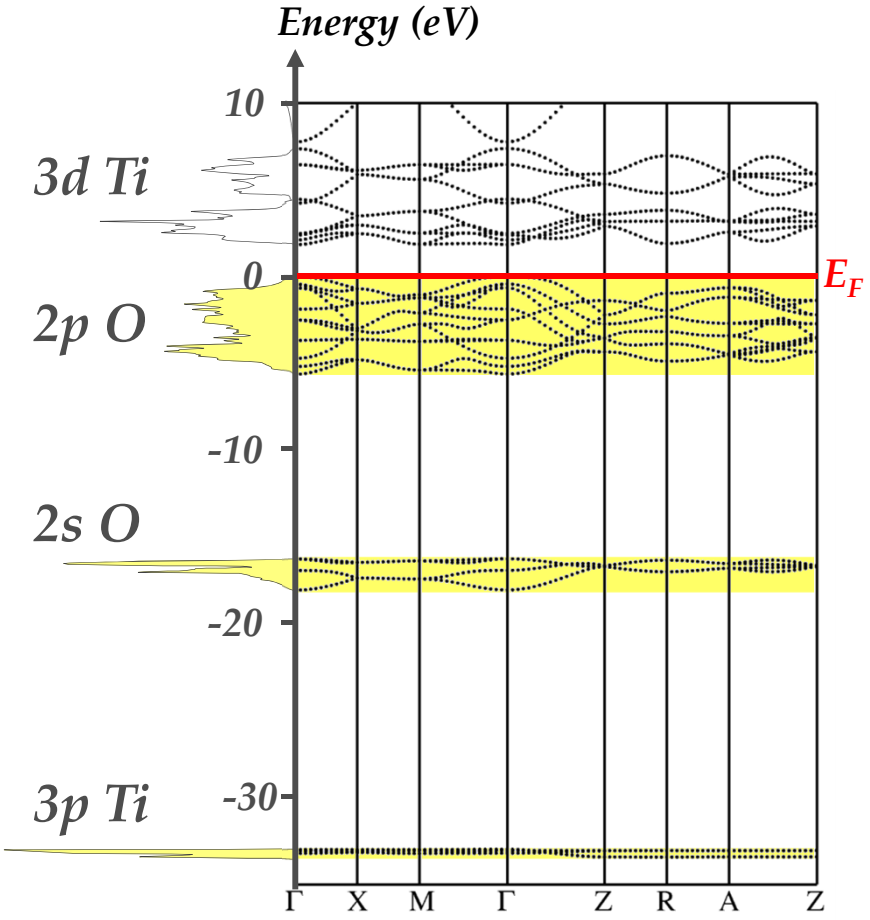

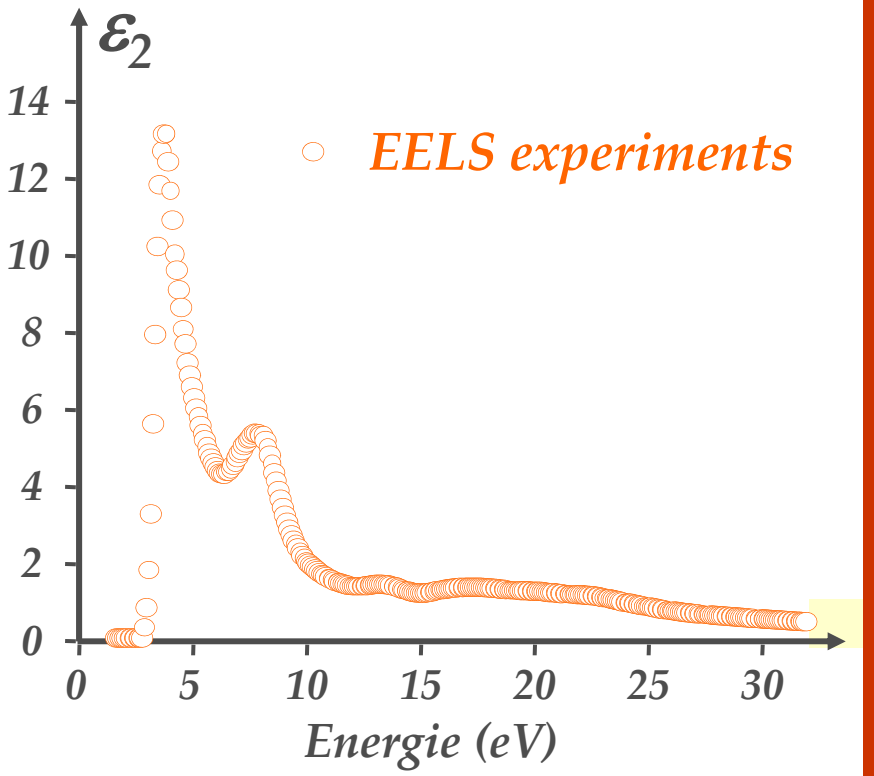

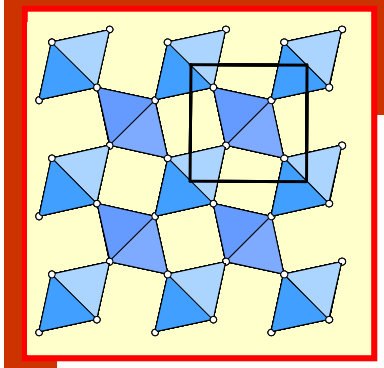

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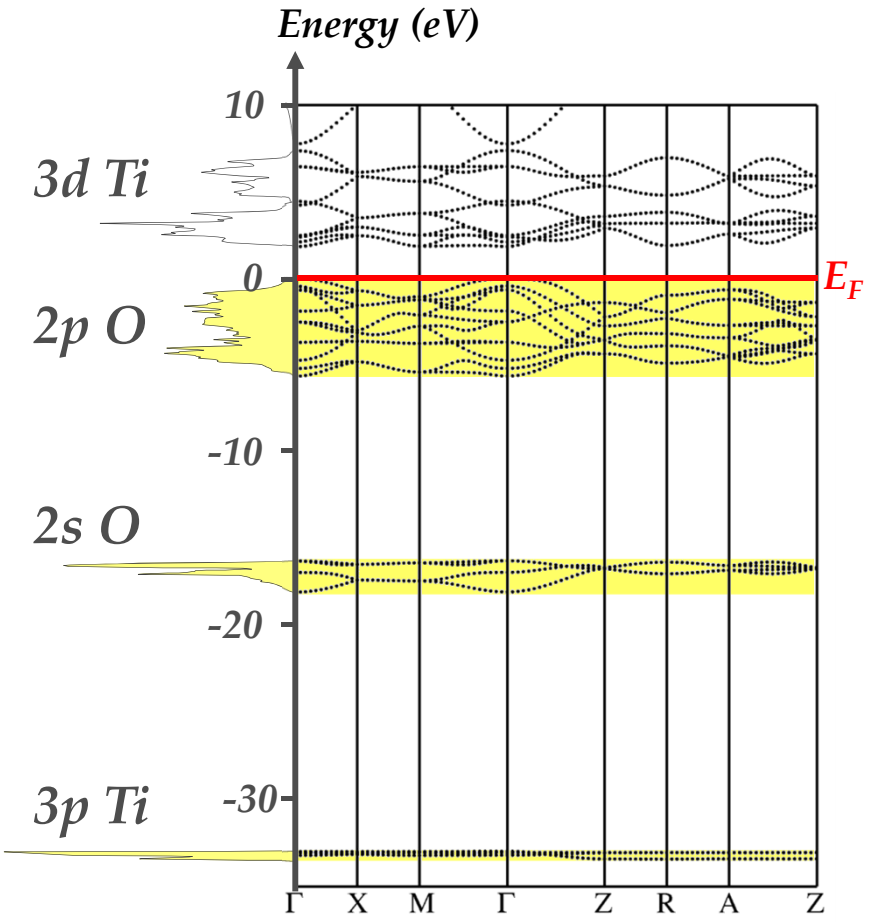
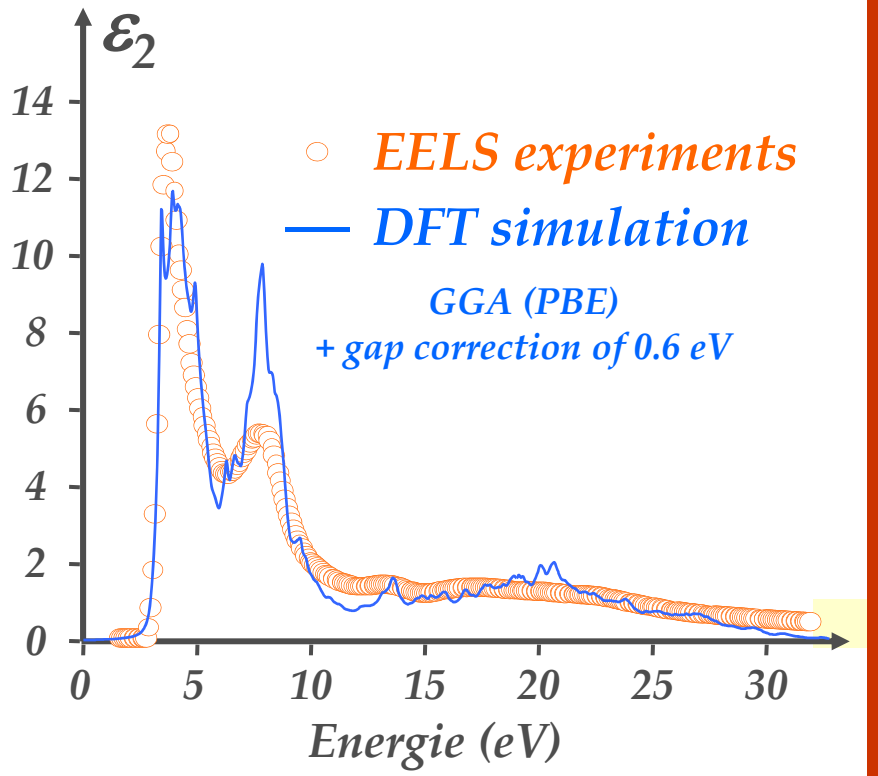
Example of the rutile phase

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

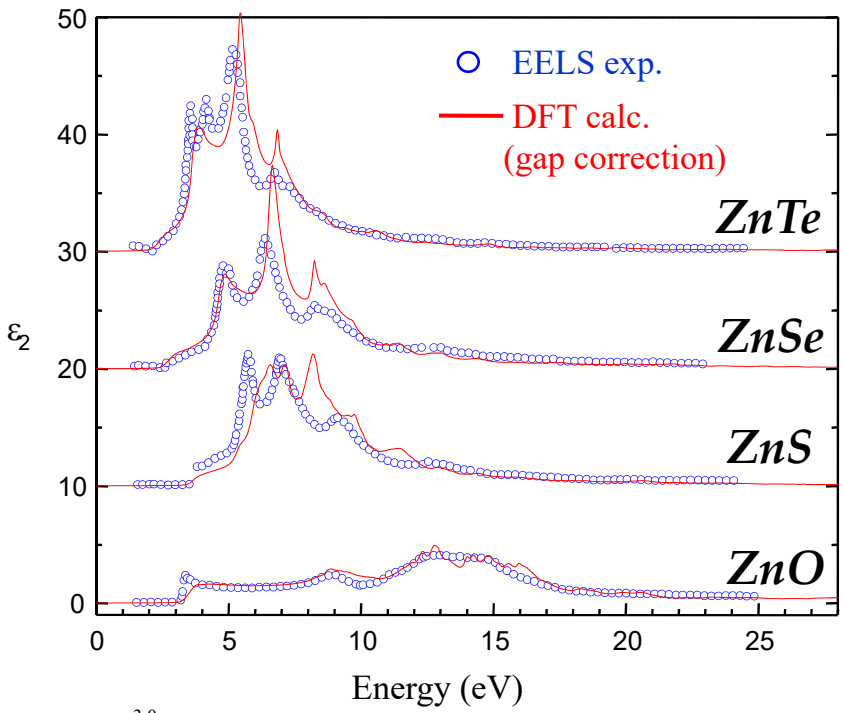
Files generated by:

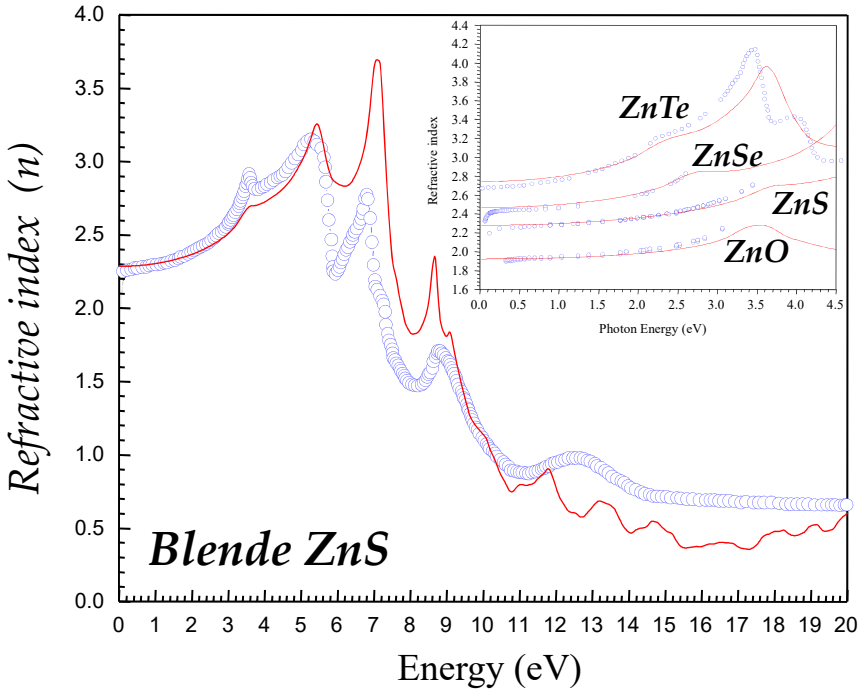
x optic → TiO2-RUT.symmat
→ TiO2-RUT.mommat

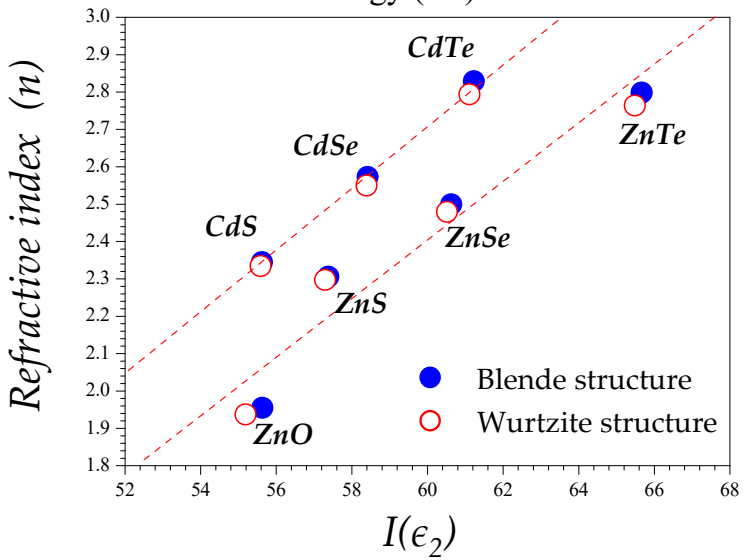
x joint → TiO2-RUT.joint

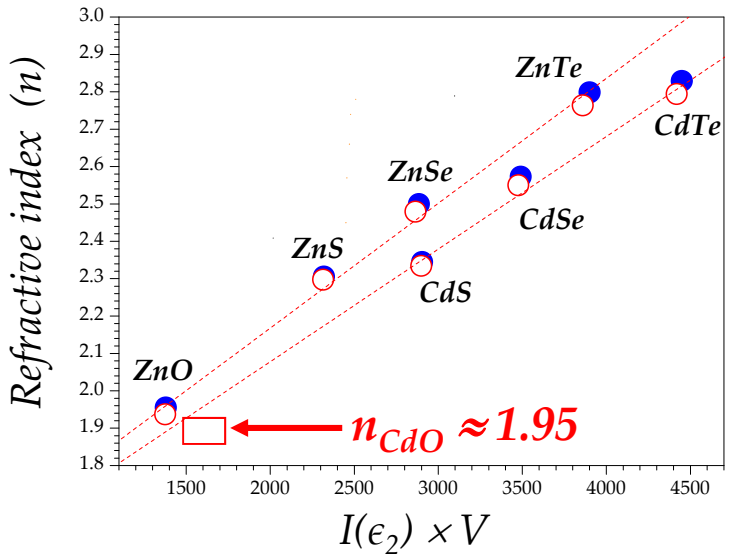
x kram → TiO2-RUT.epsilon
→ TiO2-RUT.sigmak
→ TiO2-RUT.refraction
→ TiO2-RUT.absorption
→ TiO2-RUT.eloss

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







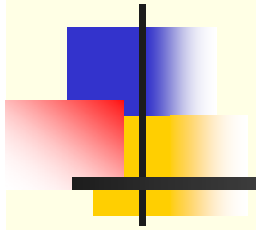


7 – Some limitations of DFT simulation of optical properties

- **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…**



Core level spectroscopy
XES, XAS, EELS, XPS

Dipole transitions between core and valence
(conduction band or continuum) states

Fermi's "golden rule"

- Time dependent perturbation theory: $\hat{H}'(t) = \hat{H}'_0 \left(e^{iE_\nu t} + e^{-iE_\nu t}\right)$
- EM-radiation with energy ω, polarisation α and direction of propagation $\boldsymbol{k}$ acts on the momentum $\boldsymbol{p}$ of the electron

$$\vec{E} = \sum_{\vec{k},\alpha} \left[\vec{e}_\alpha(\vec{k}) e^{i(\vec{k}.\vec{x}-\omega t)} \right]$$

The transition probability W from state i to f is then given by **Fermi's "golden rule"** :

$$W_{f\leftarrow i} = \left\langle f_f \left| e^{i\vec{k}\cdot\vec{x}} \hat{e}_\alpha(\vec{k}) \cdot \vec{p} \right| f_i \right\rangle^2 \rho_N(E) \quad with \quad E = E_f - E_i - E_\nu$$

Number of states with energy E

E-conservation

W: proportional to the square of the transition matrix element

momentum (= dipole) matrix elements:

momentum of photons << momentum of e^-;

momentum conservation ⟹ e^- cannot change its momentum

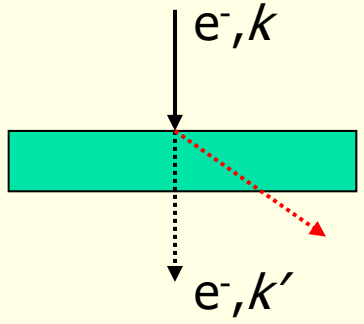
$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{x} + \ldots$$

dipole quadrupole … approximation

$$e^{i\vec{k}\cdot\vec{r}} \approx 1$$

1-3% error (even for keV X-rays), but:
EELS (electron energy loss spectr.) may violate dipole approximation (selection rules!!)

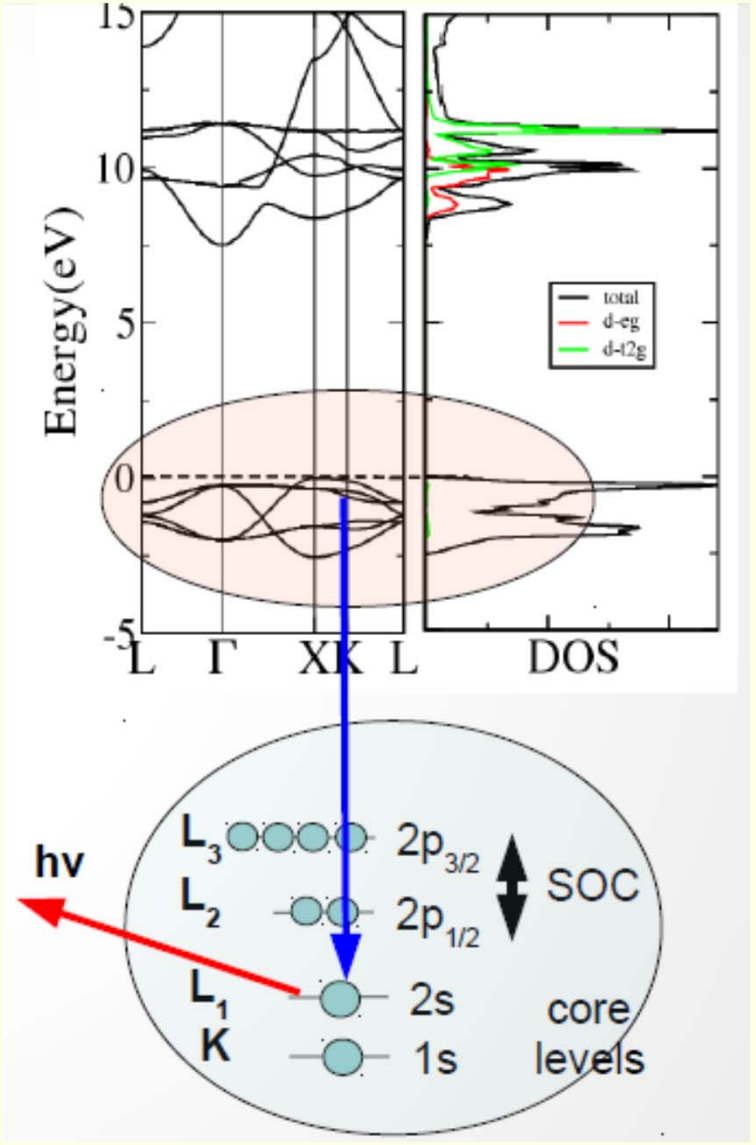
$$\left\langle f_f \left| \hat{H}' \right| f_i \right\rangle = \hat{e}_\alpha \left\langle f_f \left| \vec{p} \right| f_i \right\rangle = \hat{e}_\alpha \left\langle f_f \left| \vec{r} \right| f_i \right\rangle$$



⟹ selection rules: $\ell \pm 1$

XES (X-ray emission spectroscopy)

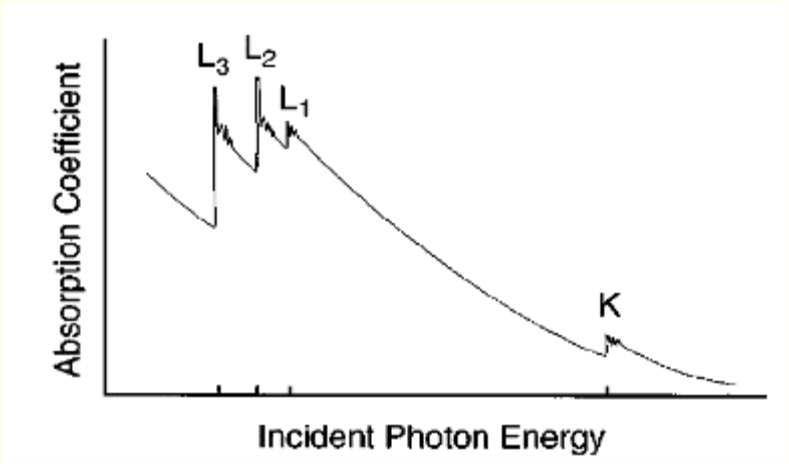
- knock out a core e^-
- valence e^- fills core hole
- measure the emitted X-ray
- XES gives the $\ell \pm \mathbf{1}$ partial DOS of the **valence** bands of the **specific atom** (with core state ℓ)

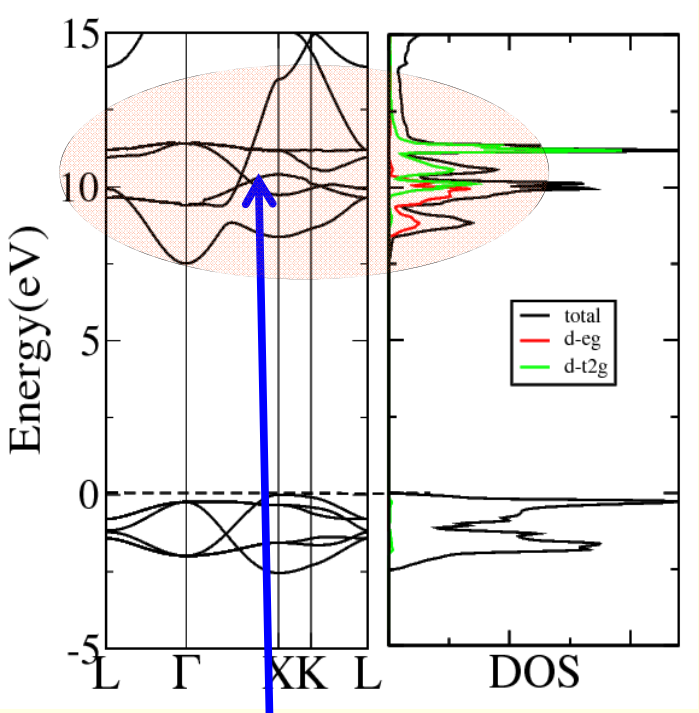


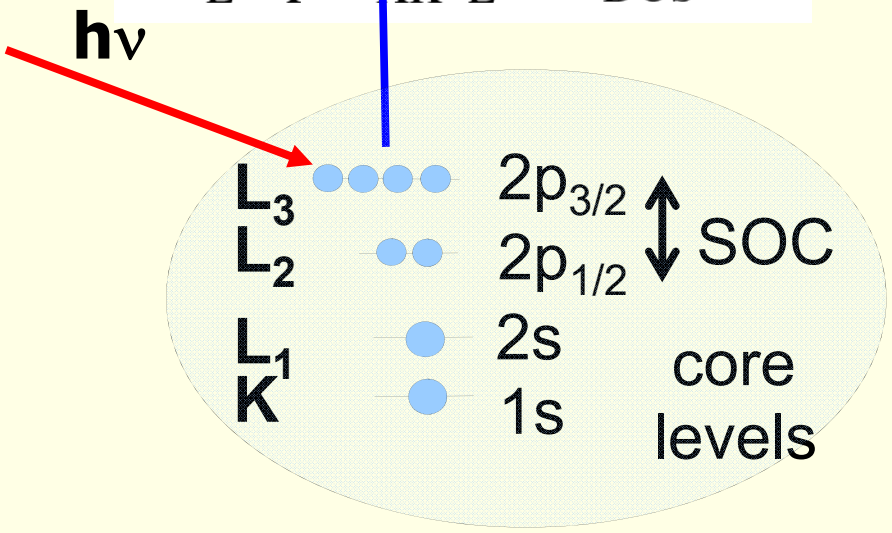
XAS (XANES), **EELS** (ELNES)

- **core electrons are excited into the conduction band**
- Each core shell introduces an absorption edge, (they are indexed by the principal number of a core level)

  K-1s, L_1-2s, L_2-$2p_{1/2}$, L_3-$p_{3/2}$







- **XAS:** XES gives the $\ell\pm\mathbf{1}$ partial DOS of the **conduction** bands of the **specific atom** (with core state ℓ)

Difference between EELS and XAS

XAS: synchrotron

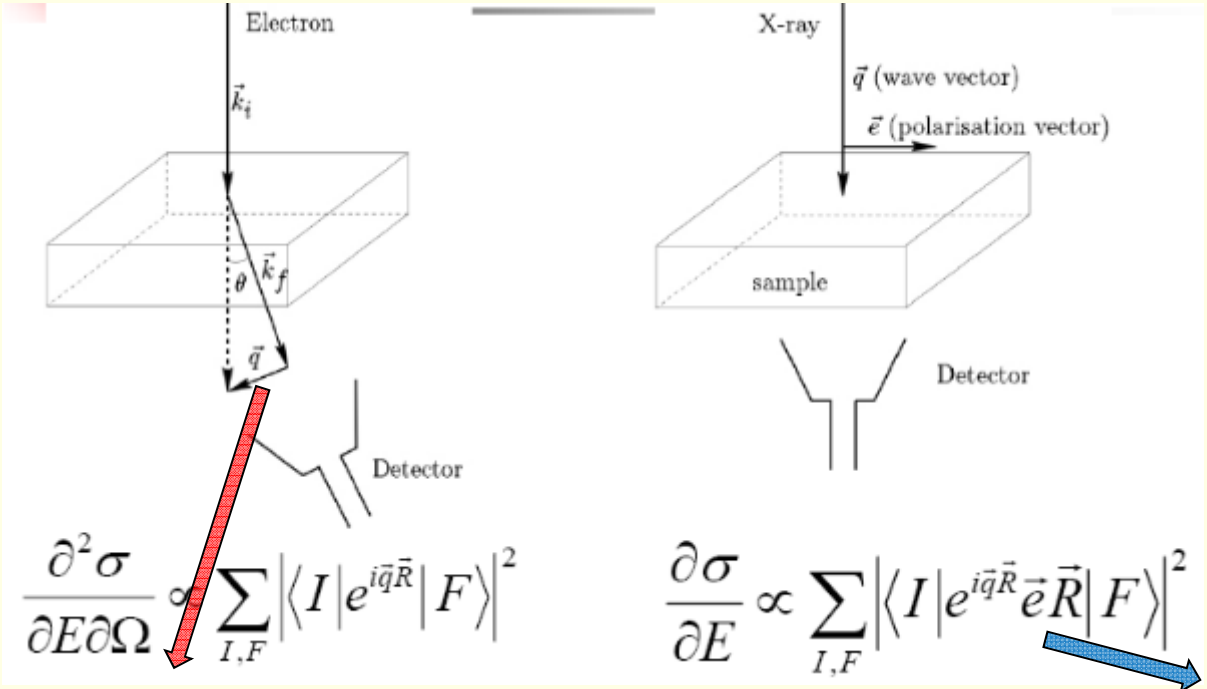
EELS: microscope

XAS vs. EELS: theory

- transition described by Fermis "golden rule" between initial (core) and final (conduction-band) state and the e^- or photon
- double differential cross section:

$$\frac{\partial^2\sigma}{\partial E\partial\Omega}(E,\boldsymbol{Q}) = \zeta\sum_{I,F}\frac{k_F}{k_I}\left|\left\langle I\,k_I\left|V\right|k_F\,F\right\rangle\right|^2\delta(E_I-E_F)$$

E - conservation



$$\frac{\partial^2\sigma}{\partial E\partial\Omega}\propto\sum_{I,F}\left|\left\langle I\left|e^{i\vec{q}\vec{R}}\right|F\right\rangle\right|^2$$

$$\frac{\partial\sigma}{\partial E}\propto\sum_{I,F}\left|\left\langle I\left|e^{i\vec{q}\vec{R}}\vec{e}\vec{R}\right|F\right\rangle\right|^2$$

single diff. cross section

momentum transfer ***q***

polarization vector ***e***

dipole approximation

$$\vec{q}\vec{R} << 1 \rightarrow e^{i\vec{q}\vec{R}} = 1 + i\vec{q}\vec{R} + \frac{(\vec{q}\vec{R})^2}{2!} + \ldots$$

EELS

$$\frac{\partial^2\sigma}{\partial E \partial\Omega} \propto \sum_{I,F} \left| \langle I | \vec{q}\vec{R} | F \rangle \right|^2$$

XAS

$$\frac{\partial^2\sigma}{\partial E \partial\Omega} \propto \sum_{I,F} \left| \langle I | \vec{\varepsilon}\vec{R} | F \rangle \right|^2$$

The polarization vector in XAS plays the same role as momentum transfer in (nonrelativistic) ELNES within the dipole approximation.

(TELNES3 can also handle non-dipole transitions + relativistic corrections)

core-valence spectroscopies give information on the local DOS (because of $\langle \Psi_{core} | r | \Psi_{val} \rangle$) of angular momentum character $\ell \pm 1$

"Final state rule":

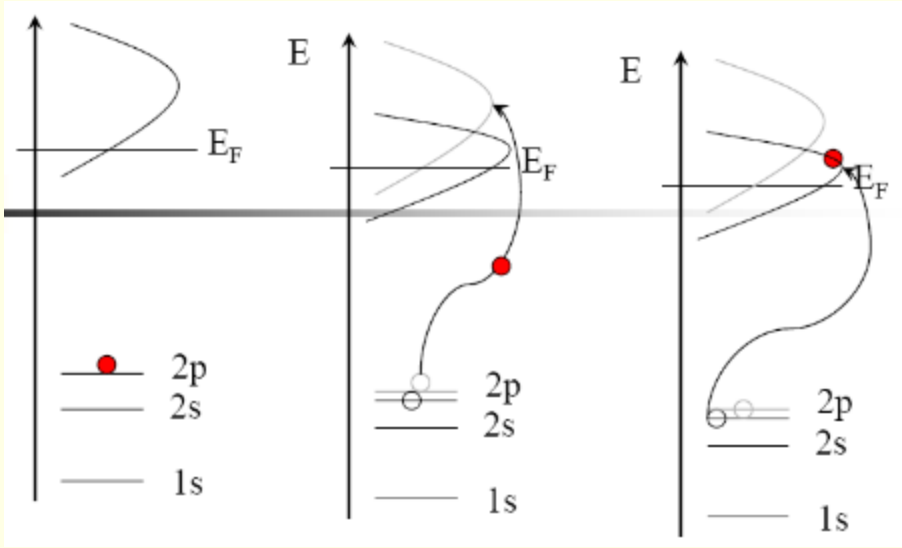
"Final state" determines the spectrum:

- Absorption spectroscopy:

  Final state has a "hole" in core state, but additional e^- in conduction band.

  Core-hole has large effect on the spectrum

  - **electron – hole interaction, "excitonic effects"**



- Emission spectroscopy:

  Final state has filled core, but valence hole.

  This is usually well screened, thus one "sees" the groundstate.

.

"Final state rule" + core hole:

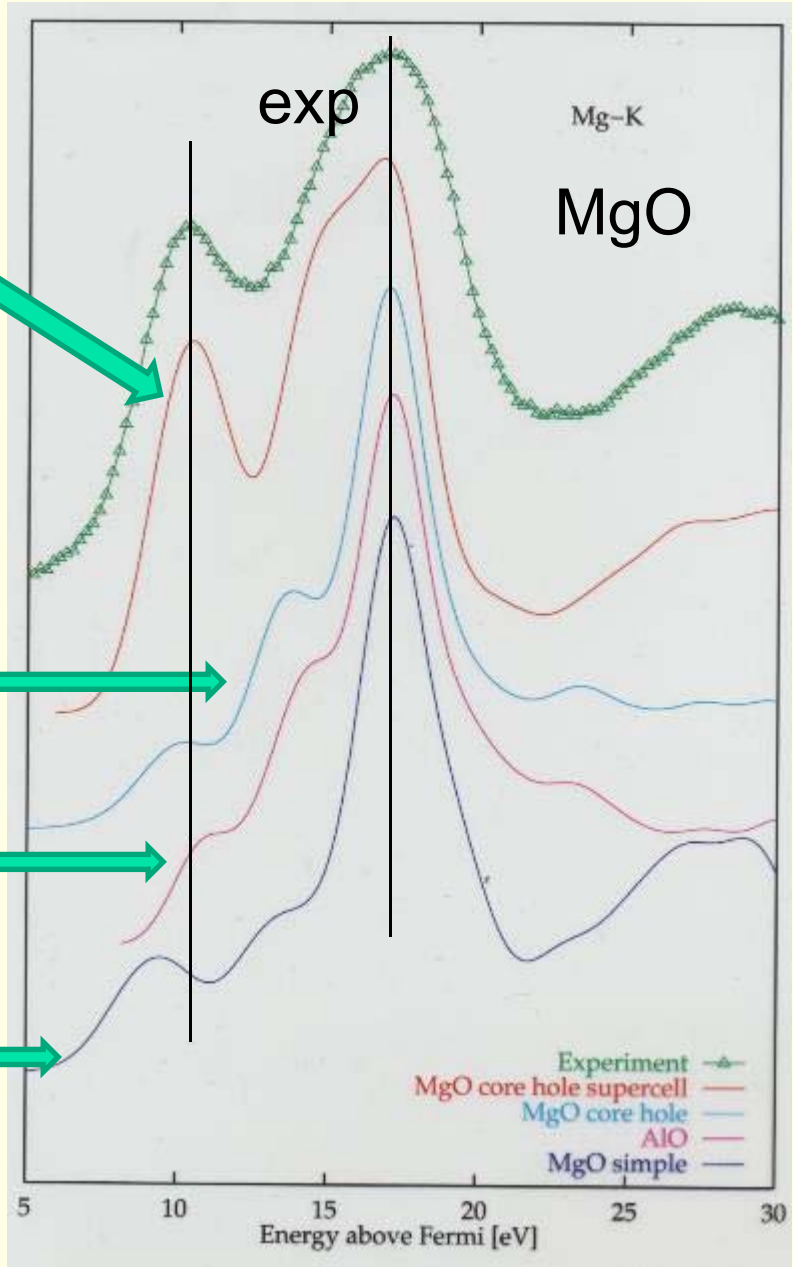
2x2x2 **supercell** calculation with core hole in **one** of the Mg atoms (add e^- to valence or "background").

This allows the conduction state to relax (adjust to the larger **effective** nuclear charge), but also to have **static screening** from the environment.

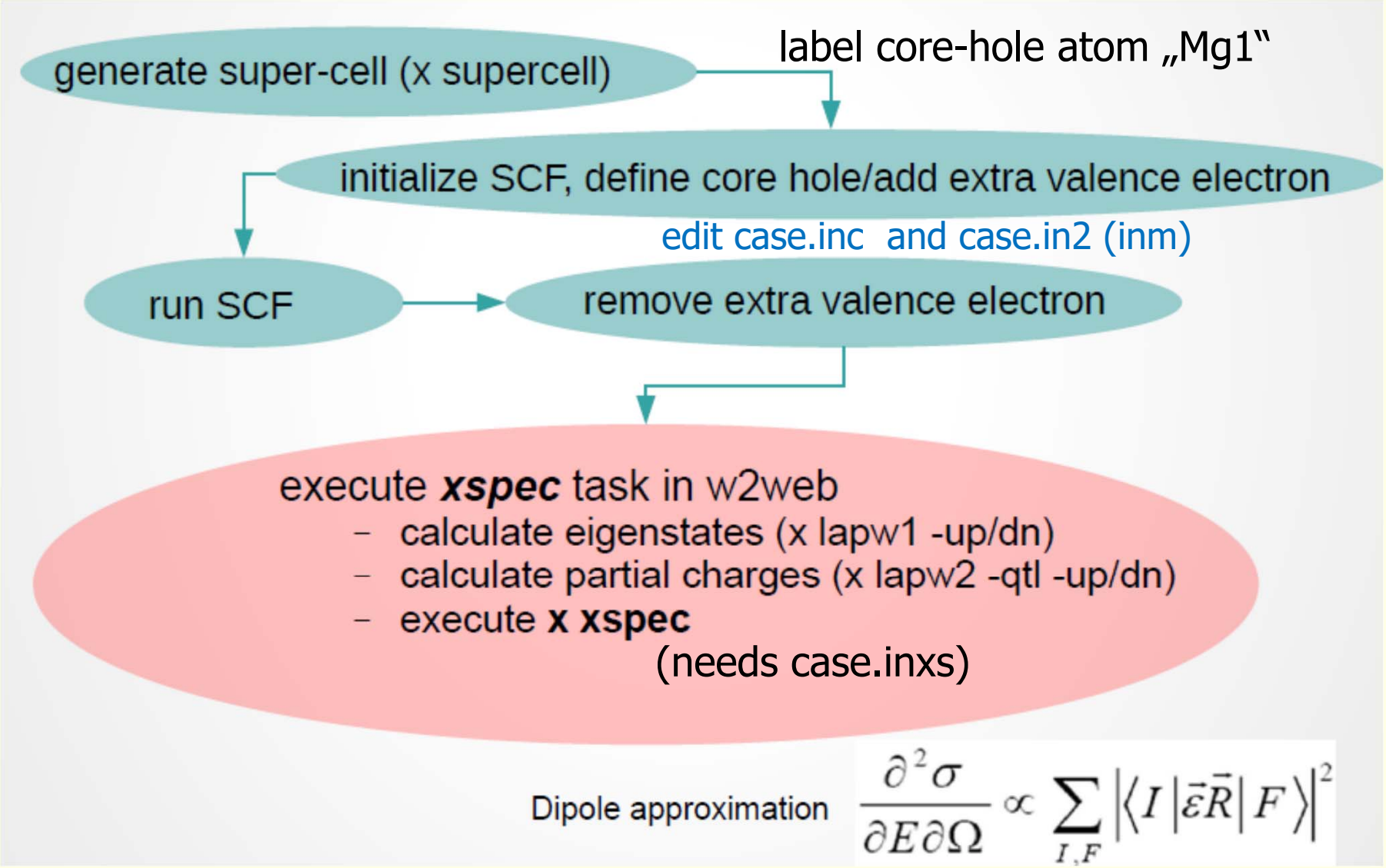
core hole, no supercell:

Z+1 (AlO)

groundstate

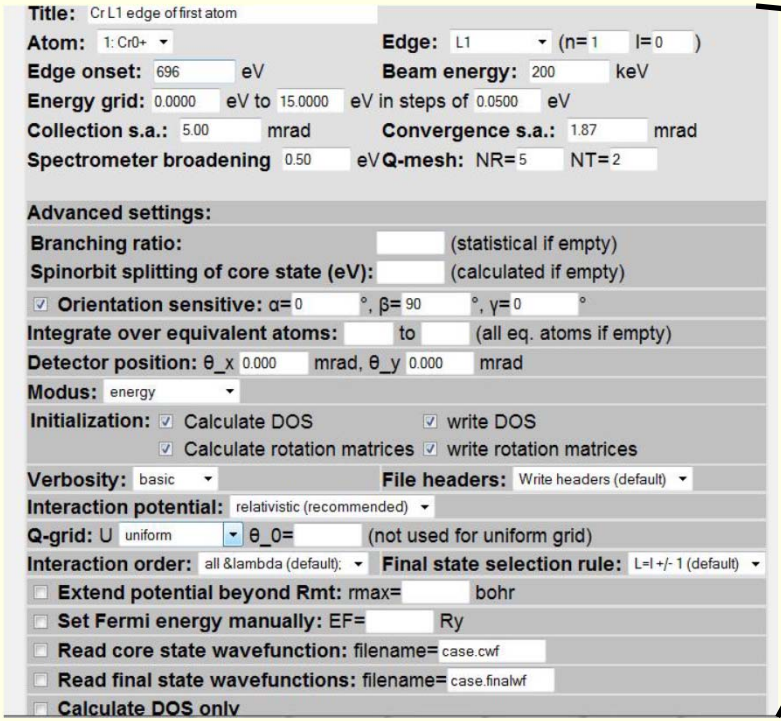


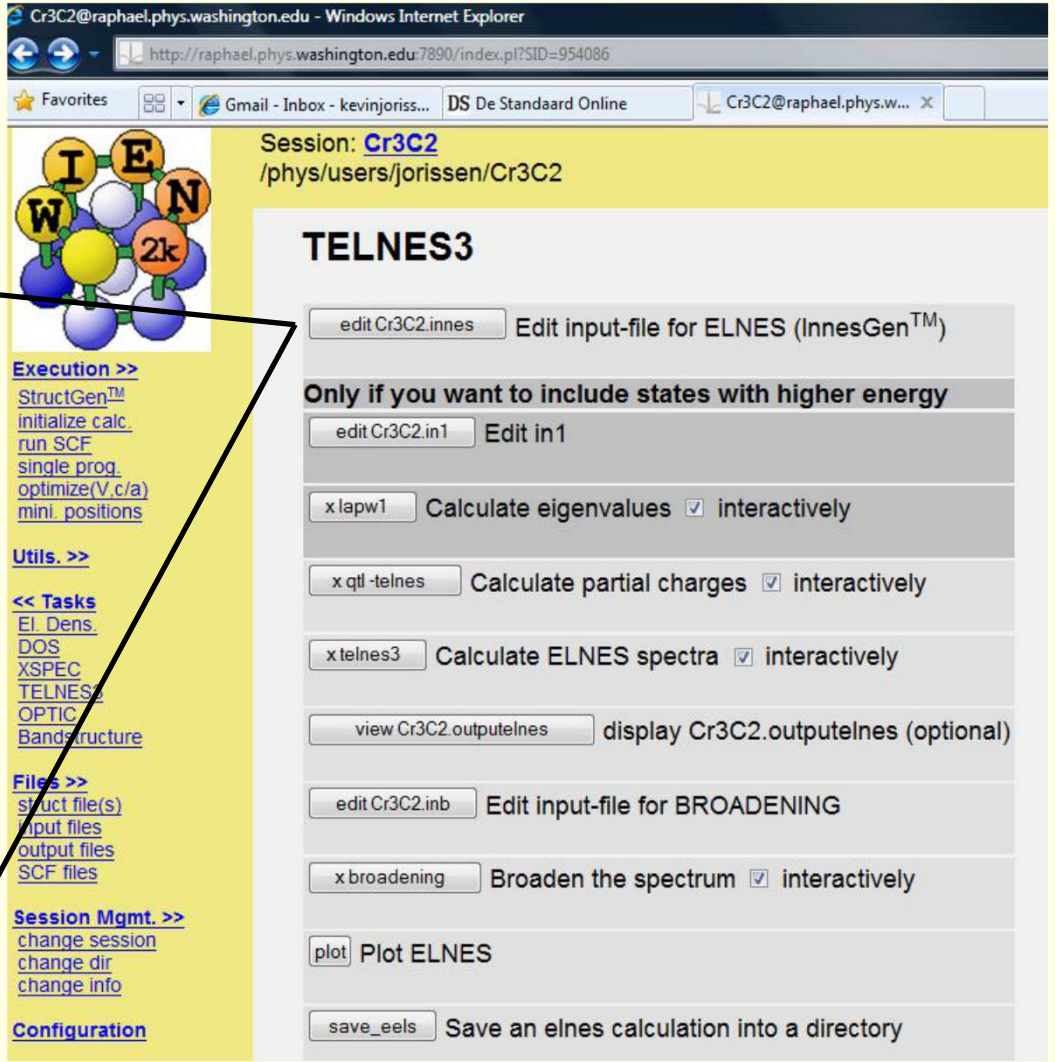
Core hole calculations in WIEN2k



EELS in WIEN2k

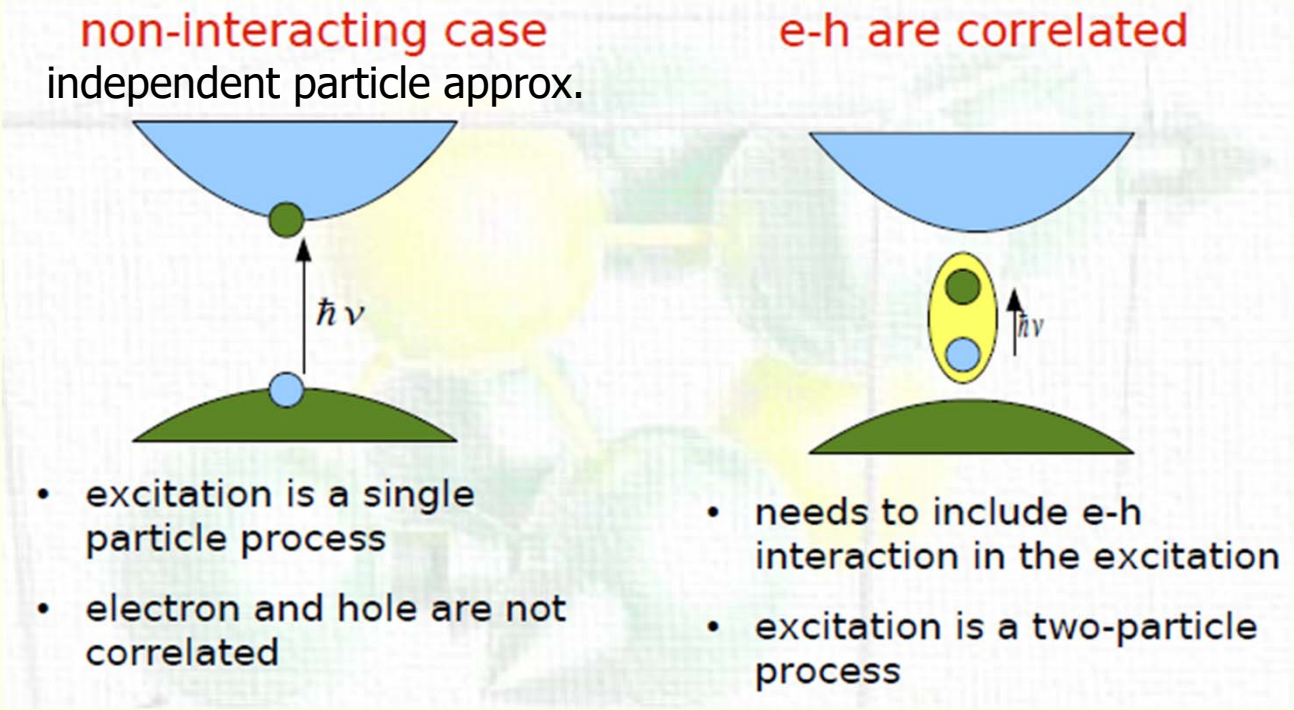
- supercell calculations as for XAS
- TELNES3 task in w2web





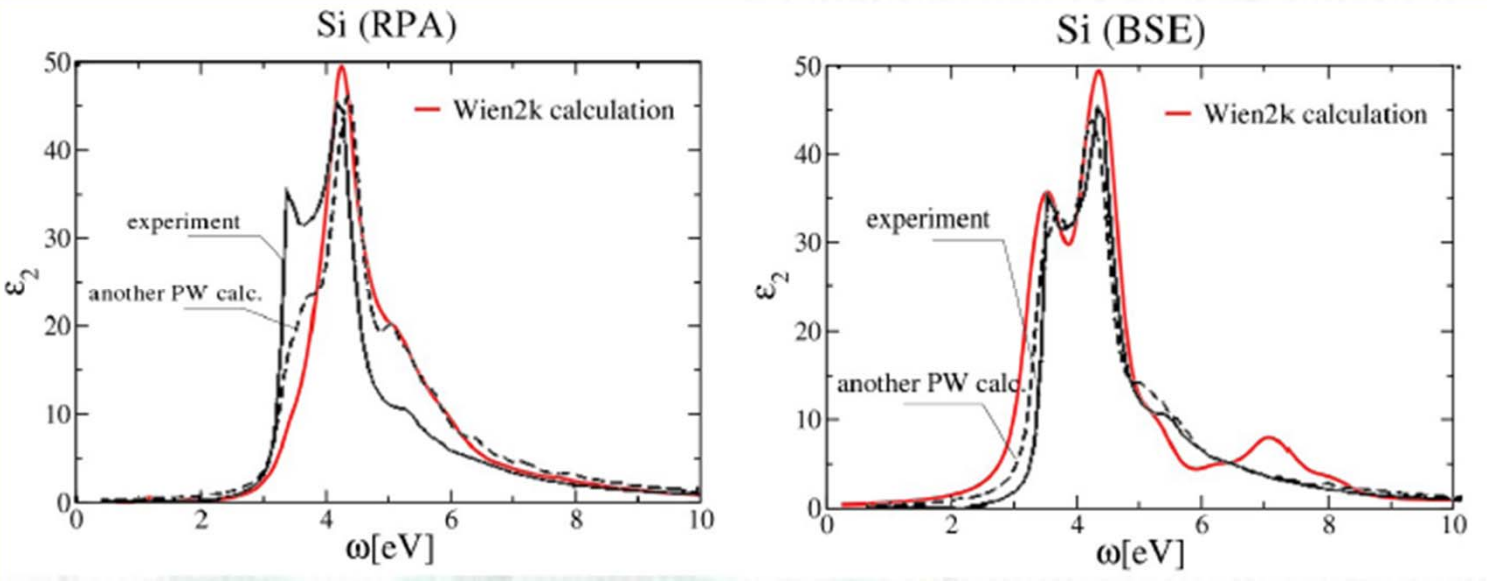
When IPA fails: Electron – hole interactions

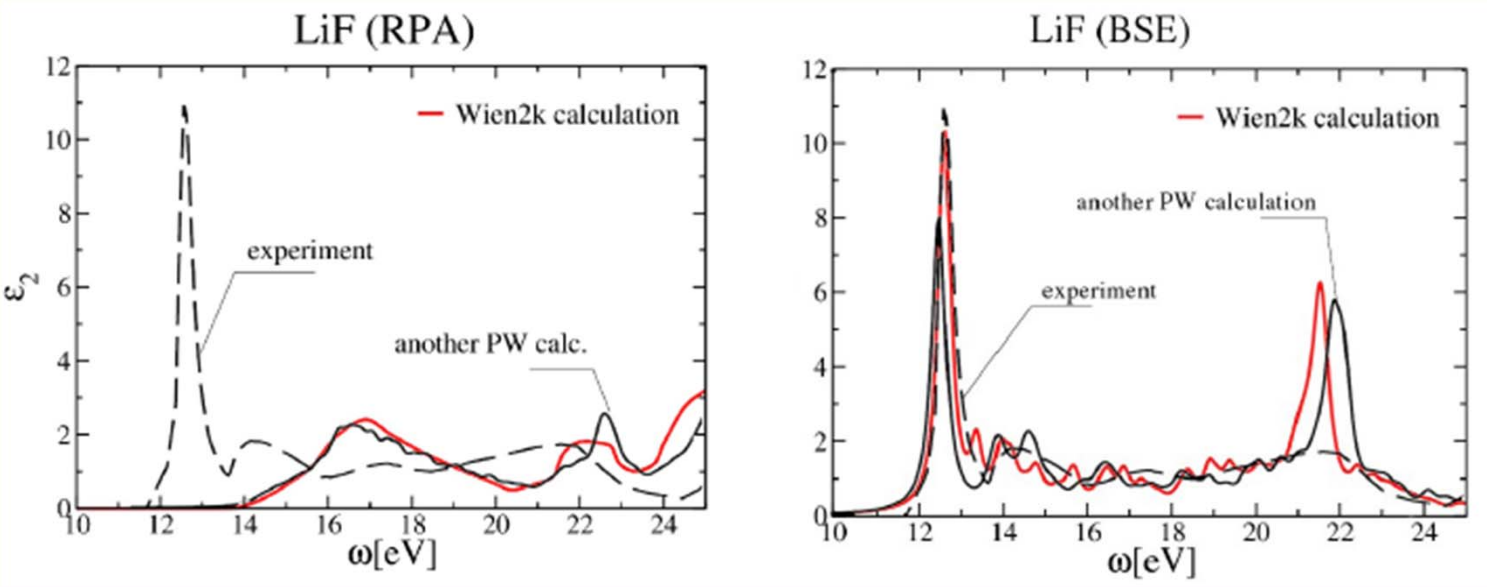
- when the e^- is not ionized, but stays in the solid:



- ⟹ **excitonic effects**
- **Frenkel (localized) and Wannier (delocalized) excitons**

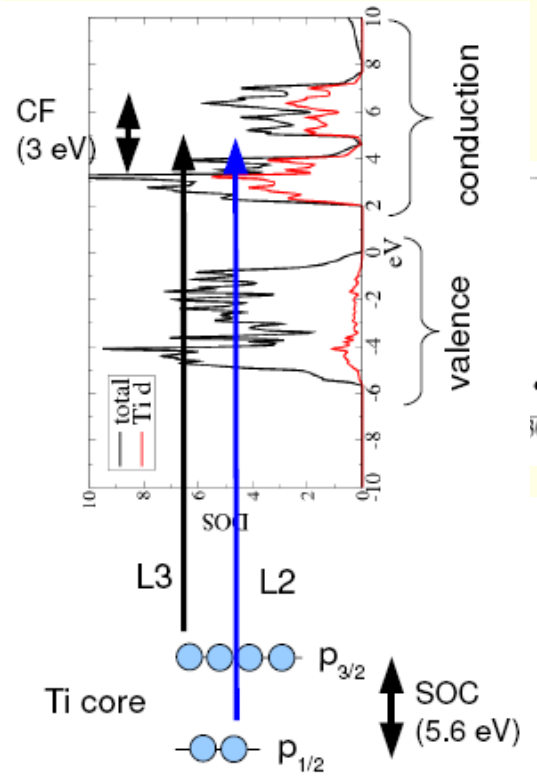
importance of excitons (BSE):



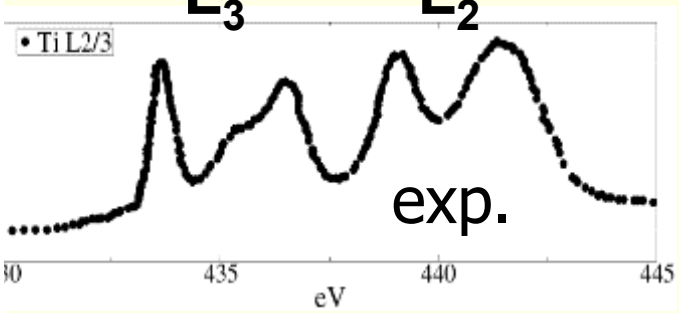


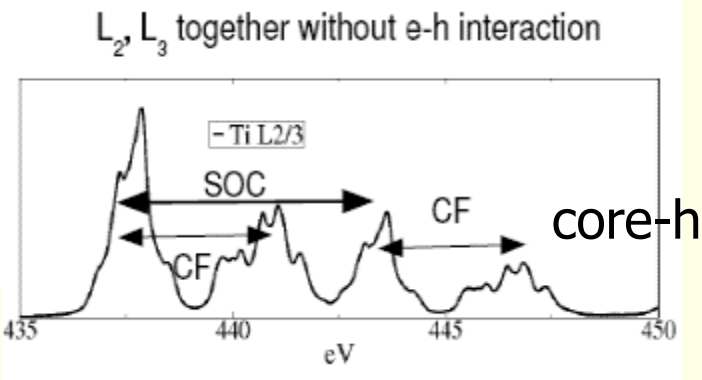
$L_{2,3}$ spectra: failure of the single particle approach

- In particular early 3d TM-compounds show a
  - *non-standard L_2/L_3 branching ratio (1:2)*
  - *sometimes a completely different lineshape (TiO_2)*
  - *„wrong" **SOC** or **CF** splittings*

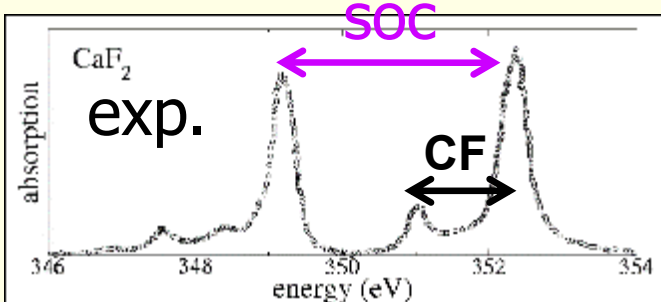


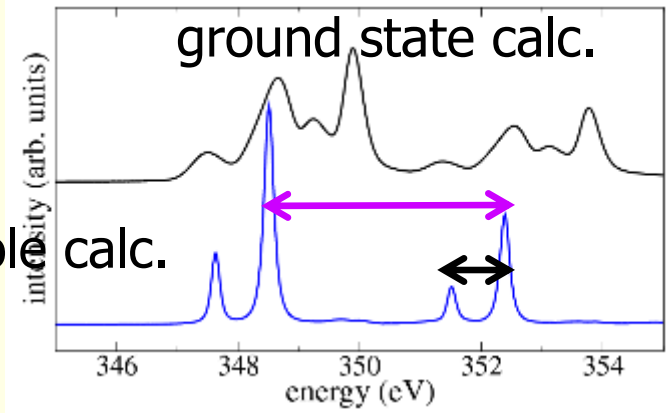
rutile TiO_2





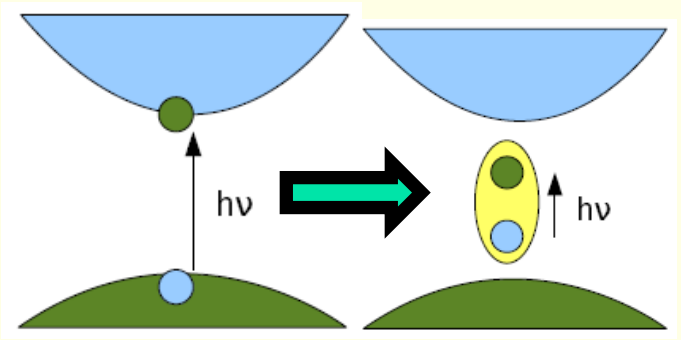
CaF_2





fully relativistic electron-hole interaction (BSE)

- *Bethe-Salpeter-equation: L(12;1'2')*
- *solving a 2-particle (e^- - h) equation of large dimension ($N_v N_c N_k \sim 100000$)*



$$\sum_{v'c'k'} (H^{eh}_{v'c'k',vck}) A^{\lambda}_{v'c'k'} = E^{\lambda} A^{\lambda}_{vck}$$

$$H^{eh} = H^{diag} + H^{dir} + 2H^{x}$$

$$H^{diag} = (E_{v,k} - E_{c,k})\delta_{cc'}\delta_{vv'}\delta_{kk'}$$

eigenvalue difference between hole (v) and electron(c) state

$$H^{dir}_{vckv'c'k'} = -\int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^{*}_{ck}(r')W(r,r')\Psi^{*}_{v'k'}(r)\Psi_{c'k'}(r')$$

attractive screened static Coulomb interaction *W; $W \sim \varepsilon^{-1}$*

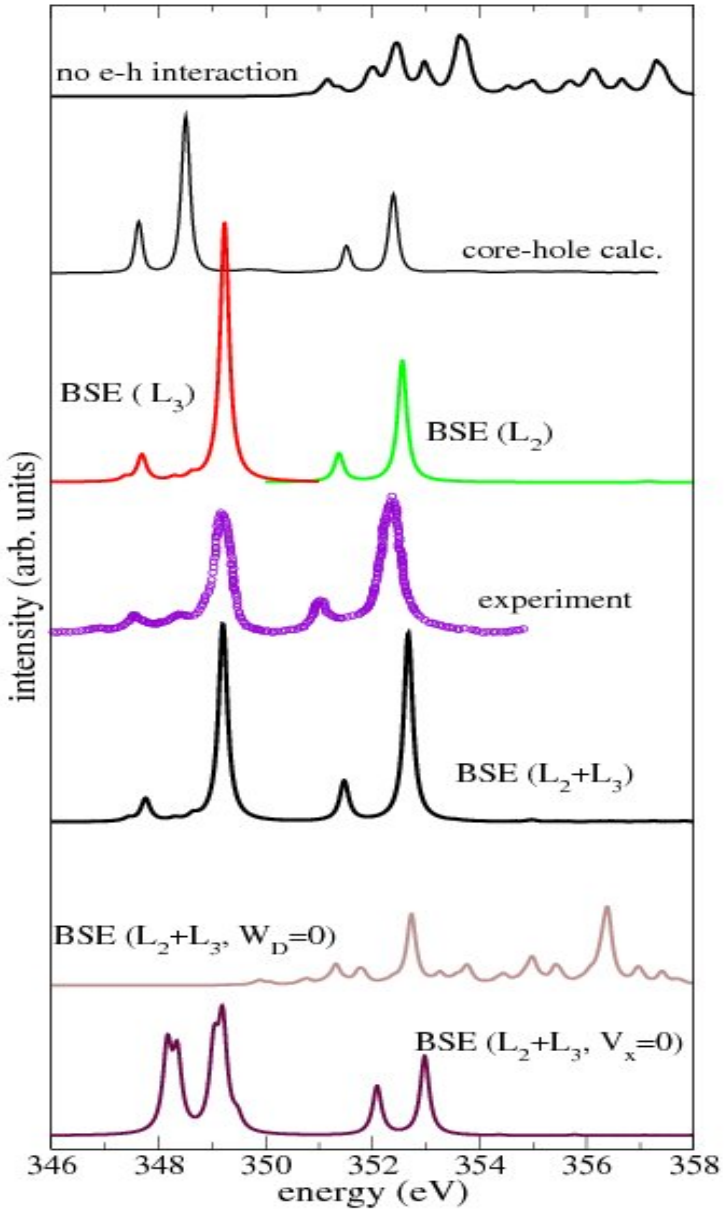
$$H^{x}_{vckv'c'k'} = \int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^{*}_{ck}(r)\bar{v}(r,r')\Psi^{*}_{v'k'}(r')\Psi_{c'k'}(r')$$

e-h exchange with bare Coulomb potential *v*

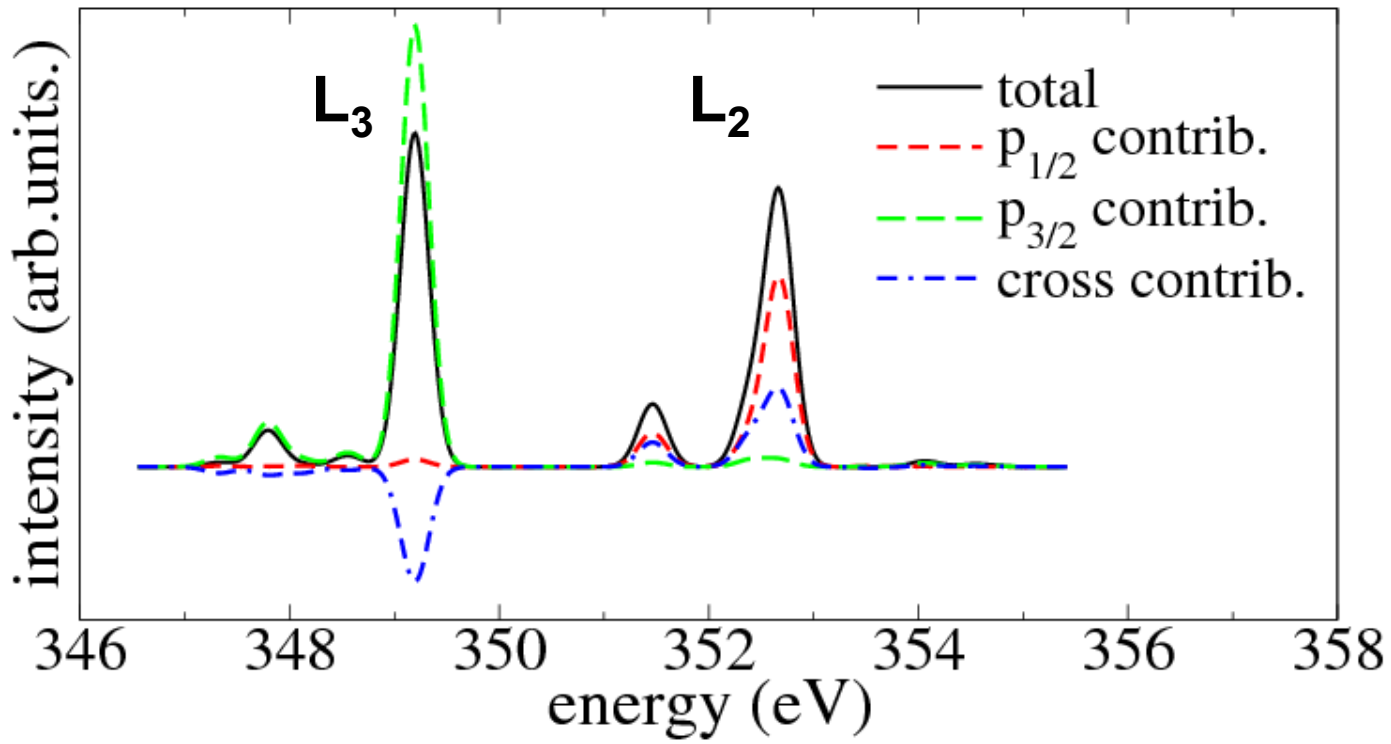
R. Laskowski, P. Blaha, Phys. Rev. B, 81, 075418 (2010)

Ca-L_{23} edge in CaF_2

- "ground-state" DOS
-
-
- **experiment**
-
-
-



$L_{2,3}$ edge for Ca in CaF_2

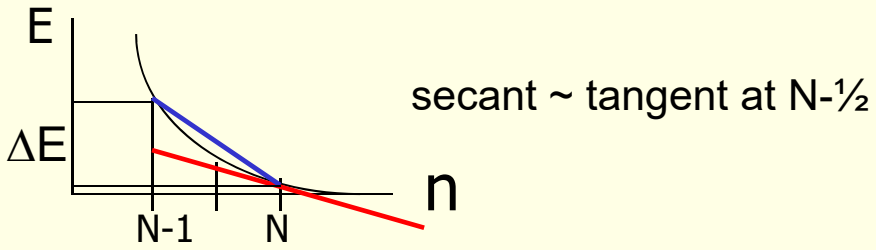


Decomposition of ϵ_2 into the excitation from $p_{1/2}$ and $p_{3/2}$ states
cross terms suppress the L_3 branch and enhance L_2

$$\varepsilon_2^{xx}(\omega) = \frac{8\pi^2}{\Omega}\sum_{\lambda}\left|\sum_{hek} A_{hek}^{\lambda}\frac{\langle hk|-i\nabla_x|ek\rangle}{\varepsilon_{ek}-\varepsilon_{hk}}\right|^2 \times \delta(E^{\lambda}-\omega)$$

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 (with respect to E_F) are NOT a good approximation:
  - $\varepsilon_i = dE/dn$ *Janak's theorem*
- Slater's "transition state": core-eigenvalues ε_i for half occupancy



- Δ-SCF-calculation with and without core-hole: $E^{tot}(N) - E^{tot}(N-1)$
  - *always use 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

Band gap problem, independent particle approx.

Ionization energy $\varepsilon_N(N) = -I$

Electron-affinity $\varepsilon_{N+1}(N+1) = -A$

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

$$E_g = \underbrace{\varepsilon_{N+1}(N) - \varepsilon_N(N)}_{\varepsilon_g} + \underbrace{\varepsilon_{N+1}(N+1) - \varepsilon_{N+1}(N)}_{\Delta_{xc}}$$

$$\boxed{E_g = \varepsilon_g + \Delta_{xc}}$$

$\boxed{\Delta_{xc}}$

shift of conduction bands: scissors operator

better local potentials: TB-mBJ

many-body perturbation theory: GW approach

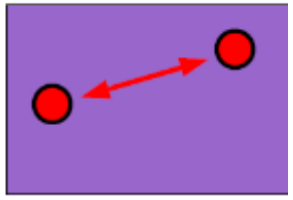
GW (MBPT on one page)

- Self-energy $\Sigma(r,r',\omega)=\frac{i}{2\pi}\int d\omega' G(r,r,\omega-\omega')W(r,r',\omega)$
- Green's function $G(\mathbf{r}_1,\mathbf{r}_2,\omega)=\sum_i \frac{\phi_i^{KS}(\mathbf{r}_1)\phi_i^{KS*}(\mathbf{r}_2)}{\omega-\epsilon_i^{KS}\pm i\eta}$ describes propagation of e^-,h^+ from $r_1 \rightarrow r_2$ with time (ω)
- screened coulomb interaction W:

Interaction between electrons in a homogeneous polarizable medium:

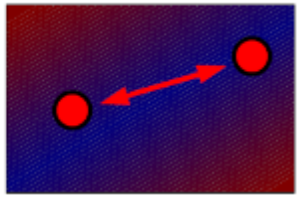
$$W(r,r')=\frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{e^2}{|r-r'|}$$

Dielectric constant of the medium

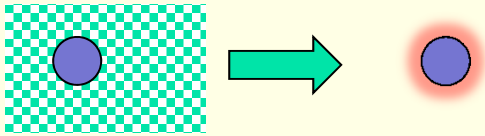


Dynamically screened interaction between electrons in a general medium:

$$W(r,r',\omega)=\frac{e^2}{4\pi\epsilon_0}\int dr'' \frac{\varepsilon^{-1}(r,r'',\omega)}{|r''-r'|}$$



- GW: screened HF approximation $\Sigma_x(\mathbf{r}_1,\mathbf{r}_2)$ + $\Sigma_c(\mathbf{r}_1,\mathbf{r}_2,\omega)$
- calculation of "quasiparticle energies":



$$\varepsilon_{nk}^{QP}=\varepsilon_{nk}^{LDA}-\langle nk|\Sigma(\varepsilon_{nk}^{QP})-V_{xc}^{LDA}|nk\rangle$$

- GW and BSE are available upon request (see „unsupported software page“ at wien2k.at

- Both calculations are **EXTREMELY** expensive
  - *Hardware: at least 128 cores with infiniband*