Structural and vibrational properties of metals from Infra-Red spectroscopy

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SAPIENZA
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OUTLINE

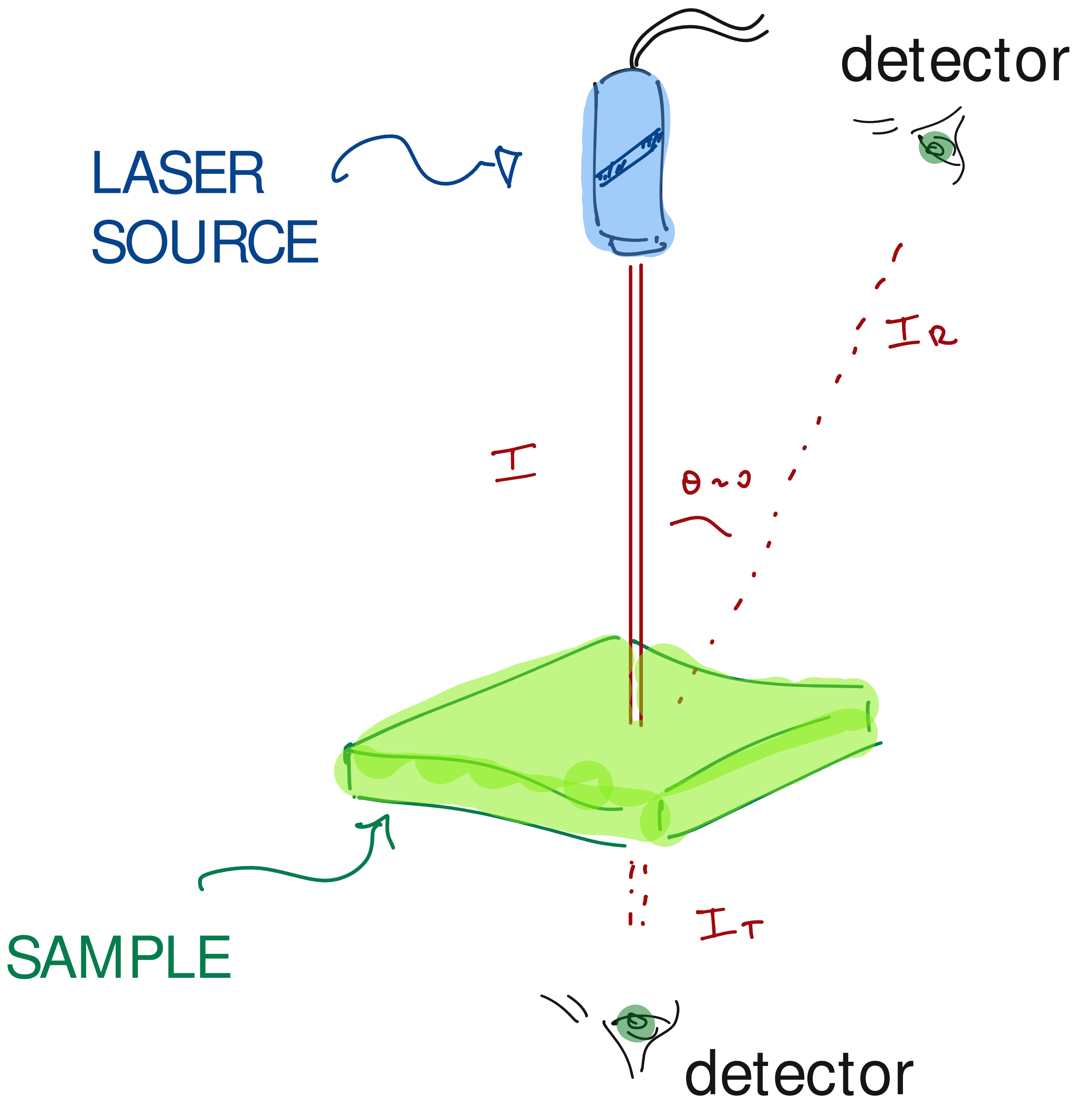
Introduction

- Infra-red spectroscopy
- Plasma reflectivity
- Bands structure and resonances
- Phonons and vibrational resonances

New approach to ab-initio linear dynamical response

- Sketch of the new approach
- Advantages of the new approach
- Comparing simulation and experiment
- New approach in more details (if there's still time and interest)

SPECTROSCOPIC SET- UP

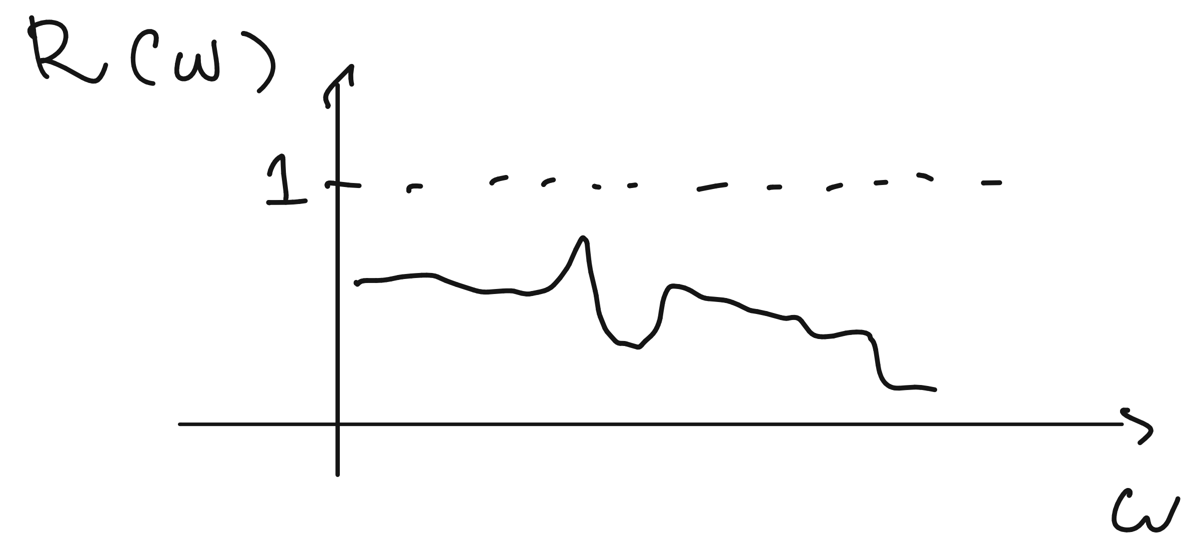


$$I = I_R + I_T + I_A$$

R : Reflected
A : Absorbed
T : Transmitted

REFLECTIVITY $\quad R := \dfrac{I_R}{I} \in [0, 1]$

Reflectivity spectrum:



Macro to micro :

REFLECTIVITY:

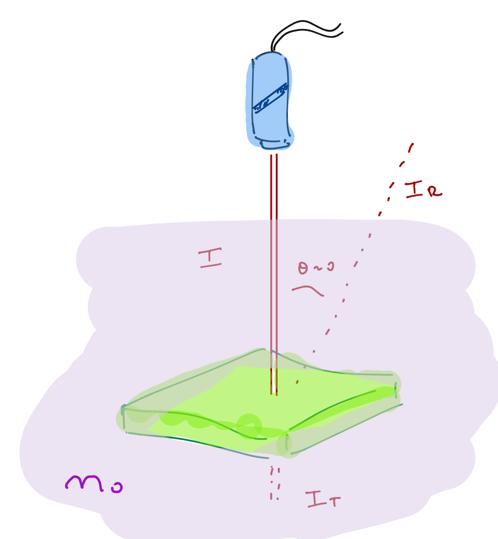
$$\boxed{R = \left| \frac{\sqrt{\varepsilon} - n_0}{\sqrt{\varepsilon} + n_0} \right|^2}$$

Total dielectric Tensor:

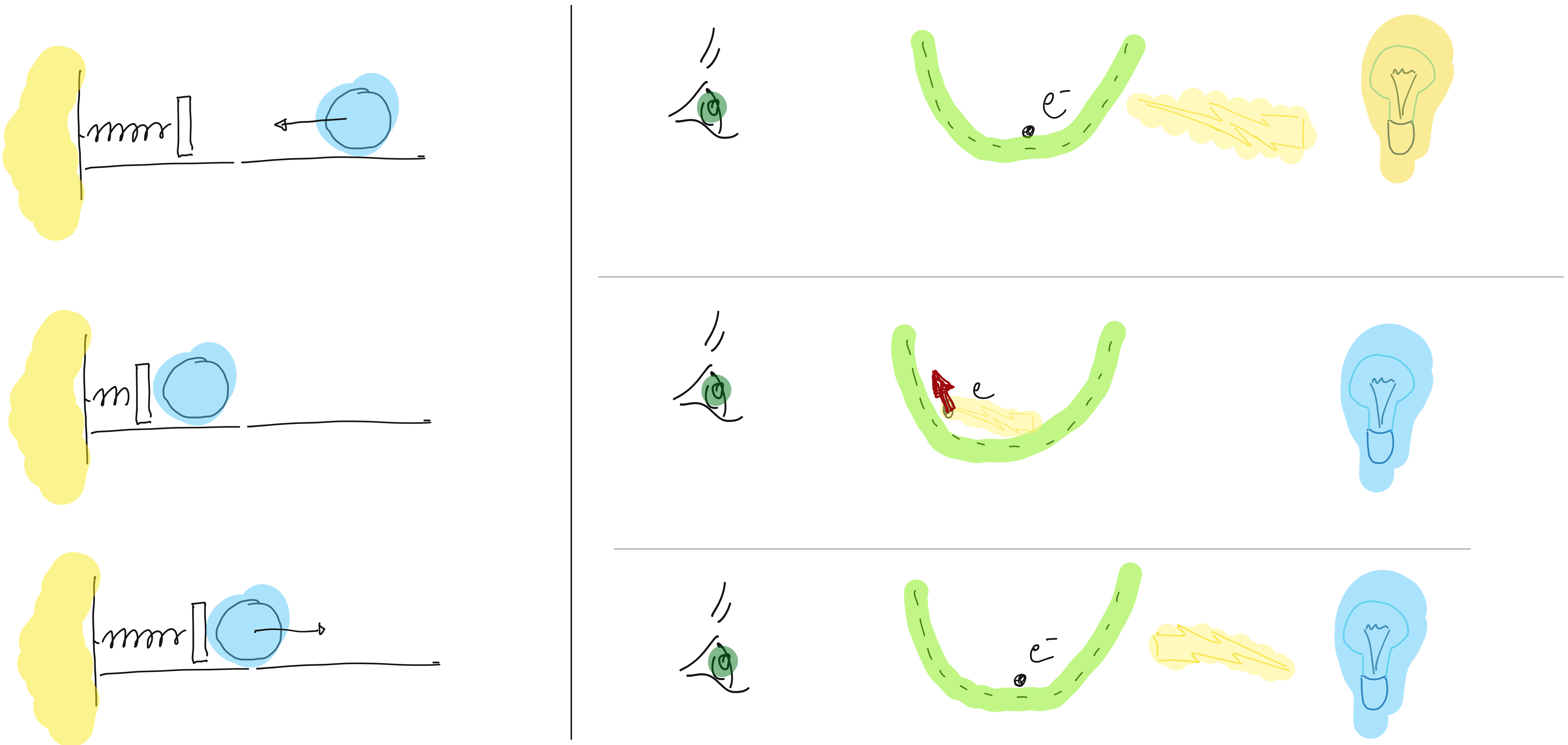
$$\boxed{\varepsilon(\omega) = 1 + 4\pi \chi^{el}(\omega) + 4\pi \chi^{ion}(\omega)}$$

Material response to Electro-Magnetic field

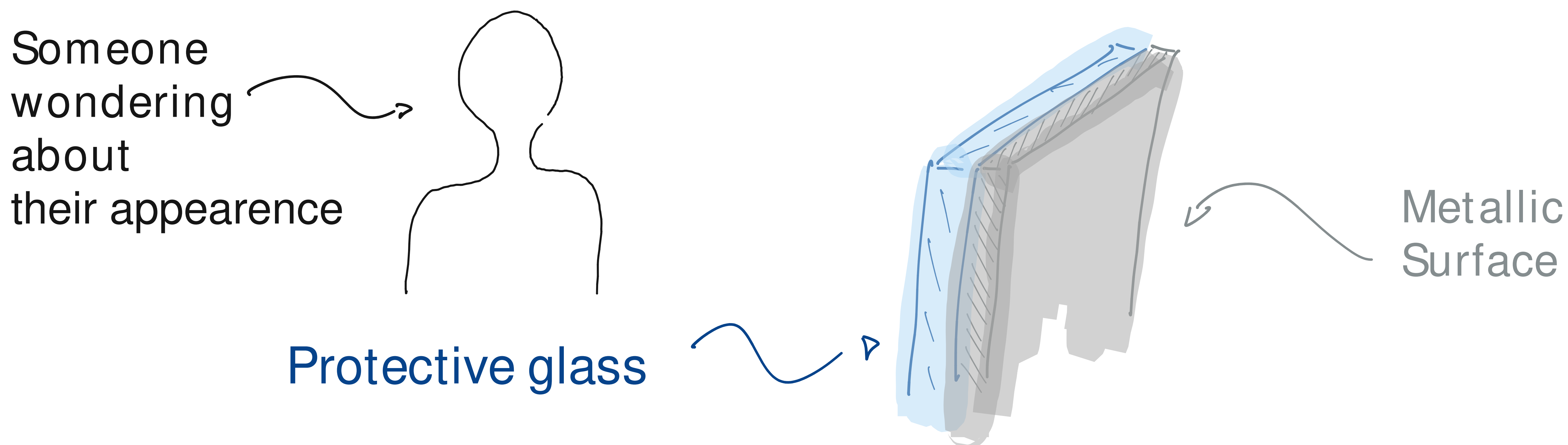
n_0 : environmental refractive index



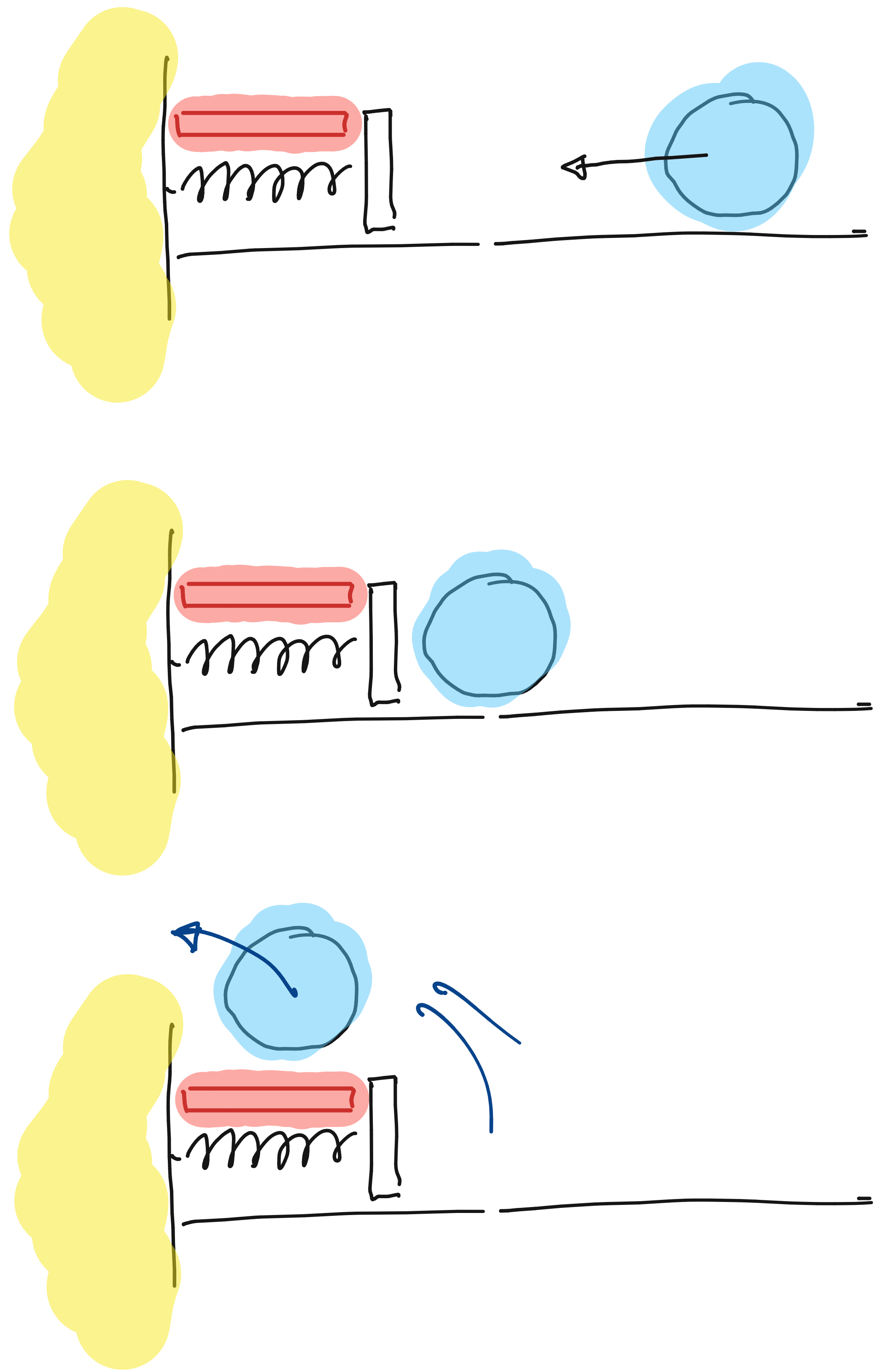
Metals: reflect

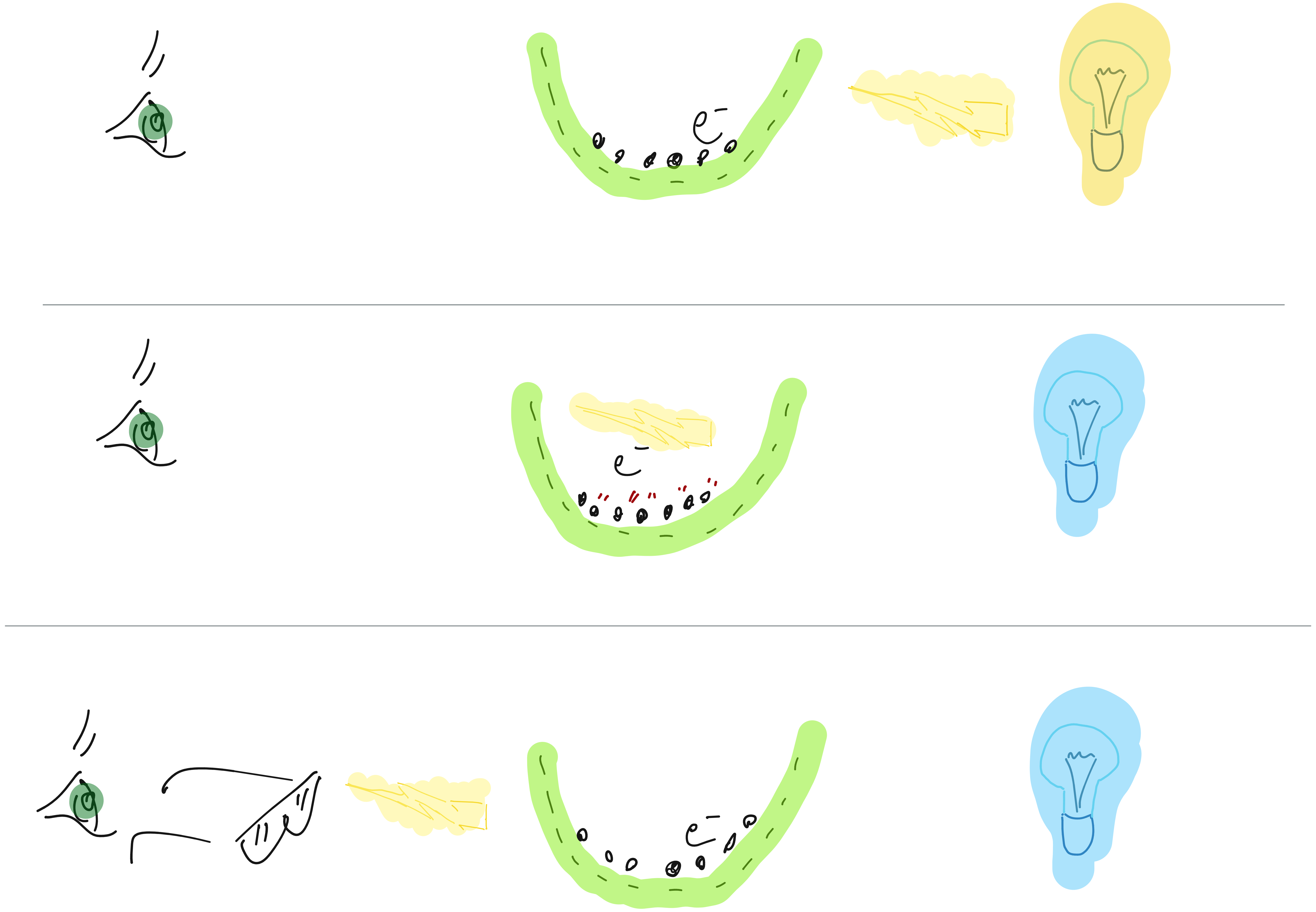


Mirrors:

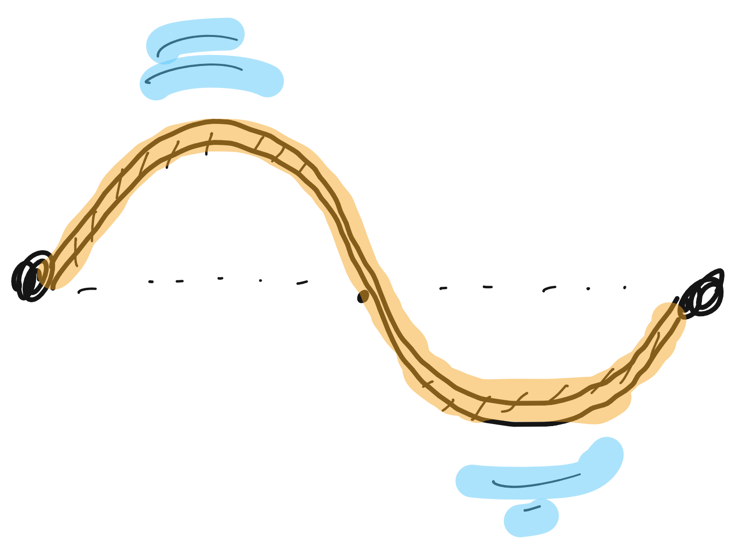


INSULATORS: do not reflect

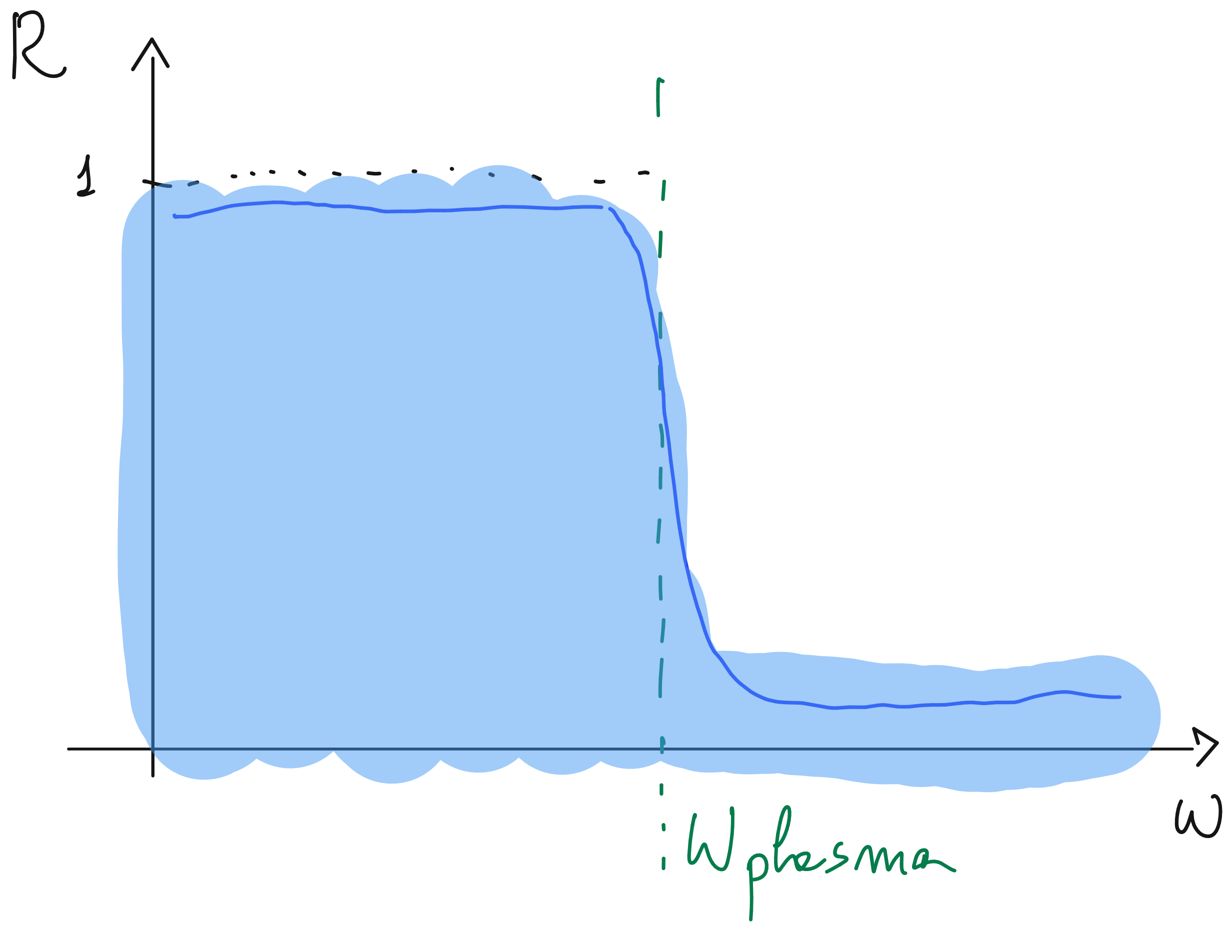


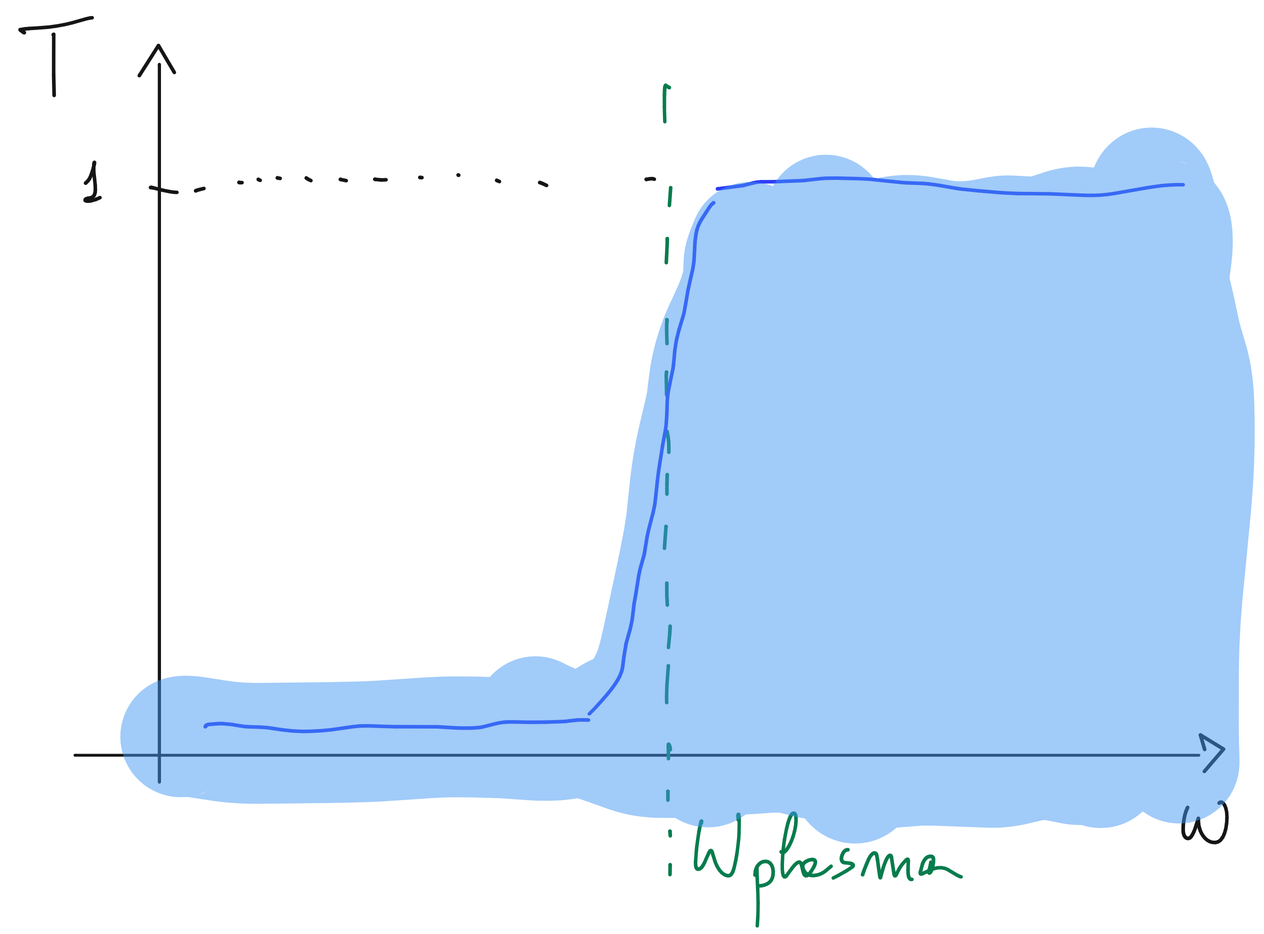


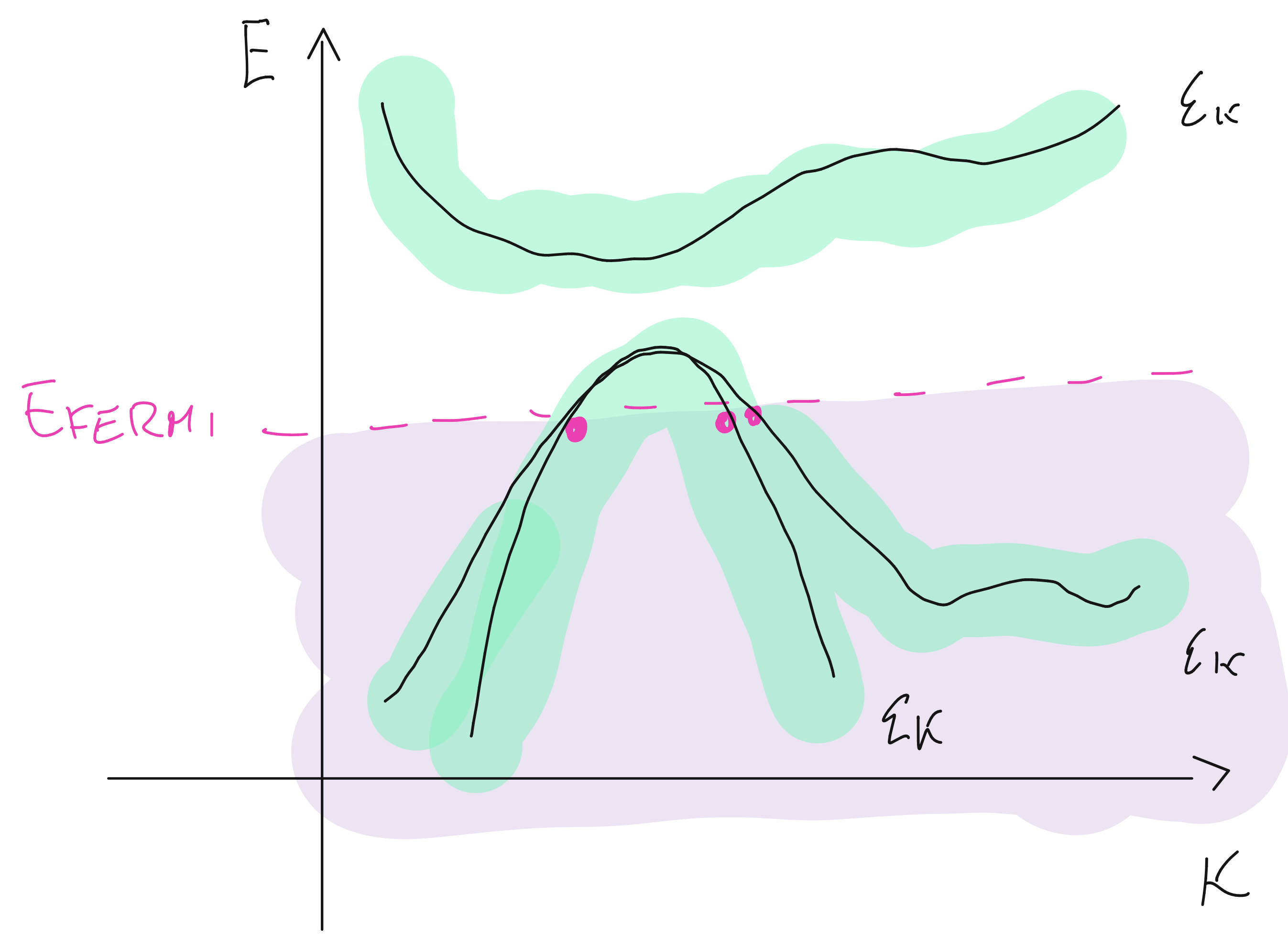
Pauli exclusion principle generates the discrete energy levels called "bands structure"
Periodicity makes completely filled (empty) bands inert.
(Perfect sinusoidal waves don't transport water, also like an oscillating rope)



METALS

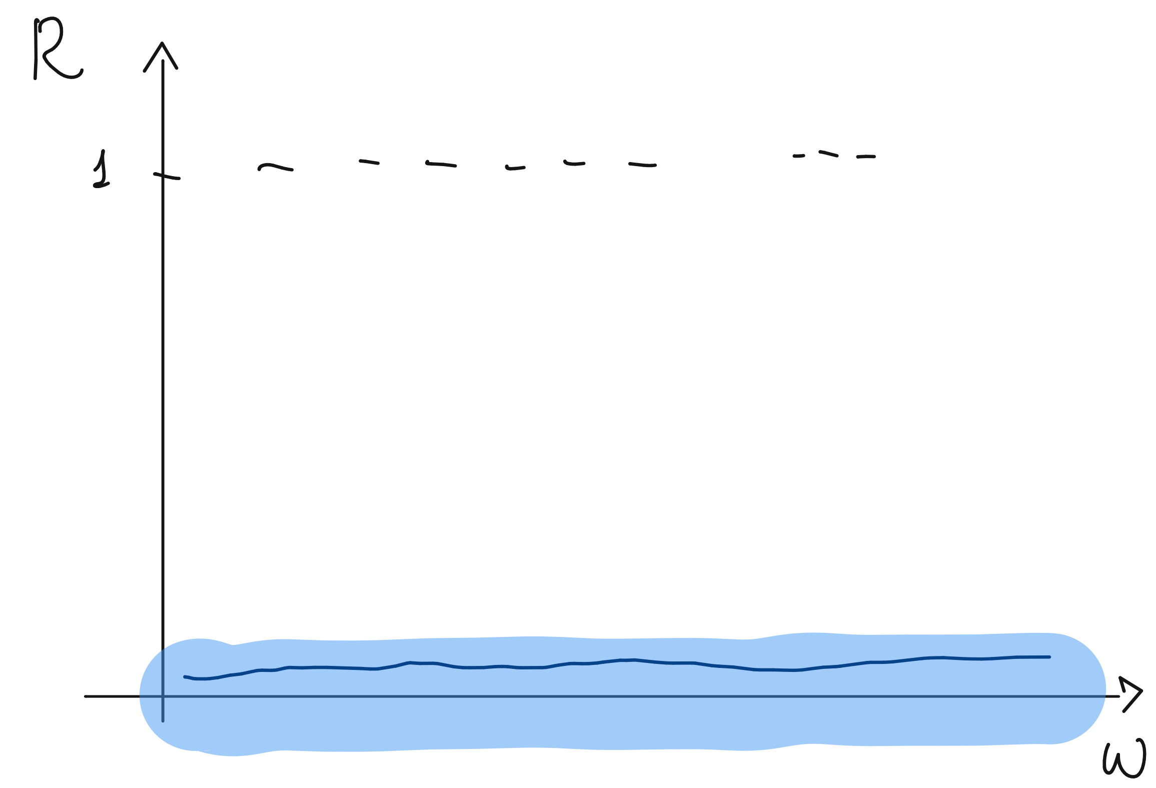


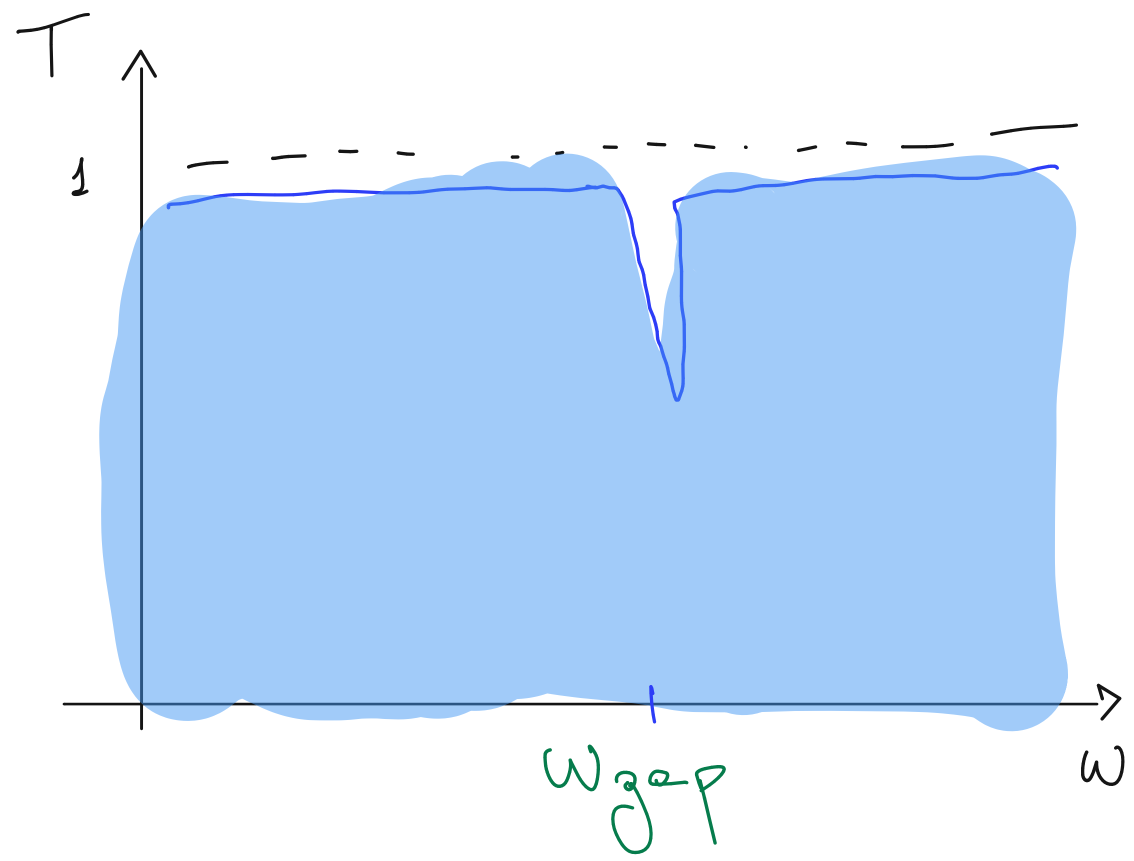


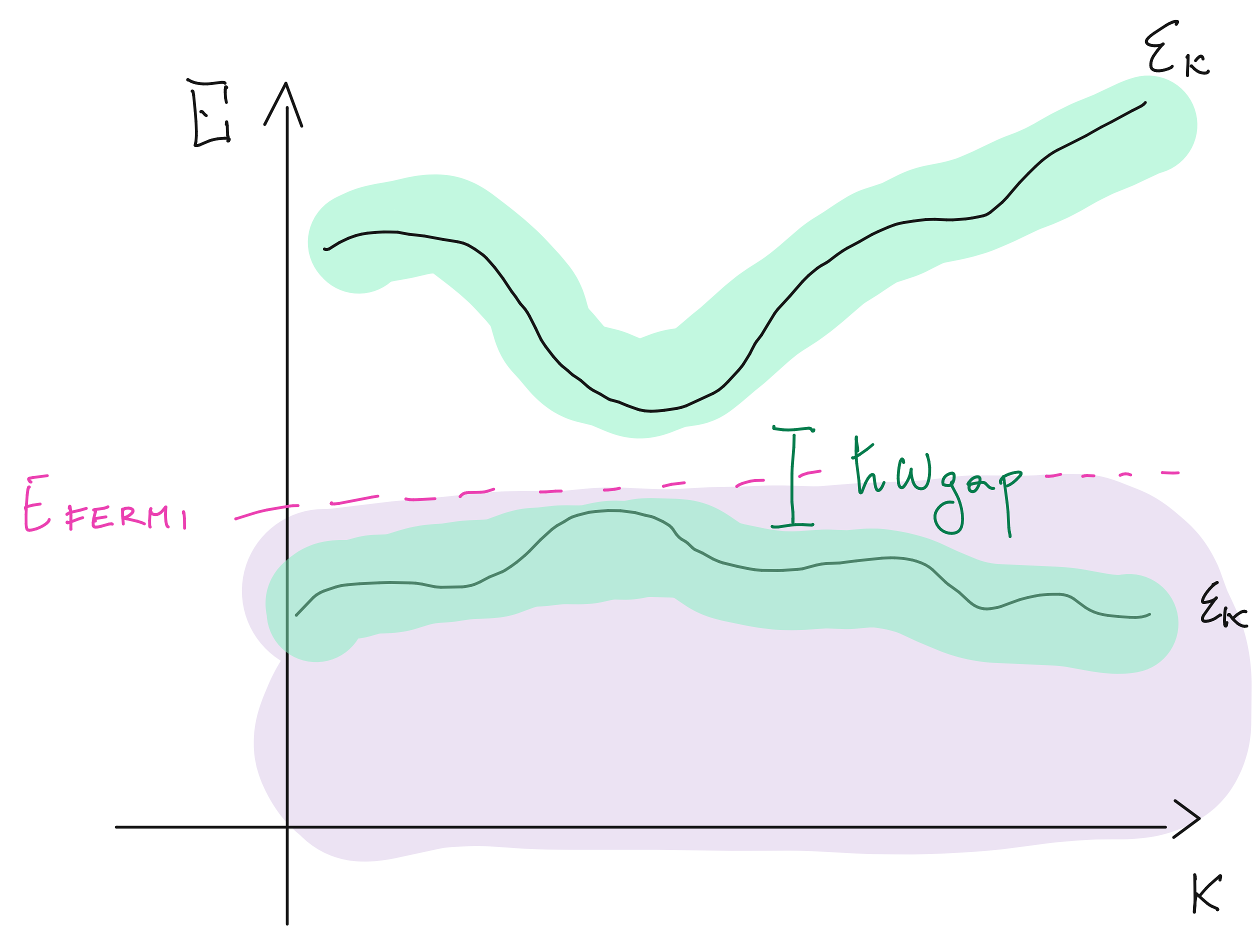


∃ Intersection: There are some "free" carriers

INSULATORS







∄ intersection: no freedom

Pauli exclusion principle generates the discrete energy levels called "bands structure"
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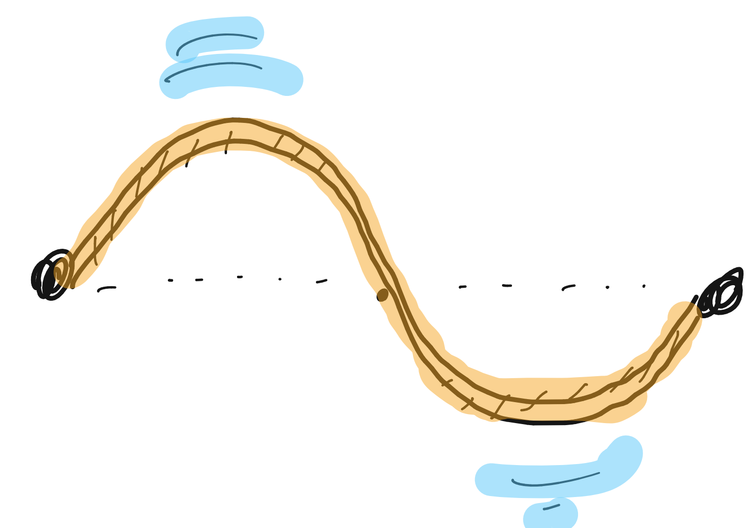
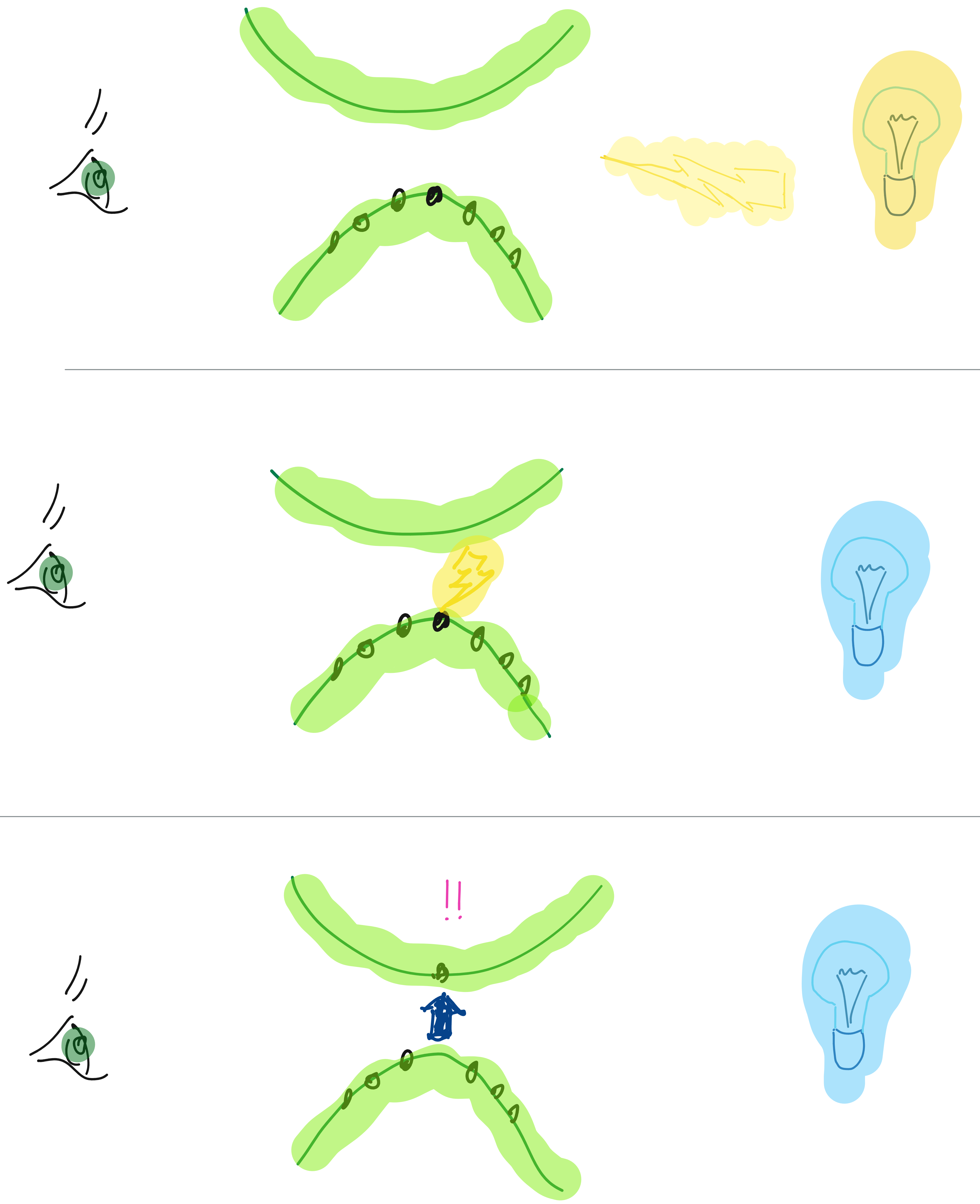
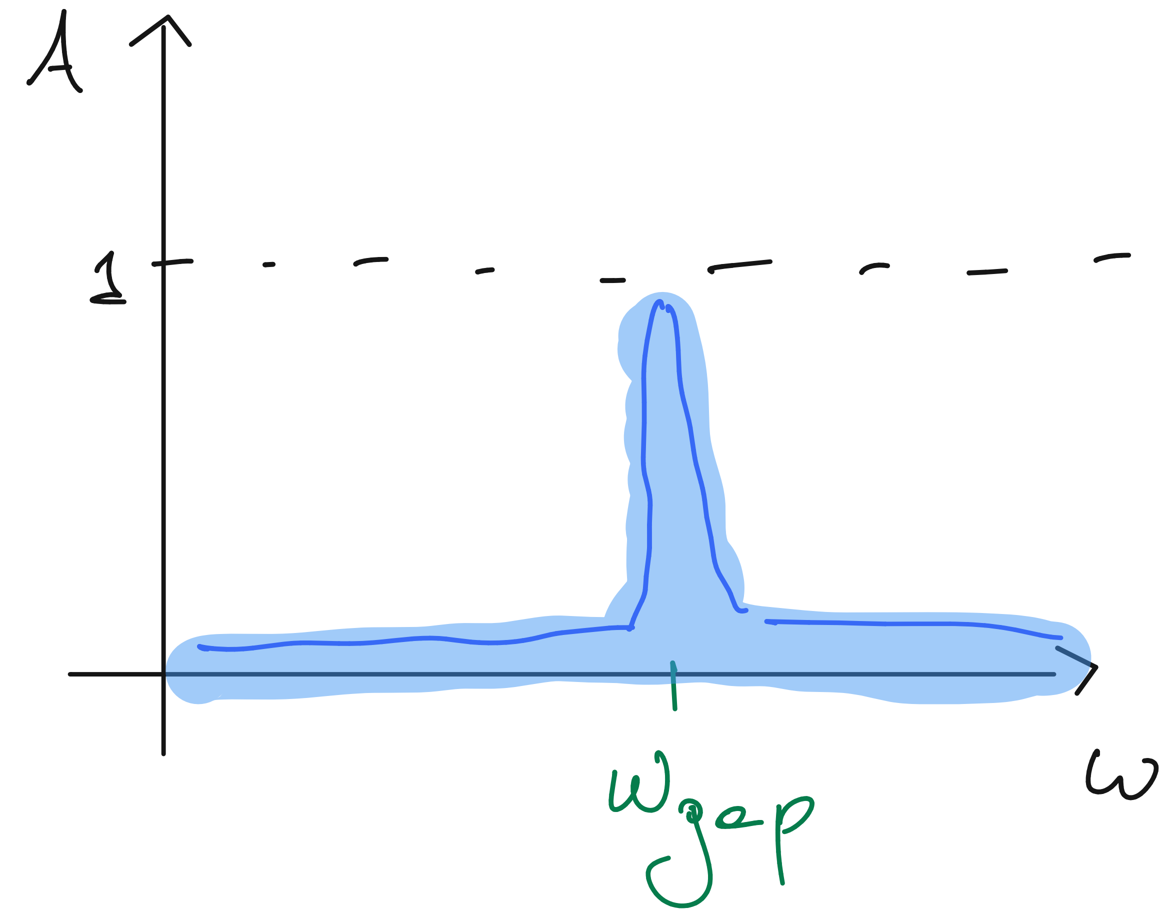


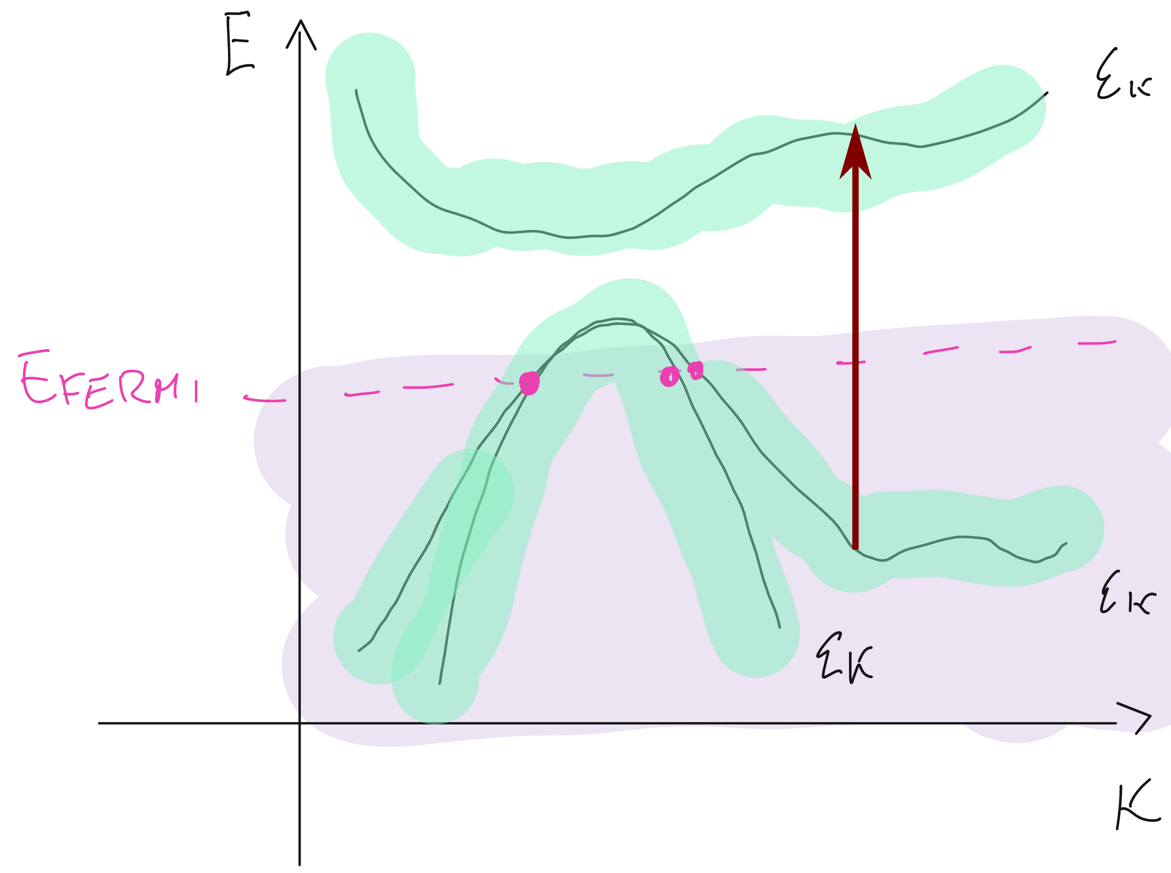
INTERBAND RESONANCE



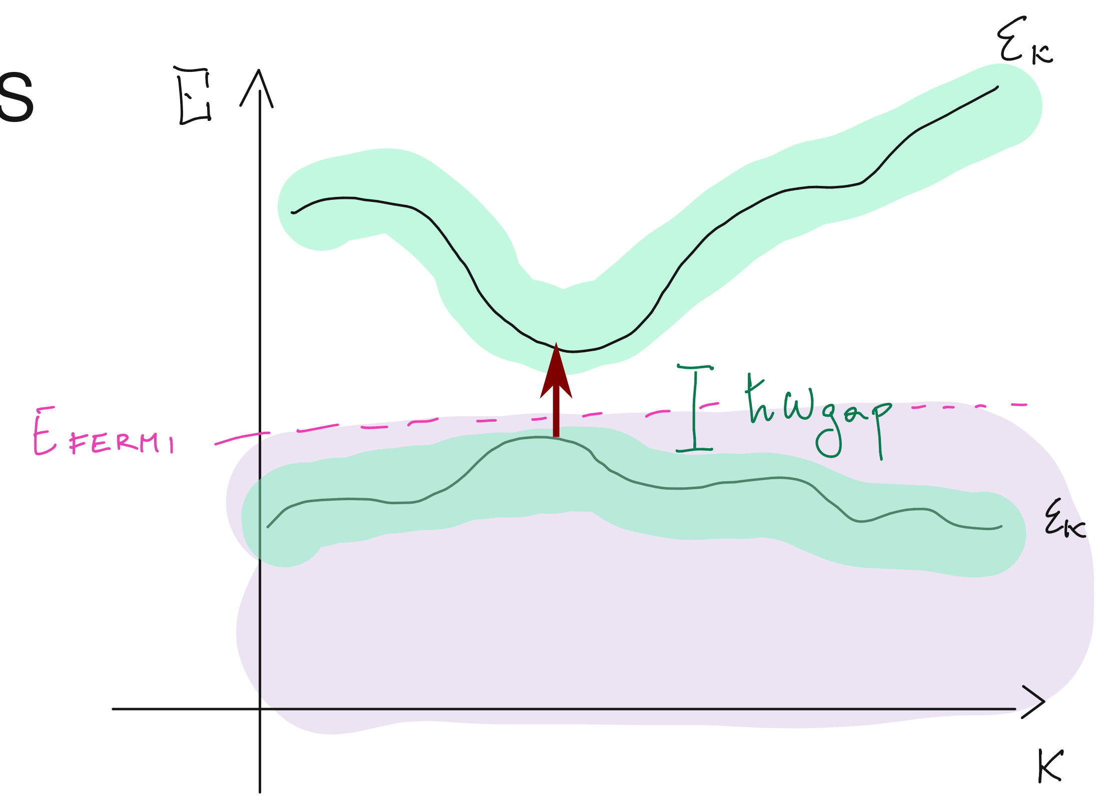
Light can be absorbed



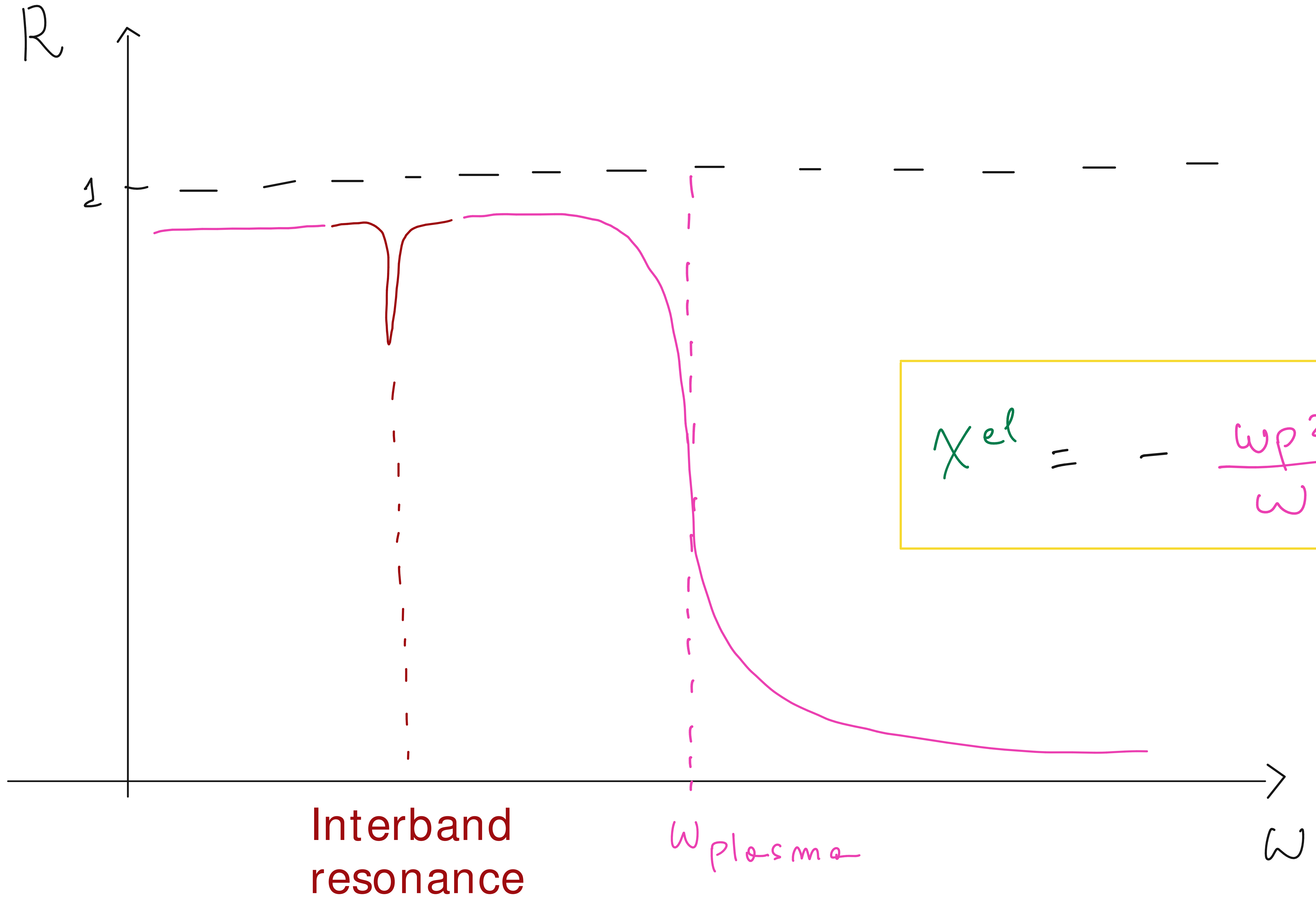
METALS



INSULATORS



TWO CONTRIBUTIONS FROM ELECTRONS



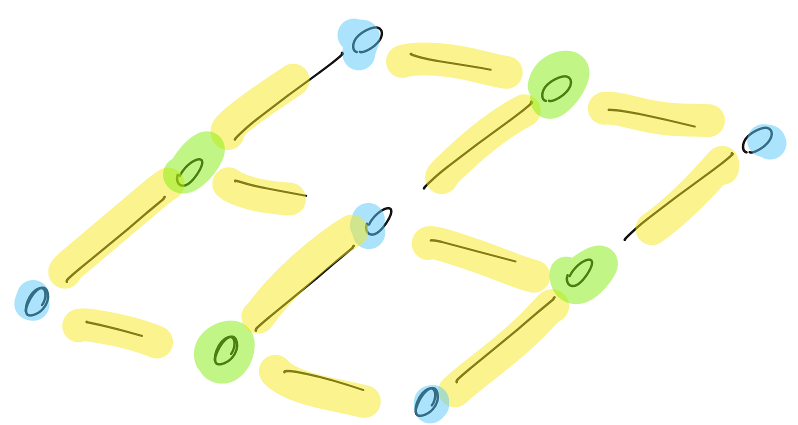
$$\boxed{\chi^{el} = -\frac{\omega_p^2}{\omega^2} + 4\pi\,\chi^{el}_{INTER}}$$

$$R = \left|\frac{\sqrt{\varepsilon} - n_0}{\sqrt{\varepsilon} + n_0}\right|^2 \qquad \varepsilon = 1 + 4\pi\,\chi^{el} + 4\pi\,\chi_{ion}$$

And the ionic contribution?

$$\varepsilon = 1 - \frac{\omega_p^2}{(\omega + i\eta)^2} \longrightarrow \varepsilon(\omega < \omega_p) < 0 \longrightarrow \sqrt{\varepsilon} \in \mathrm{Im} \Rightarrow |\sqrt{\varepsilon} - n_0| = |\sqrt{\varepsilon} + n_0| \qquad R = \left|\frac{\sqrt{\varepsilon} - n_0}{\sqrt{\varepsilon} + n_0}\right|^2 = 1$$

PHONONS



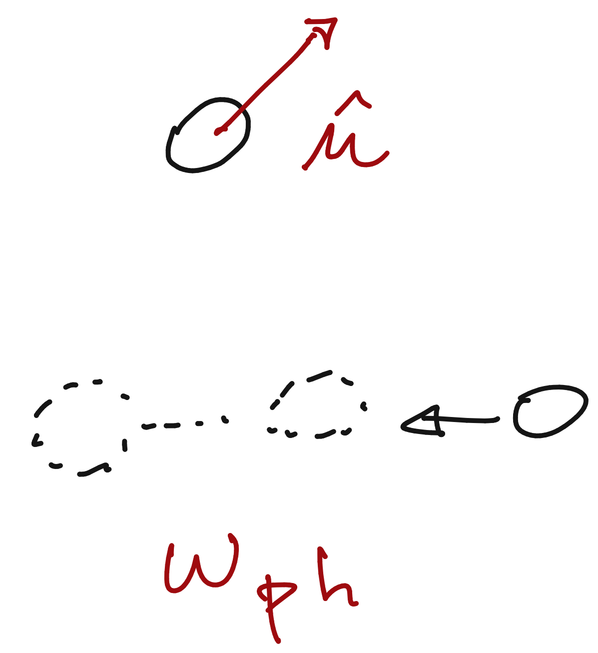
Crystal lattice

$$H = \sum \frac{p_i^2}{2m} + V$$

$$\bar{\bar{D}}_{\mu\nu} = \frac{\partial^2 V}{\partial u_\mu \, \partial u_\nu}$$

$\hat{u}$ – displacement

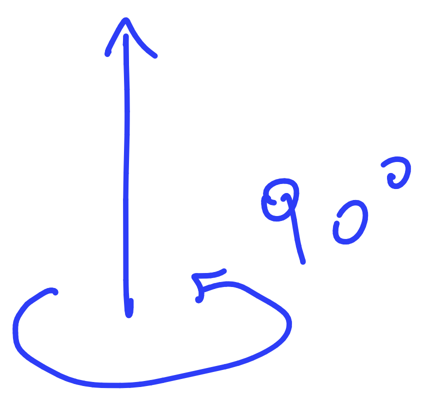
ω_{ph} – oscillation frequence



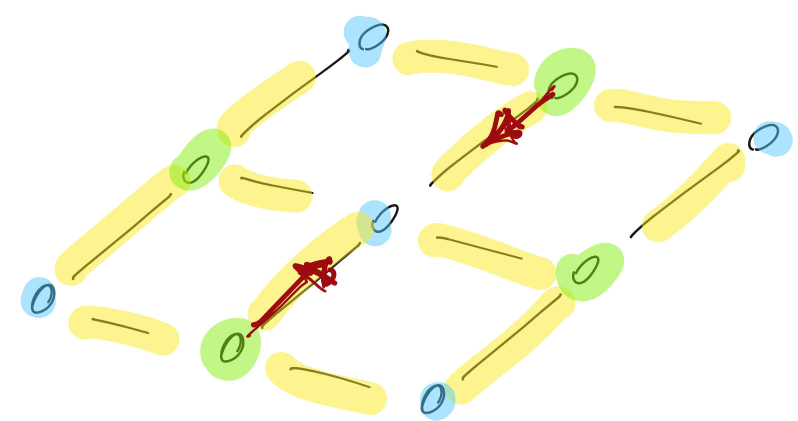
$\bar{\bar{D}} \Rightarrow$ $\hat{u}$ eigenvectors

ω_{ph} eigenvalues

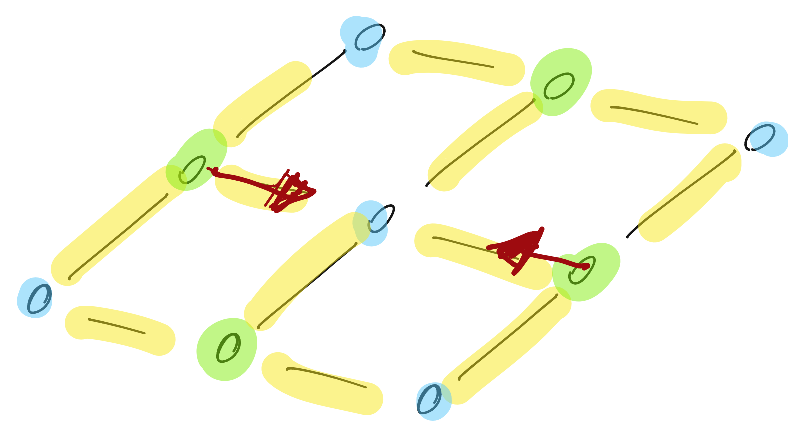
SYMMETRIES



$R_{\hat{z}}[90°] : V(r) \longrightarrow V(r)$

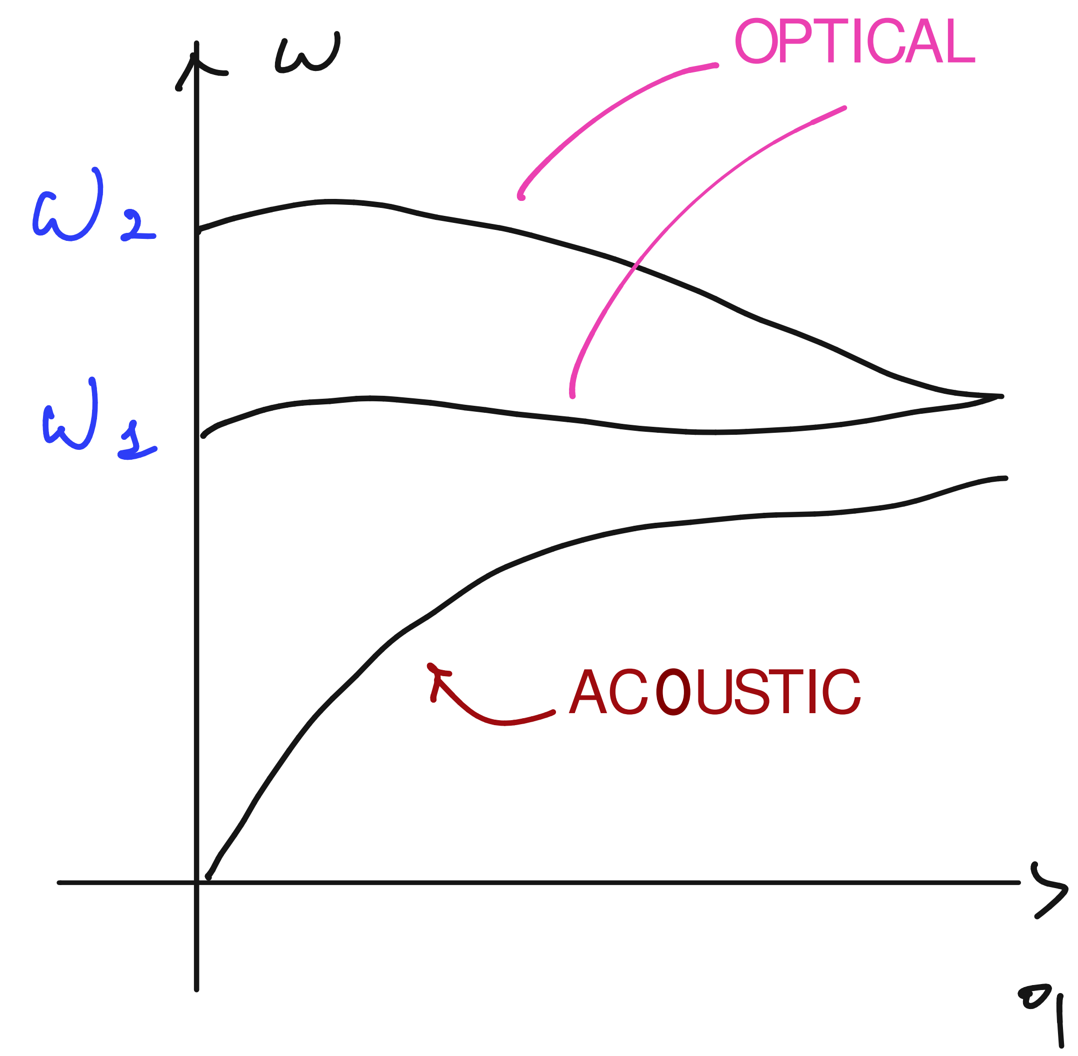


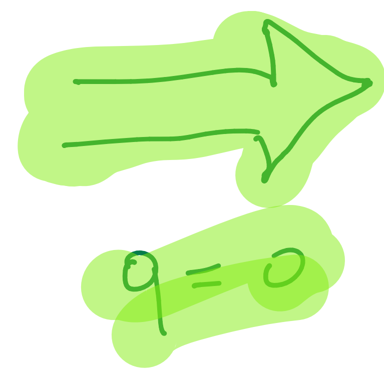
same frequency



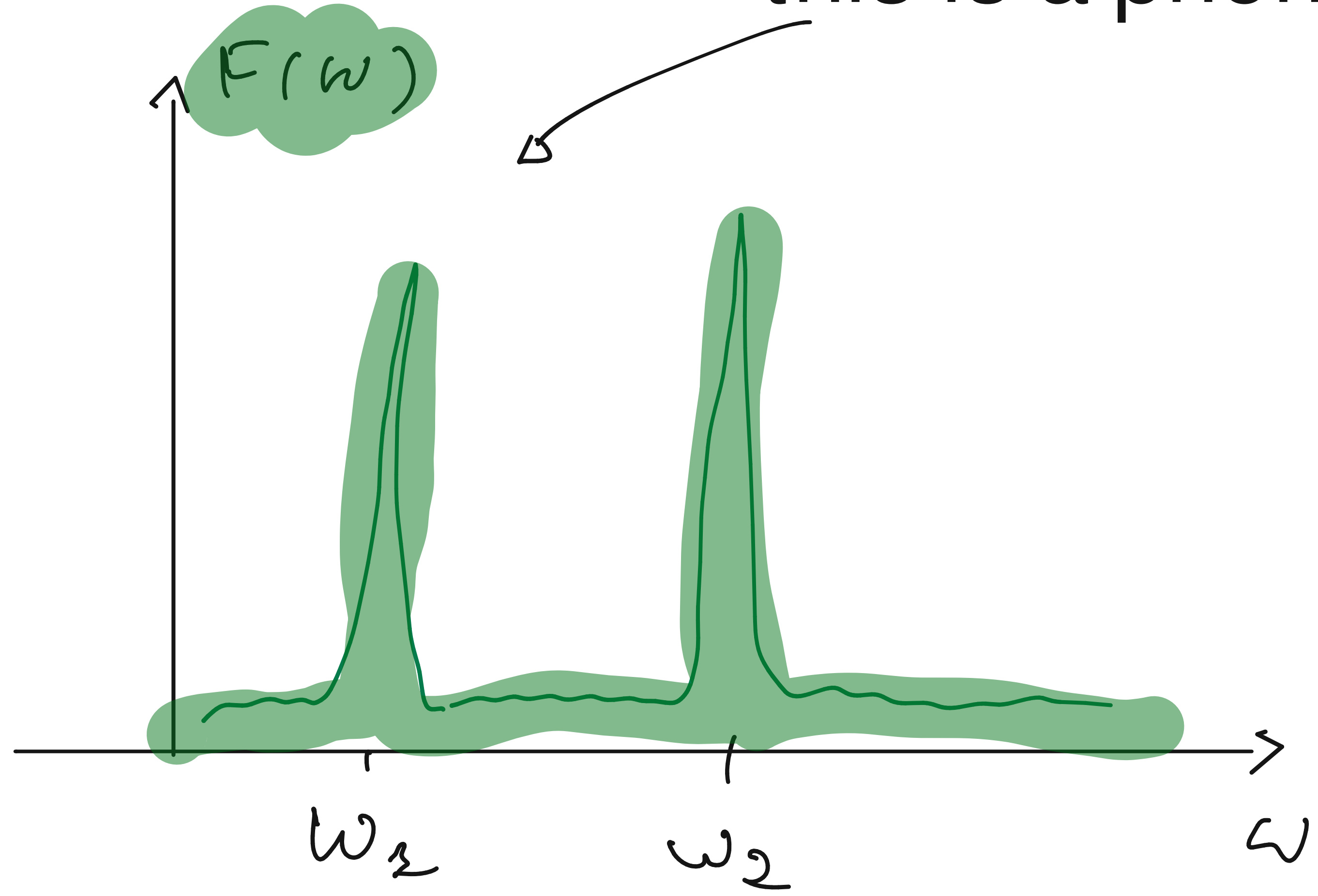
It's enough to know the symmetries of the phonons (experimentally)
to obtain information about the geometrical structure

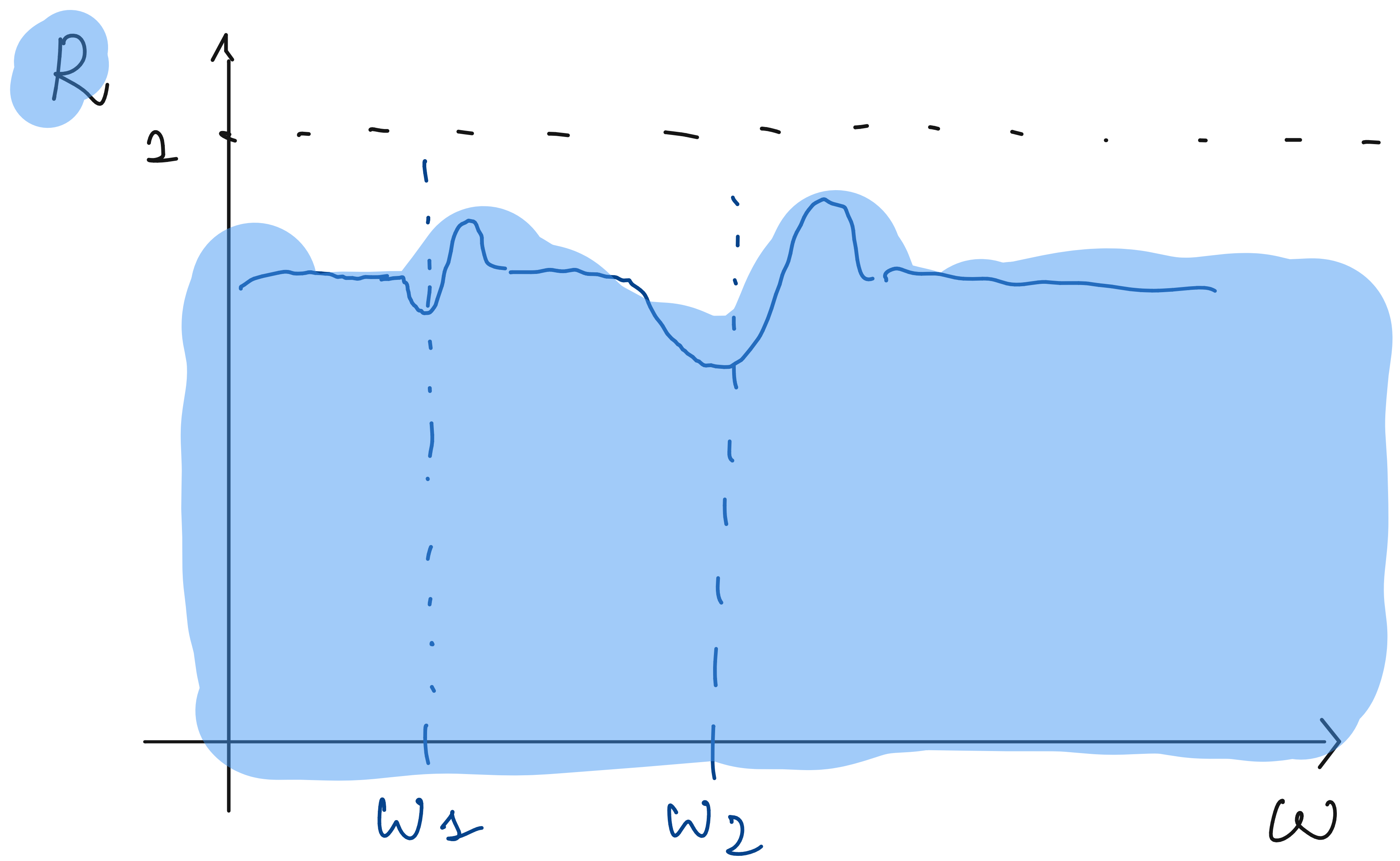
Vibrational resonances





this is a phonon

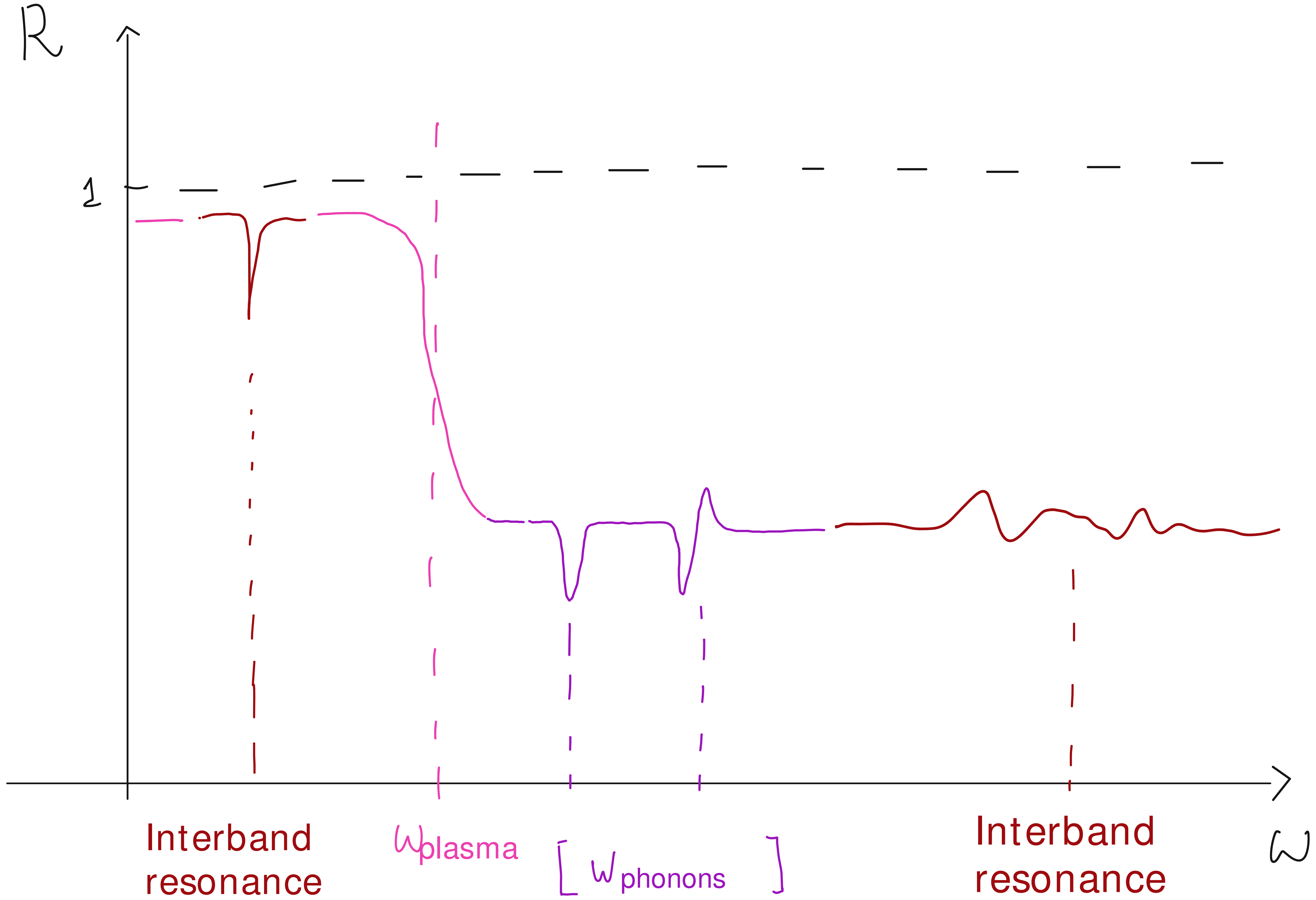


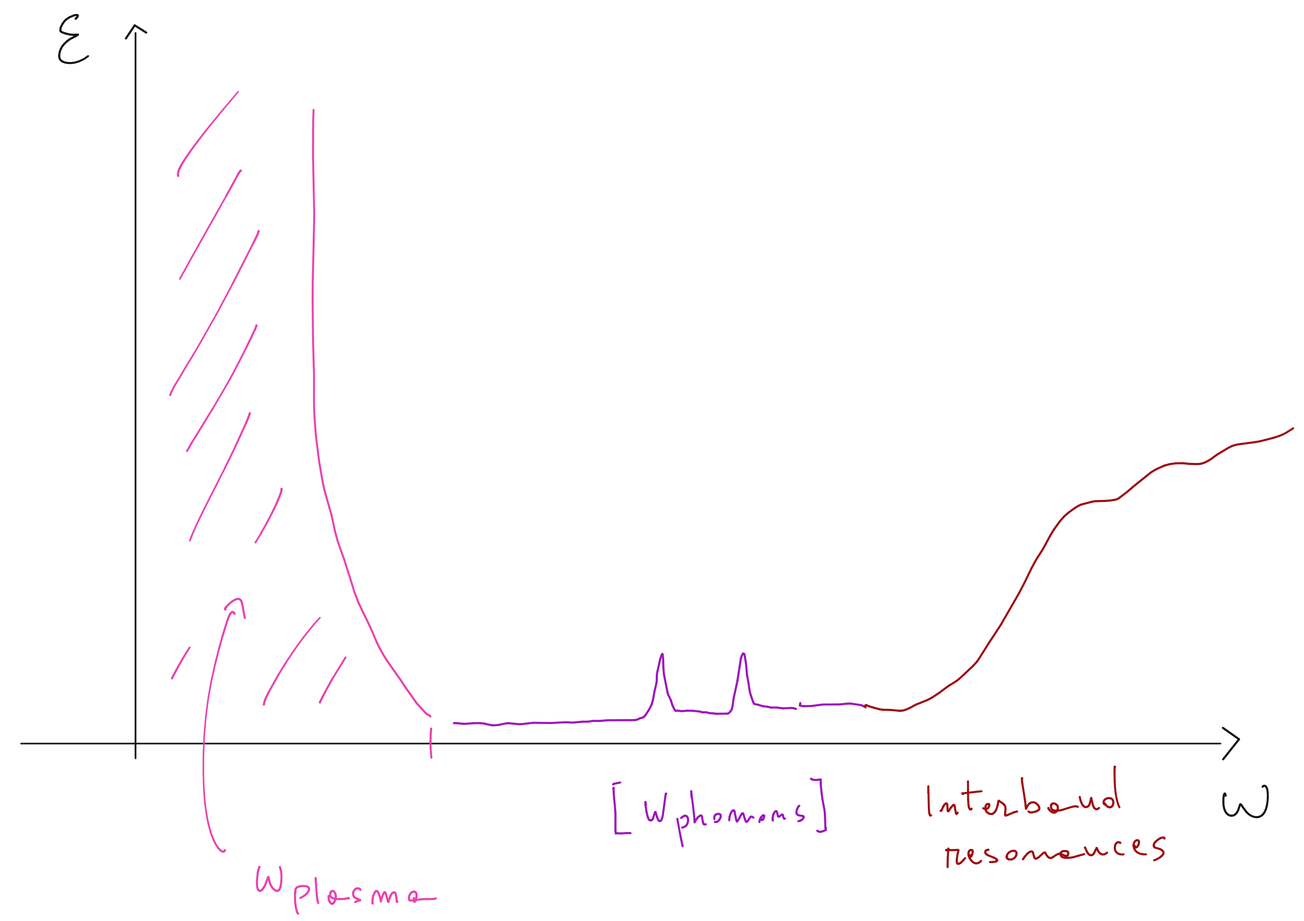


Phonons can be seen
as peaks in the reflectivity !!

$$\varepsilon(\omega) = 1 + 4\pi\,\chi^{el}(\omega) + 4\pi\,\chi^{ion}(\omega)$$

IDEAL CASE: everything clearly visible

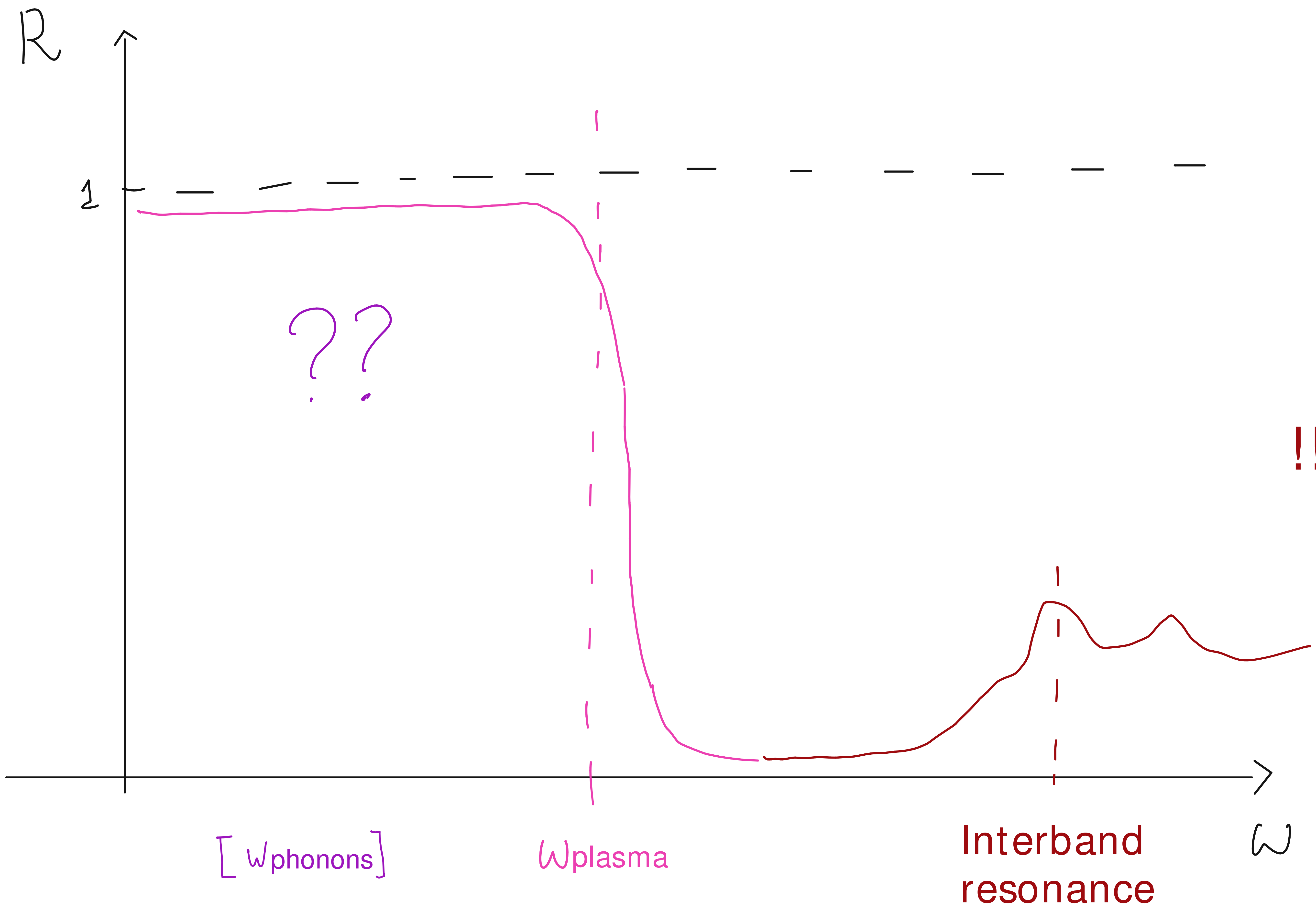


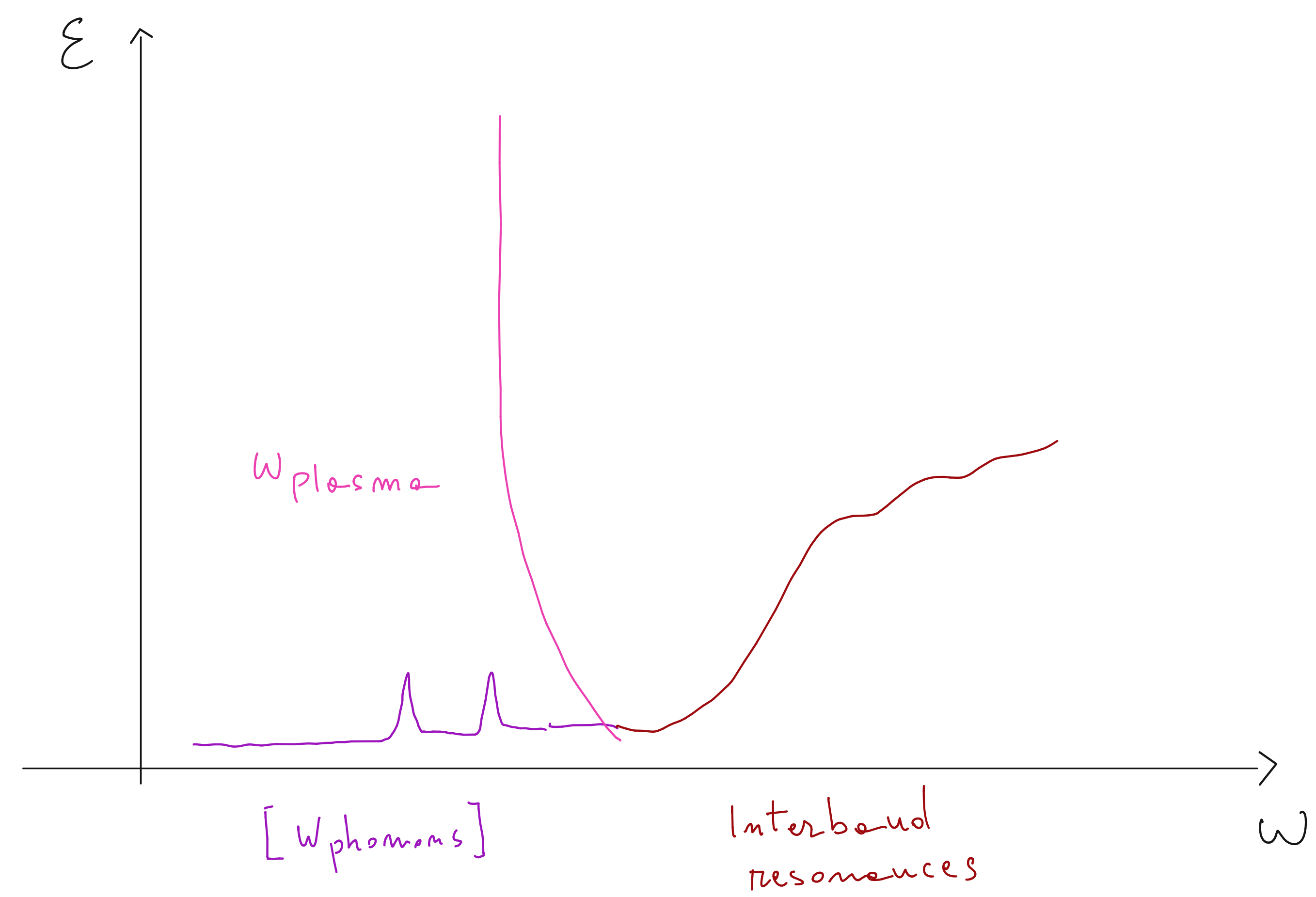


$$R = \left| \frac{\sqrt{\varepsilon} - n_0}{\sqrt{\varepsilon} + n_0} \right|^2$$

$$\varepsilon = 1 \underbrace{- \frac{\omega_p^2}{\omega^2}}_{\chi_{el}} + 4\pi \chi_{ion} + \underbrace{4\pi \chi^{el}_{INTER}}_{\chi_{el}}$$

Most metals:

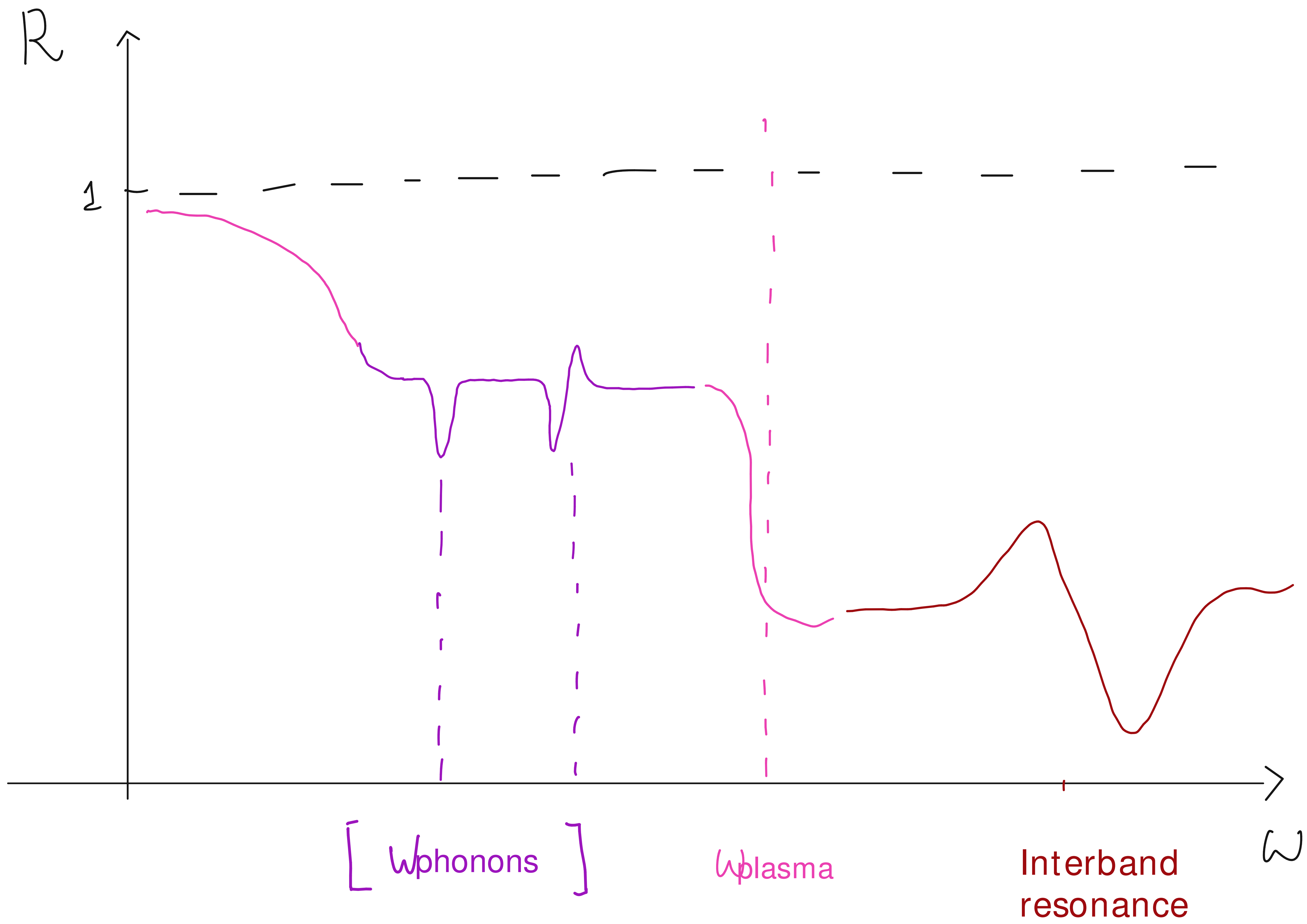




!! Impossible to see phononic features!!

$$\varepsilon = 1 + 4\pi\chi_{el} + 4\pi\chi_{ion} \simeq 1 + 4\pi\chi_{el}$$

SOME METALS:



Idea: even if there are free carriers (a plasma peak exists)
they "live" too shortly to oscillates and thus perfectly reflects light

Hence, other contributions are now visible

How to simulate IR reflectivity

"Dynamical linear response function in DFPT" (Density Functional Perturbation Theory)

- are computed straightforwardly by the canalitinel formula
- where $\{\psi_{\kappa i}\}$, $\{\varepsilon_{\kappa i}\}$ are solved SCF via $\underbrace{\text{Kohn-Sham theorem}}$

The magic behind DFT framework

Averaging over different energies

Finite Temperature

$$\chi_{el}^{AB} = \int d^3k \sum_{i,j} \frac{f(\varepsilon_{\kappa i}) - f(\varepsilon_{\kappa j})}{\varepsilon_{\kappa i} - \varepsilon_{\kappa j} - (\omega + i\eta)} \langle \psi_{\kappa i} | \partial_A H | \psi_{\kappa j} \rangle \langle \psi_{\kappa j} | \partial_B H | \psi_{\kappa i} \rangle$$

Averaging over reciprocal space

Energy Conservation

My Work:

- there are already packages to compute these properties
- Not feasible to apply them to metals
  - Using a straightforward implementation requires too many resources to be applied to the hard case of metals

[Metals depends more on frequency]

For each w: a very expensive calculation

($\frac{\partial H}{\partial A}(w)$: is computed self-consistently)

Self-consistent cycle:

$$H = \sum \frac{p^2}{2m} + V_{SCF}$$

$$\Delta V_{SCF} = \Delta V_{ext} + \int K_{Hxc}(r) \cdot \Delta\rho(r)$$

$$\Delta\psi(r) = \sum \frac{\langle\psi'|\Delta V|\psi\rangle}{\varepsilon - \varepsilon_0} |\psi'\rangle$$

$$\Delta\rho = \sum \langle\psi|r\rangle\langle r|\psi\rangle$$

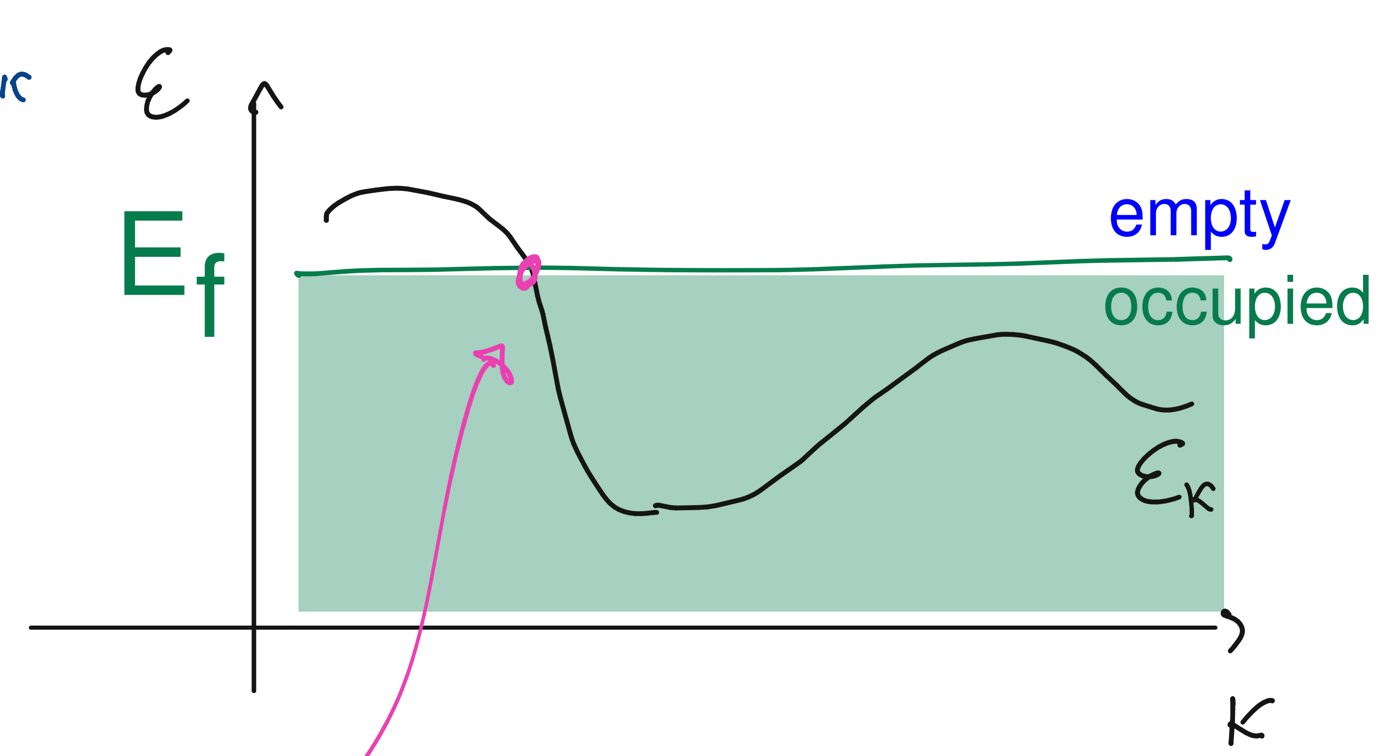
My Work:

- there are already packages to compute these properties
- Not feasible to apply them to metals
  - Using a straightforward implementation requires too many resources to be applied to the hard case of metals

! sampling is a bottleneck

$$\int d^3K \ldots \simeq \frac{1}{N_K}\sum_{K=1}^{N_K}$$

Metals need very high N_K



idea:

Smooth ≡ easy to sample

Efermi intersection ≠ smooth features
a lot changes between "ABOVE" and "BELOW"

New approach → new software

1] No self-consistent

2] Quick computation on many k-points

(thanks to Wannier interpolation)

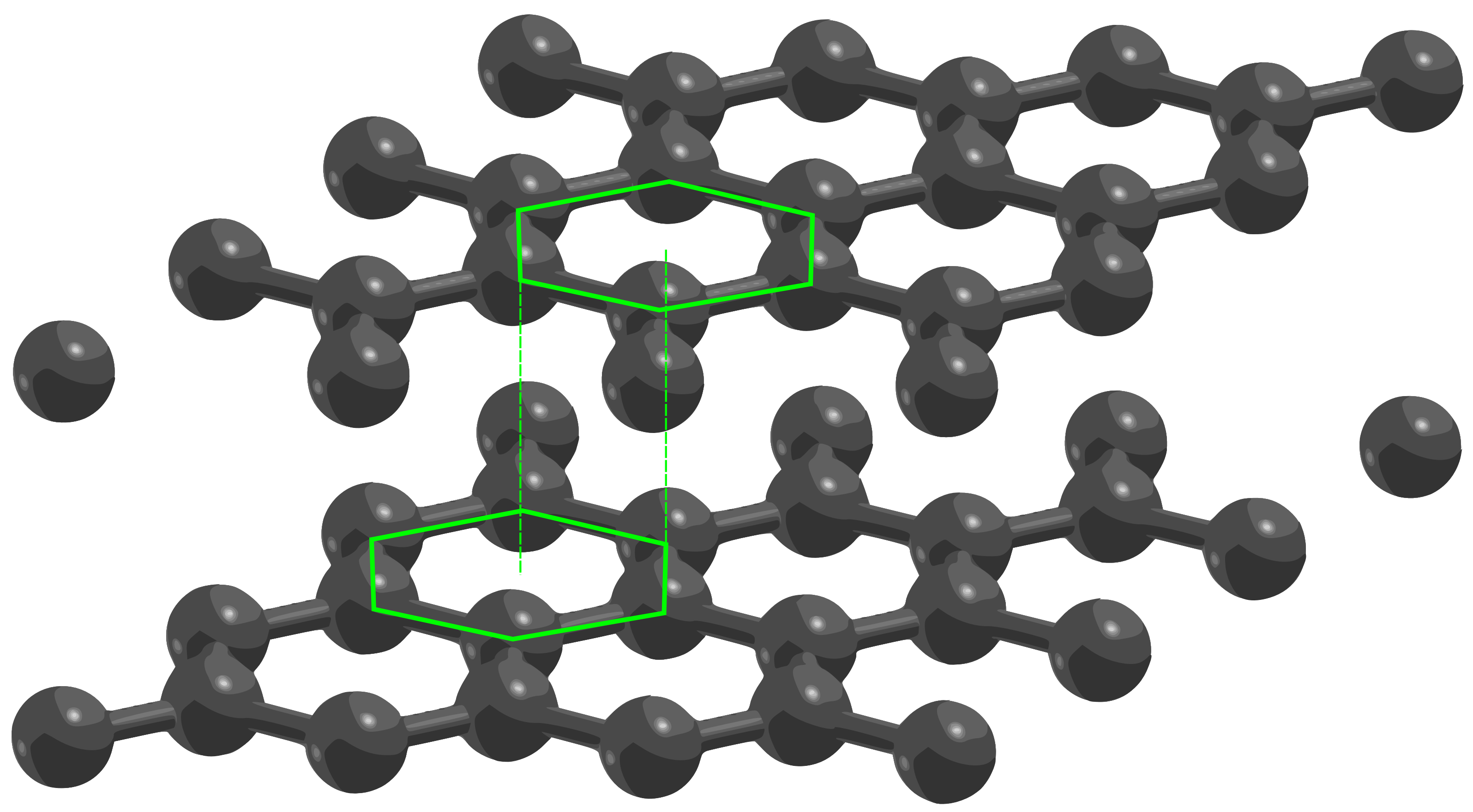
At the price of adding only a quadratic error !!!

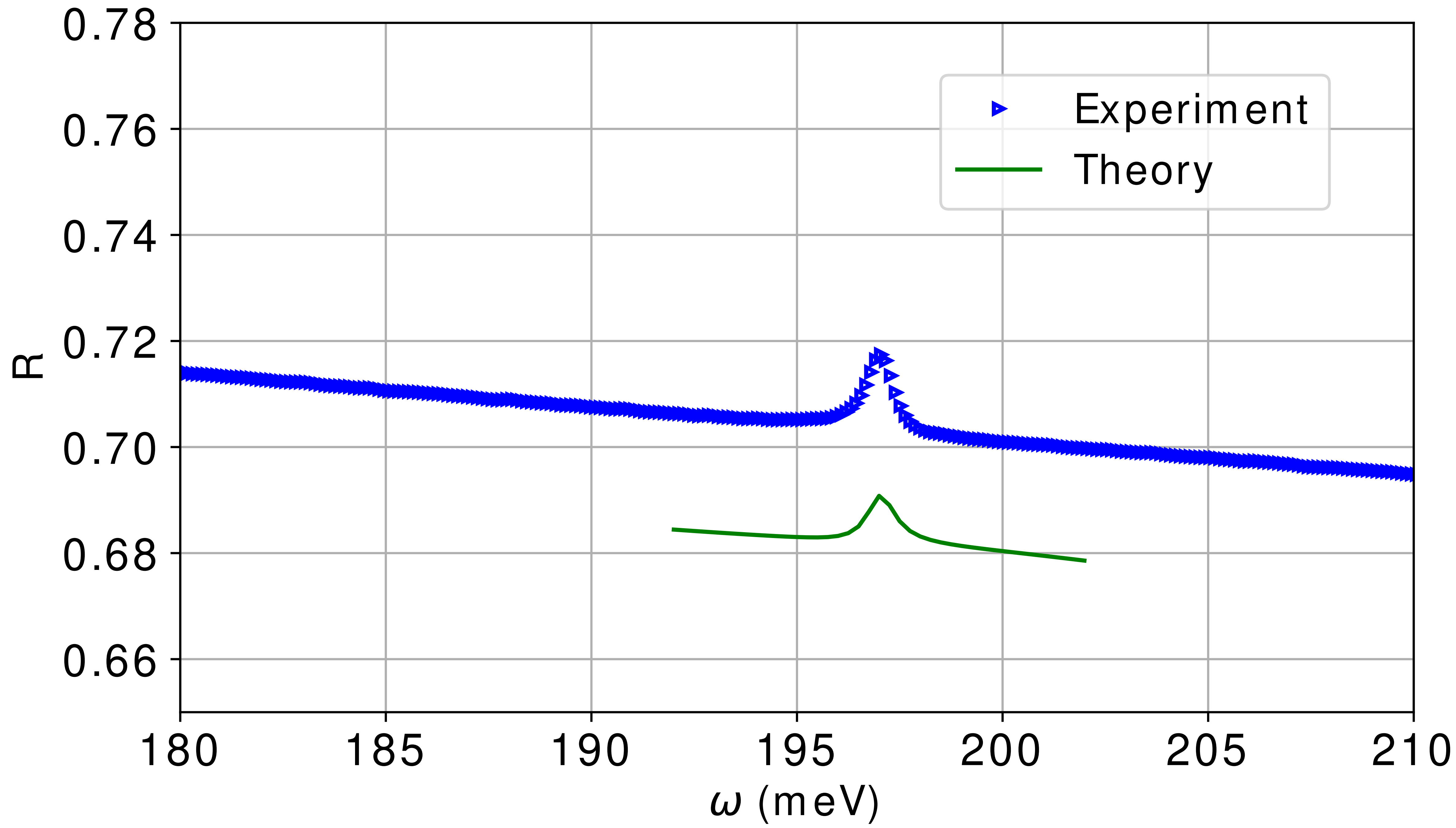
Quick layout: Thanks to a simple rewriting of χ_{AB}

- one SCF calculation for easy parameters
- refine the preliminary scf with nscf calculation

RESULTS:

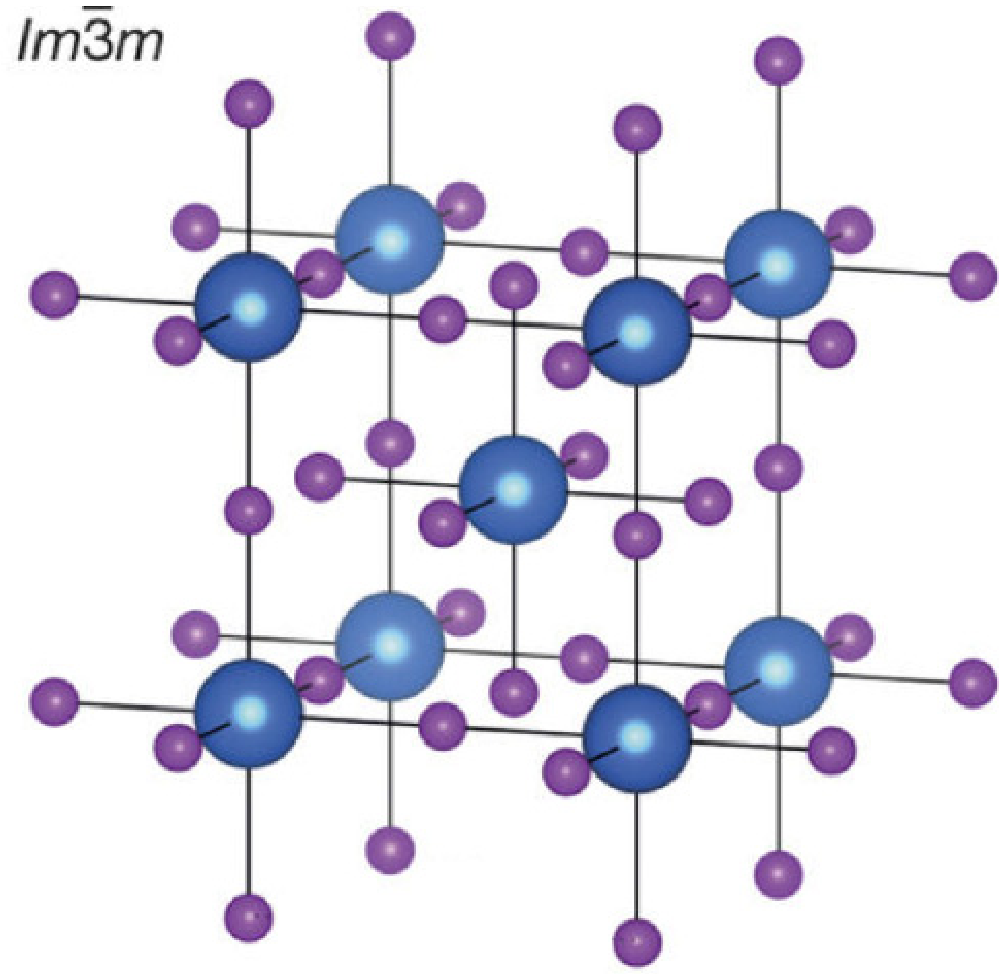
Graphite

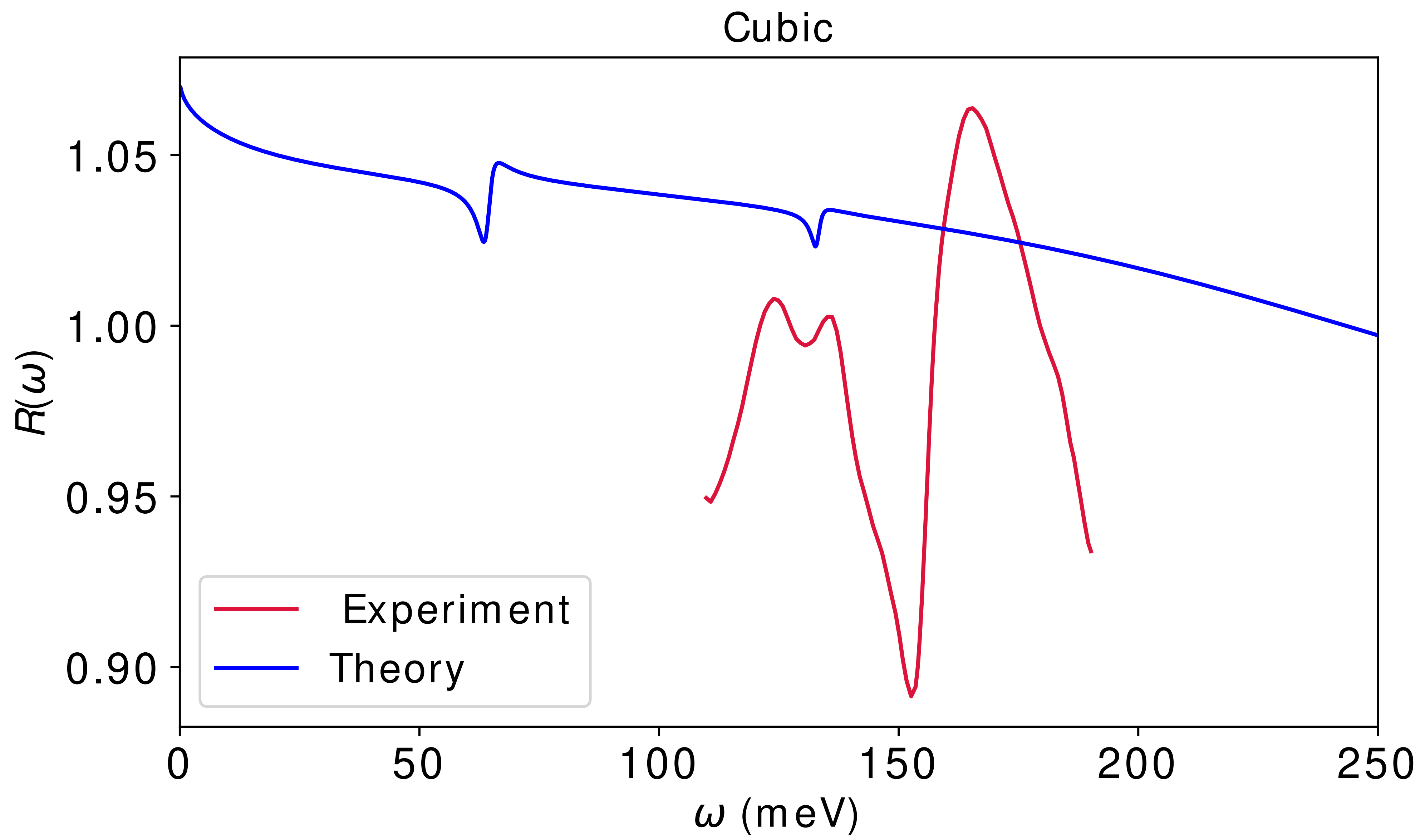


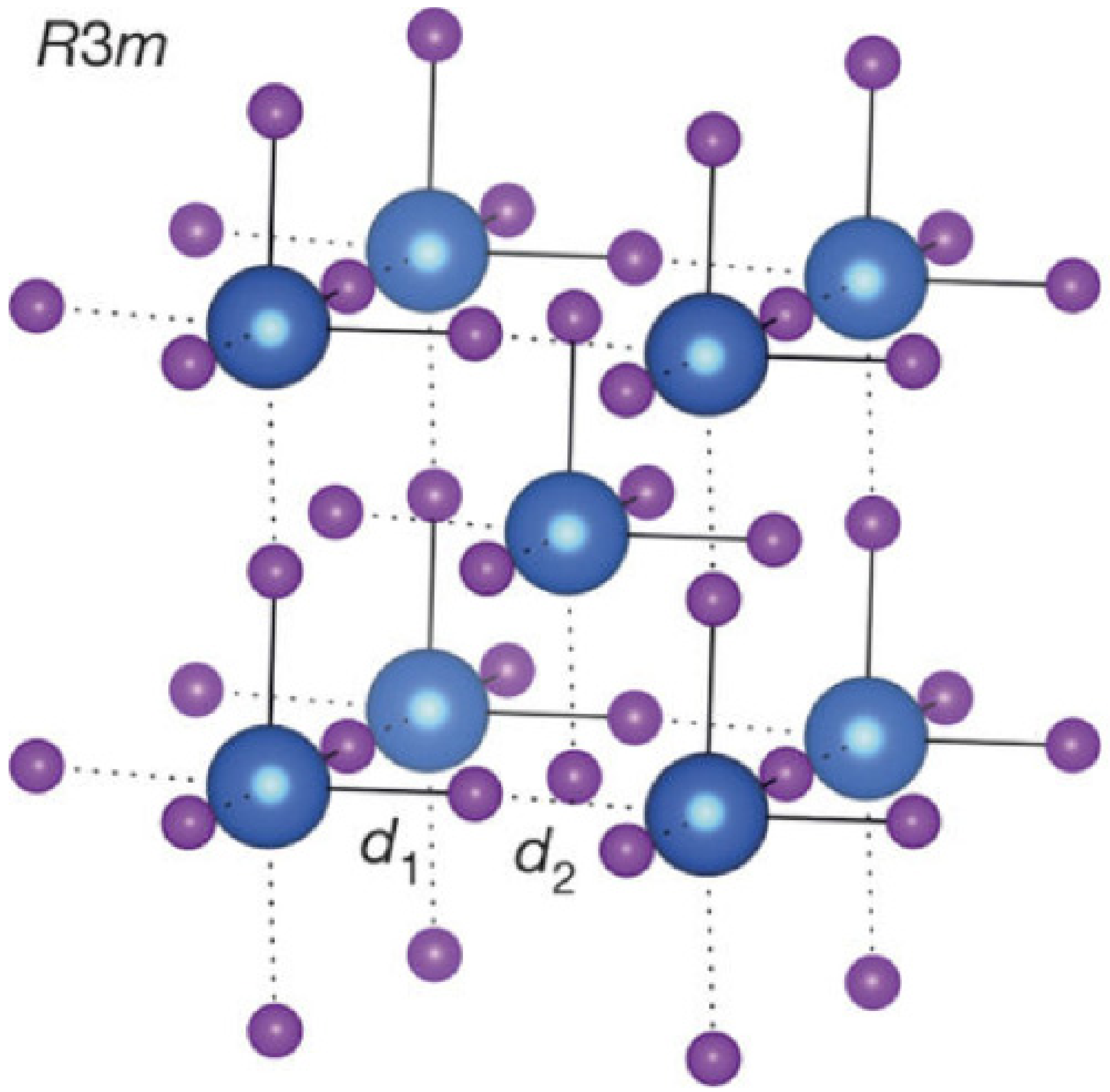


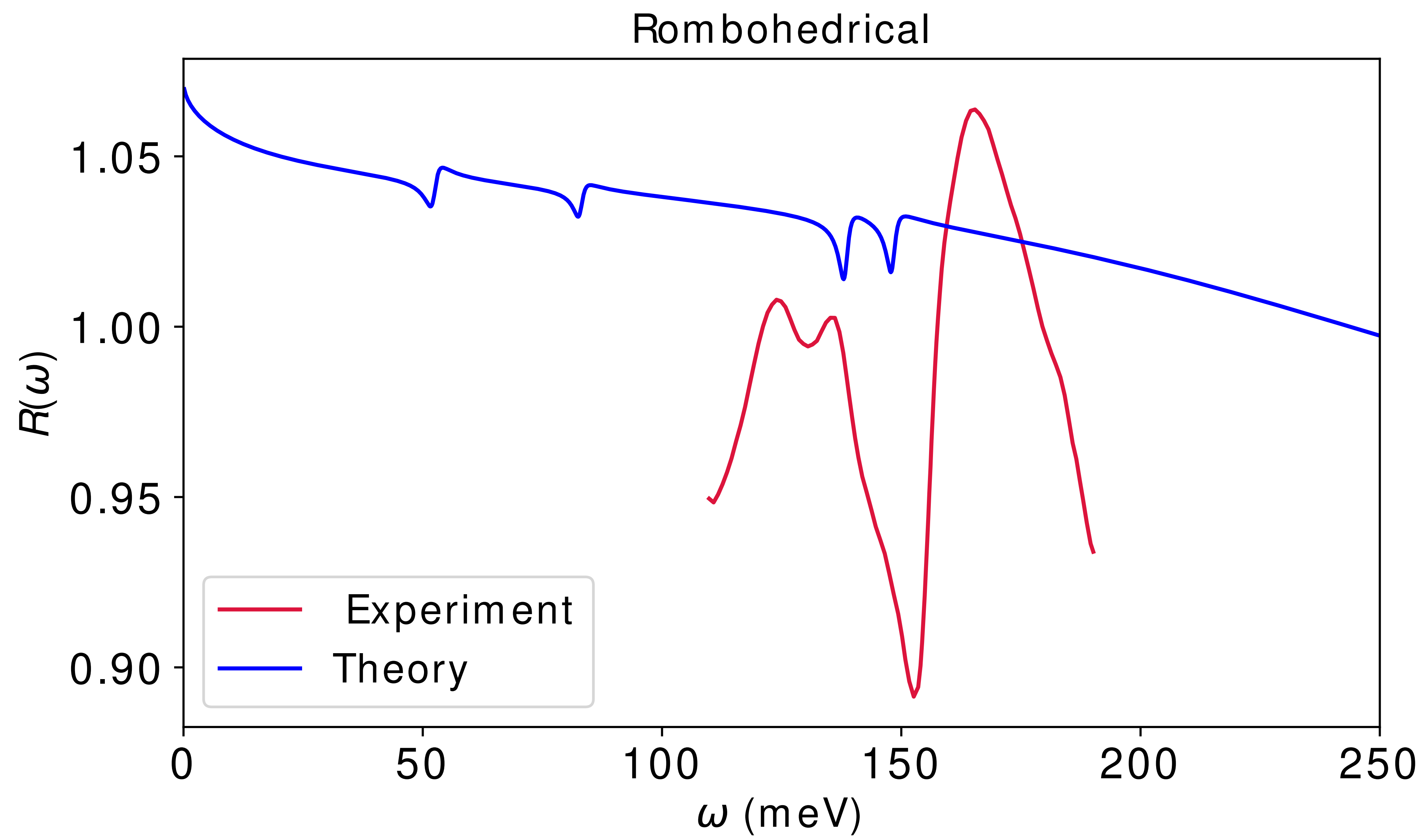
RESULTS:

H_3S


$Im\bar{3}m$


Cubic
1.05
1.00
0.95
0.90
$R(\omega)$
Experiment
Theory
0
50
100
150
200
250
ω (meV)


$R3m$
d_1
d_2


Rombohedrical
1.05
1.00
0.95
0.90
$R(\omega)$
Experiment
Theory
0
50
100
150
200
250
ω (meV)

CONCLUSION

Hopes

you got a little more familiar with electrons, phonons, bands structures, reflectivity resonances....

I found soon I way to get a better agreement with the experimental data and pubblish a good paper

thank you for your attention!!

More details about the new approach

$$R = \left| \frac{\sqrt{\varepsilon} - n_0}{\sqrt{\varepsilon} + n_0} \right|^2$$

$$\varepsilon(w) = 1 + 4\pi\chi^{el}(w) + 4\pi\chi^{vib}(w)$$

$$\chi^{el}_{\alpha,\beta} = \frac{1}{\Omega}\frac{1}{N_k}\sum_{k,l,m}^{N_k(T)} \left\langle \psi^l_k \middle| v_\alpha \middle| \psi^m_k \right\rangle \left\langle \psi^m_k \middle| v_\beta + (\varepsilon^m_k - \varepsilon^l_k) V^{(E)}_{hxc} \middle| \psi^l_k \right\rangle \frac{f(\varepsilon^l_k) - f(\varepsilon^m_k)}{(\varepsilon^l_k - \varepsilon^m_k)^2} \frac{1}{(\varepsilon^l_k - \varepsilon^m_k) + z}$$

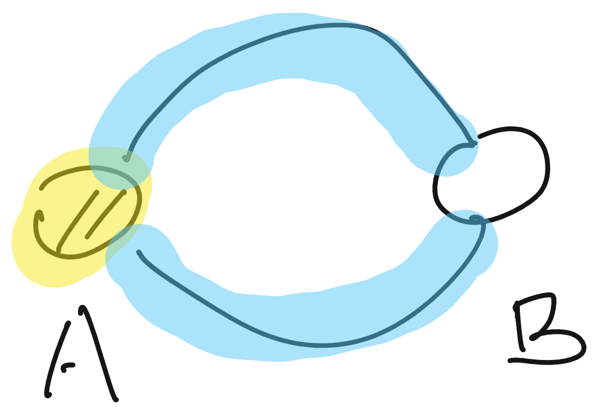
$$\chi^{vib}_{\alpha\beta}(z) = \frac{1}{N_k\Omega}\sum_s \frac{d^s_\alpha d^s_\beta}{w_s^2 - z^2}$$

$$Z^s_{\alpha,\beta} = Z^s_{ion}\delta_{\alpha,\beta} + \frac{1}{N_k}\sum_{k,l,m}^{N_k(T)} \left\langle \psi^l_k \middle| v_\alpha \middle| \psi^m_k \right\rangle \left\langle \psi^m_k \middle| \frac{\partial V_{ks}}{\partial u^s_\beta} \middle| \psi^l_k \right\rangle \frac{f(\varepsilon^l_k) - f(\varepsilon^m_k)}{\varepsilon^l_k - \varepsilon^m_k} \frac{1}{(\varepsilon^l_k - \varepsilon^m_k) + z}$$

More details about the new approach

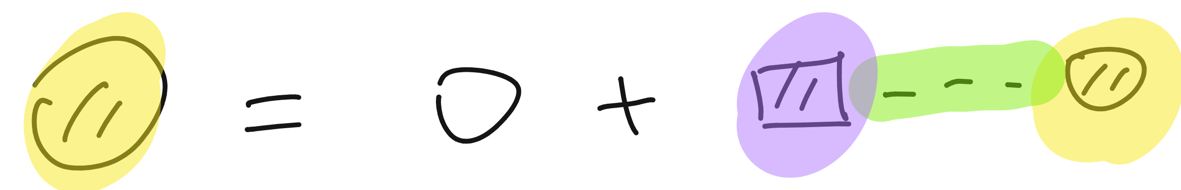
$$\chi_{el} = \int d^3k \sum_{i,j} \frac{f(\varepsilon_{ki}) - f(\varepsilon_{kj})}{\varepsilon_{ki}-\varepsilon_{kj}-(\omega+i\eta)} \langle \psi_{ki} | \underbrace{V^A_{ext} + V^A_{SCF}(\omega)}_{\text{A.K.A. Dressed vertex}} | \psi_{kj}\rangle \langle \psi_{kj} | V^B_{ext} | \psi_{ki}\rangle$$

=

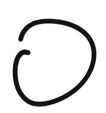


with the dressing defined as:

$$V^A_{dress} = \int K_{Hxc} \cdot \rho^A(\omega)$$

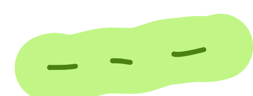


Legend

 $= V^A_{ext}$

 $= V^A_{ext} + V^A_{dress}(\omega)$

 $= \rho^{(A)}(\omega)$

 $= K_{Hxc} = \dfrac{\partial^2 V_{KS}}{\partial\rho\,\partial\rho}$

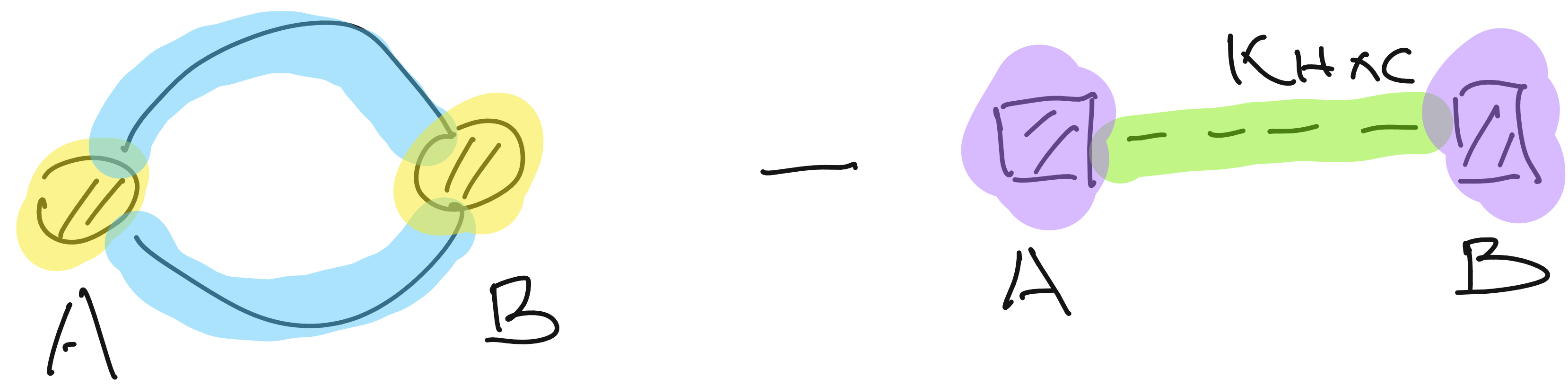
 = depends on ω

More details about the new approach

New formulation

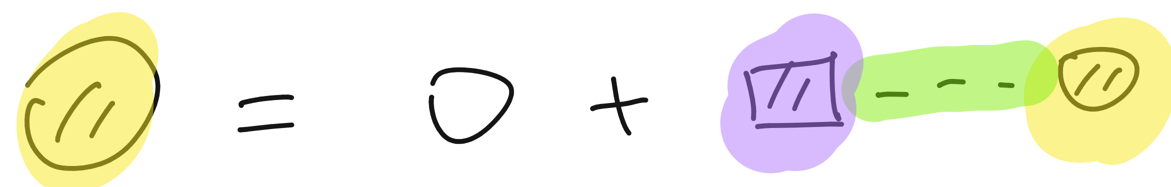
$$\chi_{el} = \int d^3k \sum_{i,j} \frac{f(\varepsilon_{ki}) - f(\varepsilon_{kj})}{\varepsilon_{ki} - \varepsilon_{kj} - (\omega + i\eta)} \langle \psi_{ki} | V_{ext}^{A} + V_{SCF}^{A}(\omega) | \psi_{kj} \rangle \langle \psi_{kj} | V_{ext}^{B} + V_{SCF}^{B}(\omega) | \psi_{ki} \rangle$$

$$- \int dr\, dr'\, \rho^{(A)}(\omega, r)\, K_{Hxc}(r, r')\, \rho^{(B)}(\omega, r')$$

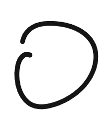
$=$ 

with the dressing defined as:

$$V_{dress}^{A} = \int K_{Hxc} \cdot \rho^{A}(\omega)$$

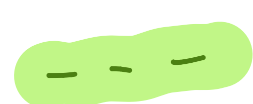


Legend

 $= V_{ext}^{A}$

 $= V_{ext}^{A} + V_{dress}^{A}(\omega)$

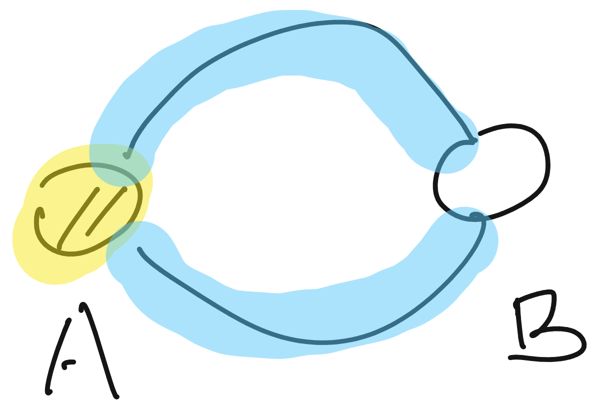
 $= \rho^{(A)}(\omega)$

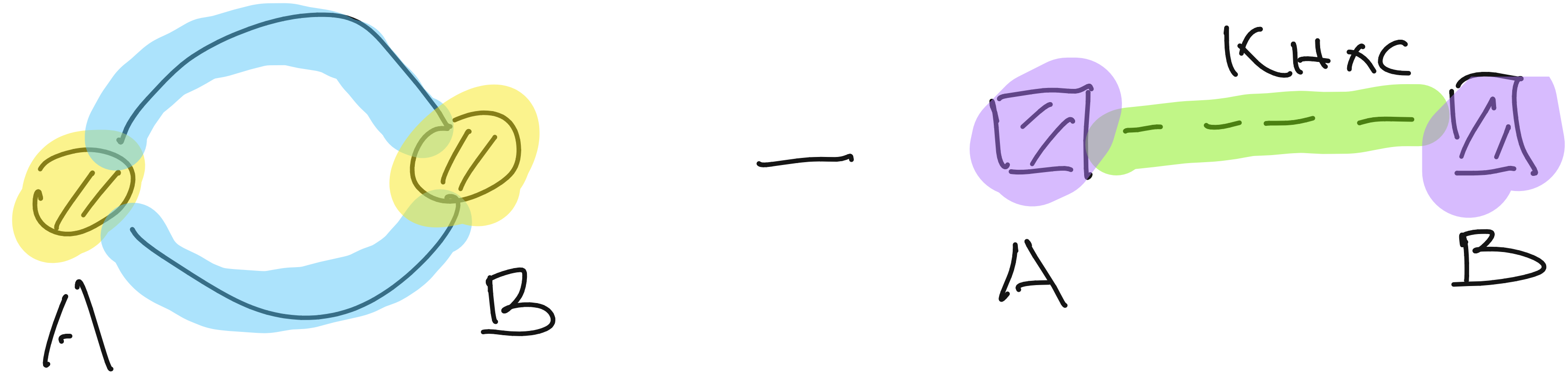
 $= K_{Hxc} = \dfrac{\partial^2 V_{KS}}{\partial \rho\, \partial \rho}$

 = depends on ω

More details about the new approach

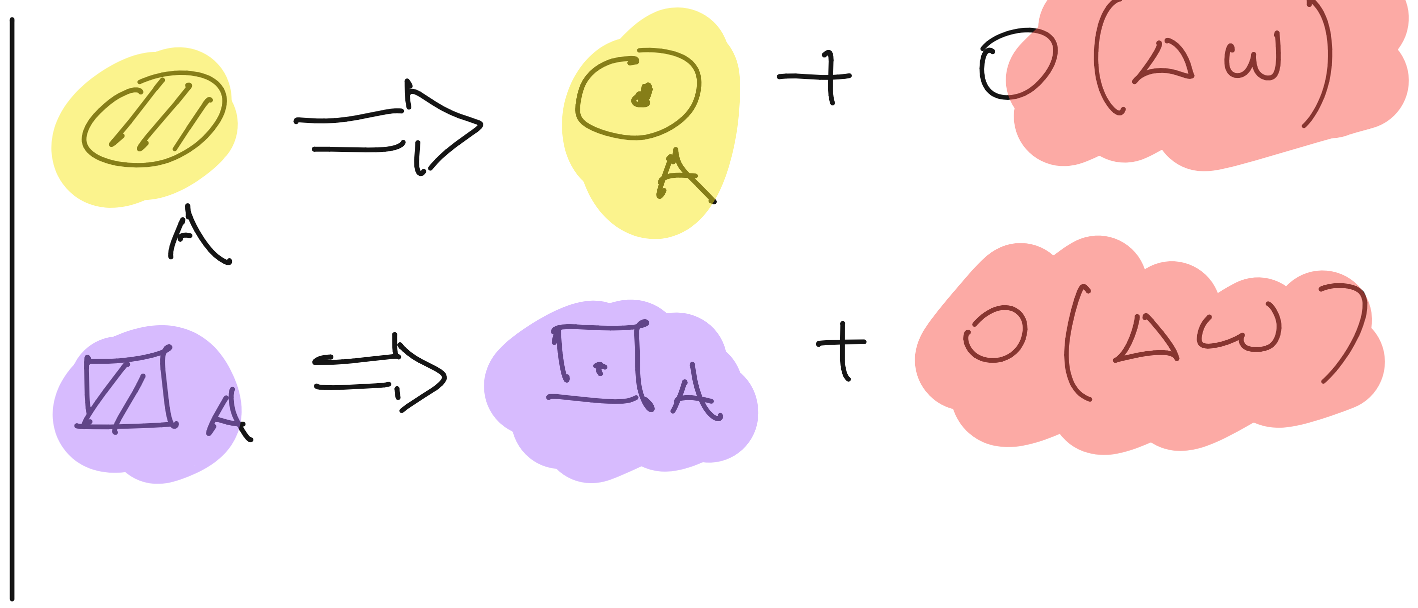
Comparison

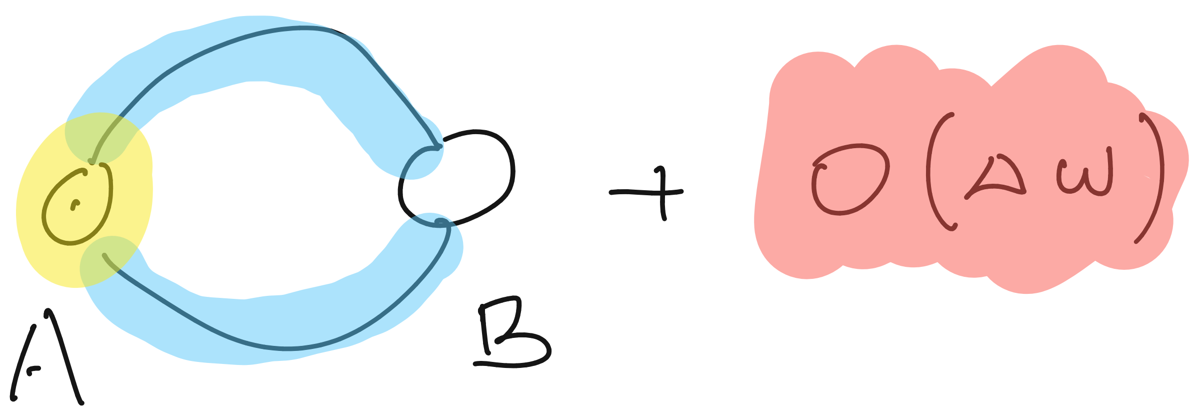


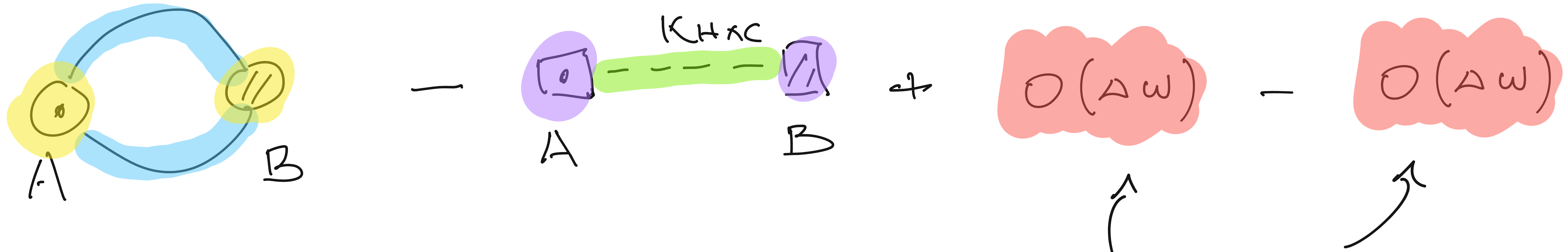


IDEA: Advantage whenever approximating

HP: use inexact frequency In one vertex $\longleftrightarrow \omega = \omega_0 + \Delta\omega \iff$







cancels out

$\mathrm{ERR} = O(\Delta\omega)$

$\mathrm{ERR} = O(\Delta\omega^2)$