Real space investigation of local field effects on surfaces

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Outline

- Surfaces, Super-cells and Local Field Effects
- Effect of the vacuum on spectra
- 1D Real Space treatment
- Local Field Effects on Surfaces

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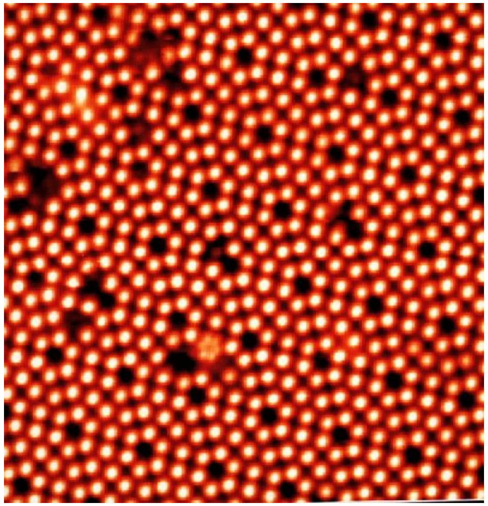
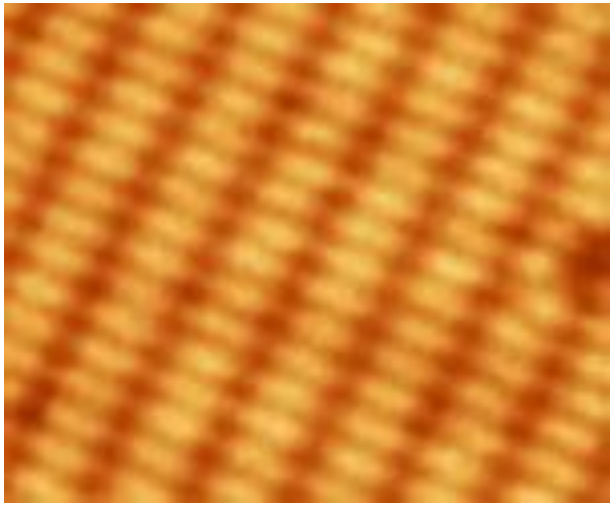
Surfaces

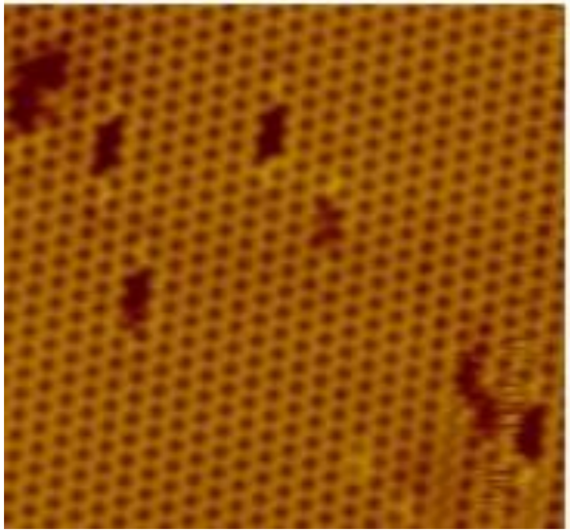
Different surfaces for the same material (e.g. Silicon)



Si(111) 7x7

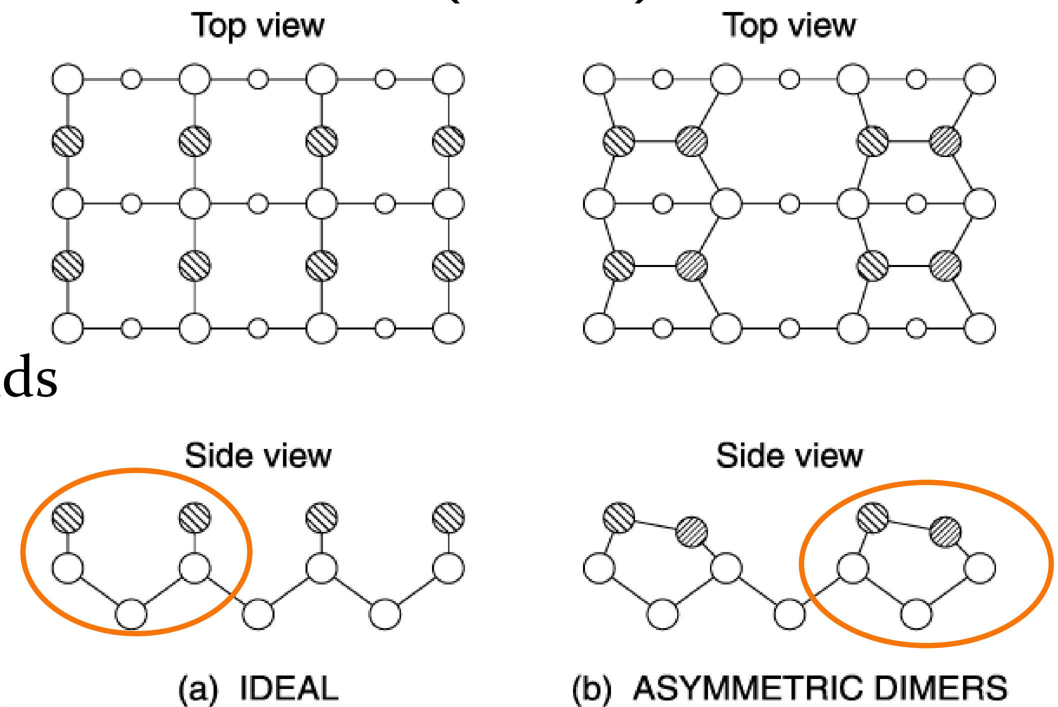


Si(001) 2x1



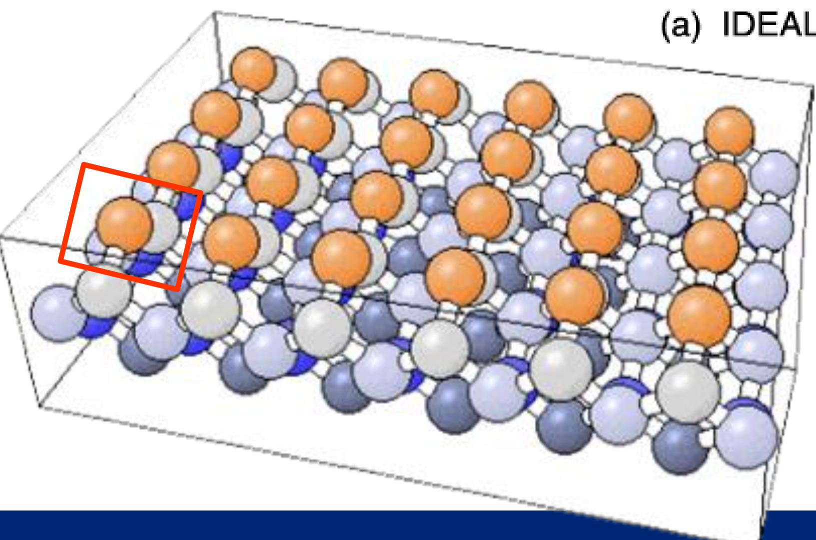
Si(001) 4x2

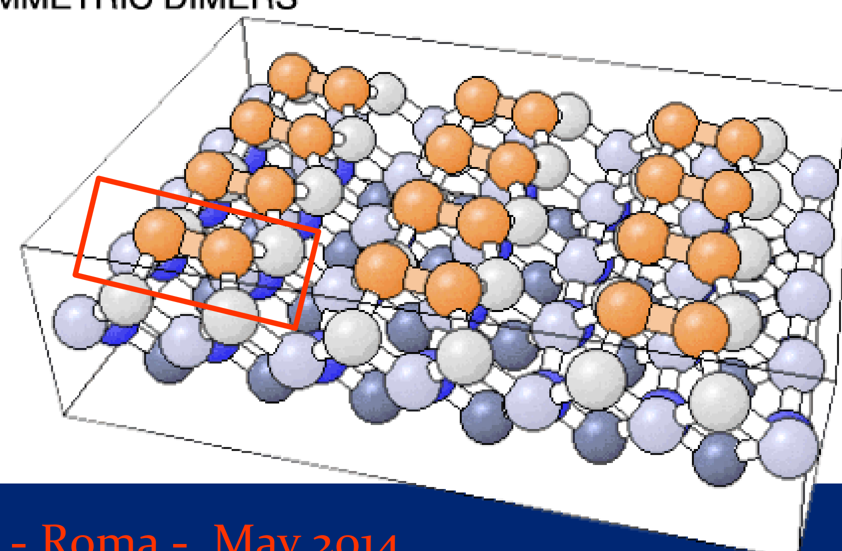
Example of surface reconstruction : Si(001)2x1



Dangling bonds

Asymmetric dimers





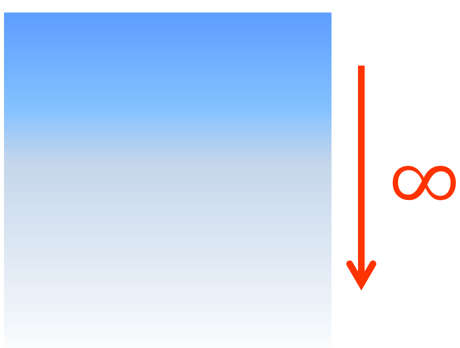
Model of surface – Super-cells Ground state calculation

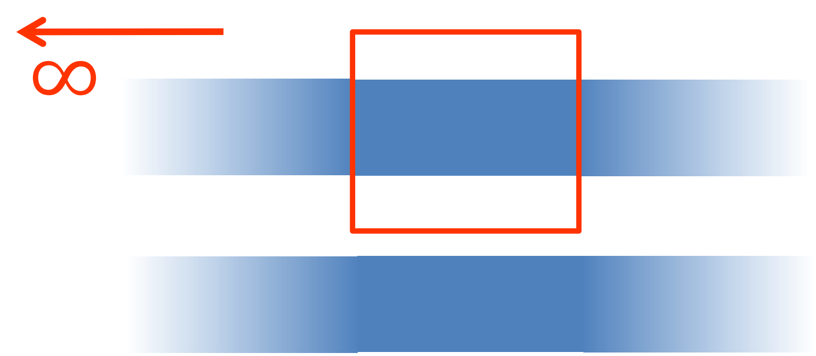
What we want → Surface

Plane waves → Supercell

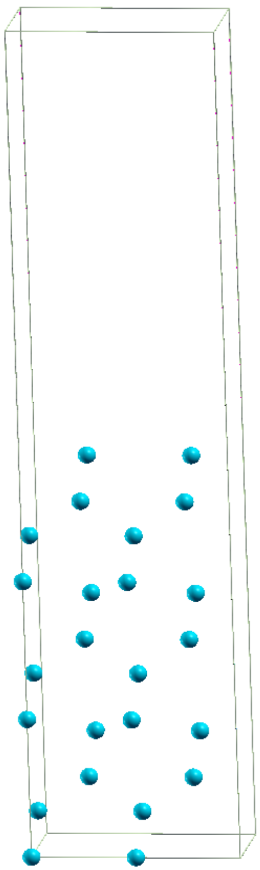
Best representation of a surface → System with 2 surfaces (slab)

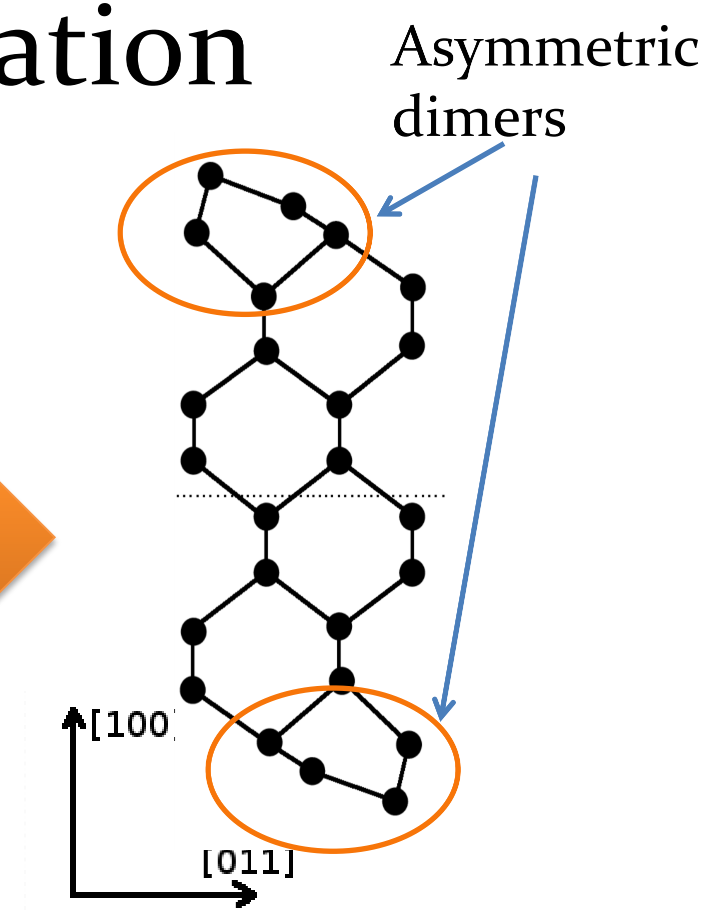
Surface → Supercell → System with 2 surfaces (slab)





Model of surface – Super-cells
Ground state calculation





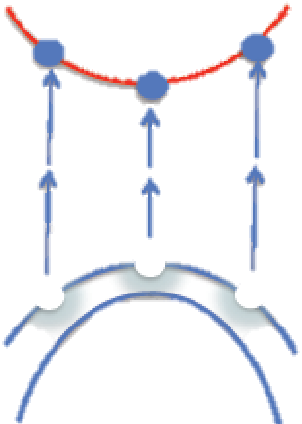
Construction of super-cell (atoms + vacuum) → Reconstruction of the surface → System with 2 surfaces (slab)

Optical properties in TDDFT

$$\chi^{(0)}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{V}\sum_{i,j}(f_i - f_j)\frac{\langle\phi_j|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\phi_i\rangle\langle\phi_i|e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}}|\phi_j\rangle}{E_i - E_j - \omega - i\eta}$$

Independent Particles (IPA)

$$\epsilon^{IPA}_M(\mathbf{q},\omega) = 1 - v_0\chi^{(0)}(\mathbf{q},\omega)_{00}$$



(No Local Field Effects)

Random Phase Approximation (RPA)

$$\chi_{\mathbf{G},\mathbf{G}'} = \chi^{(0)}_{\mathbf{G},\mathbf{G}'} + \sum_{\mathbf{G}''}\chi^{(0)}_{\mathbf{G}\mathbf{G}''}v_{\mathbf{G}''}\chi_{\mathbf{G}'',\mathbf{G}'}$$

+

$$\epsilon^{RPA}_M(\mathbf{q},\omega) = \frac{1}{1 + v_0\chi(\mathbf{q},\omega)_{00}}$$

(Local Field Effects included)

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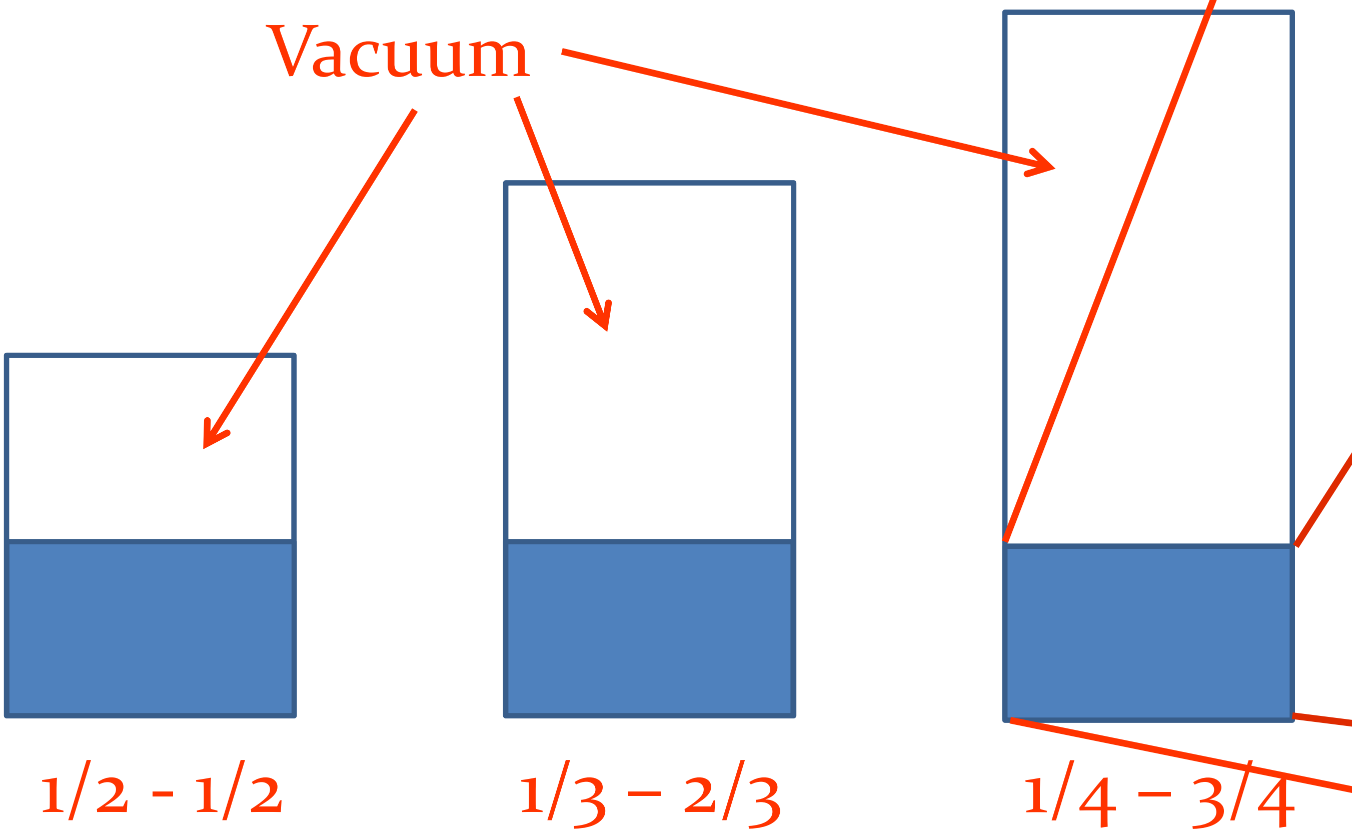
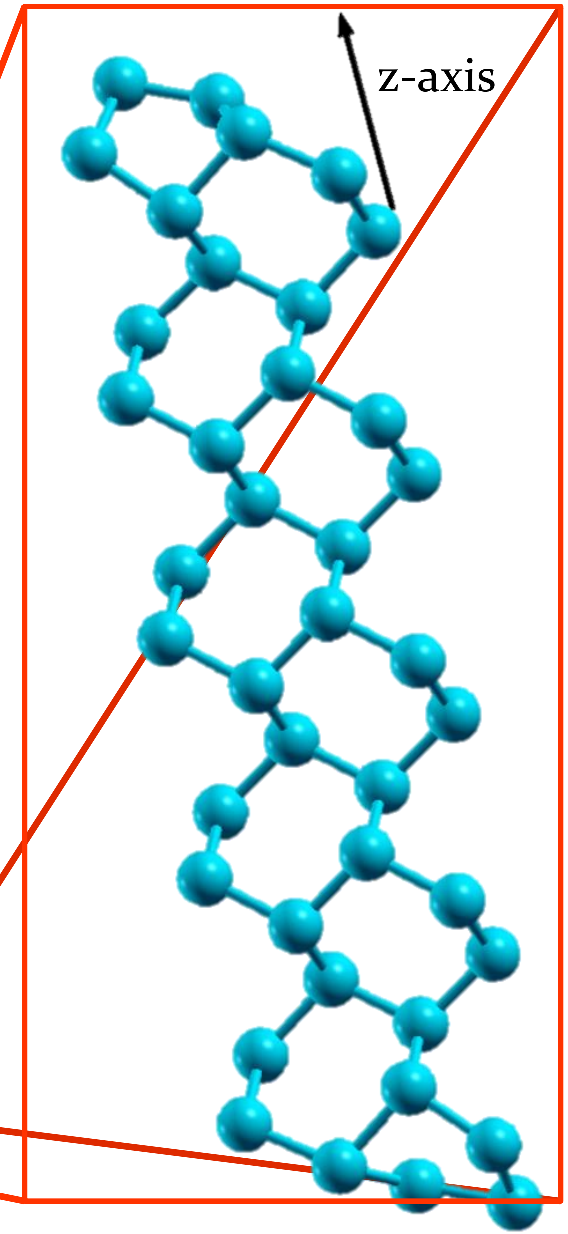
Effect of the vacuum on the spectra

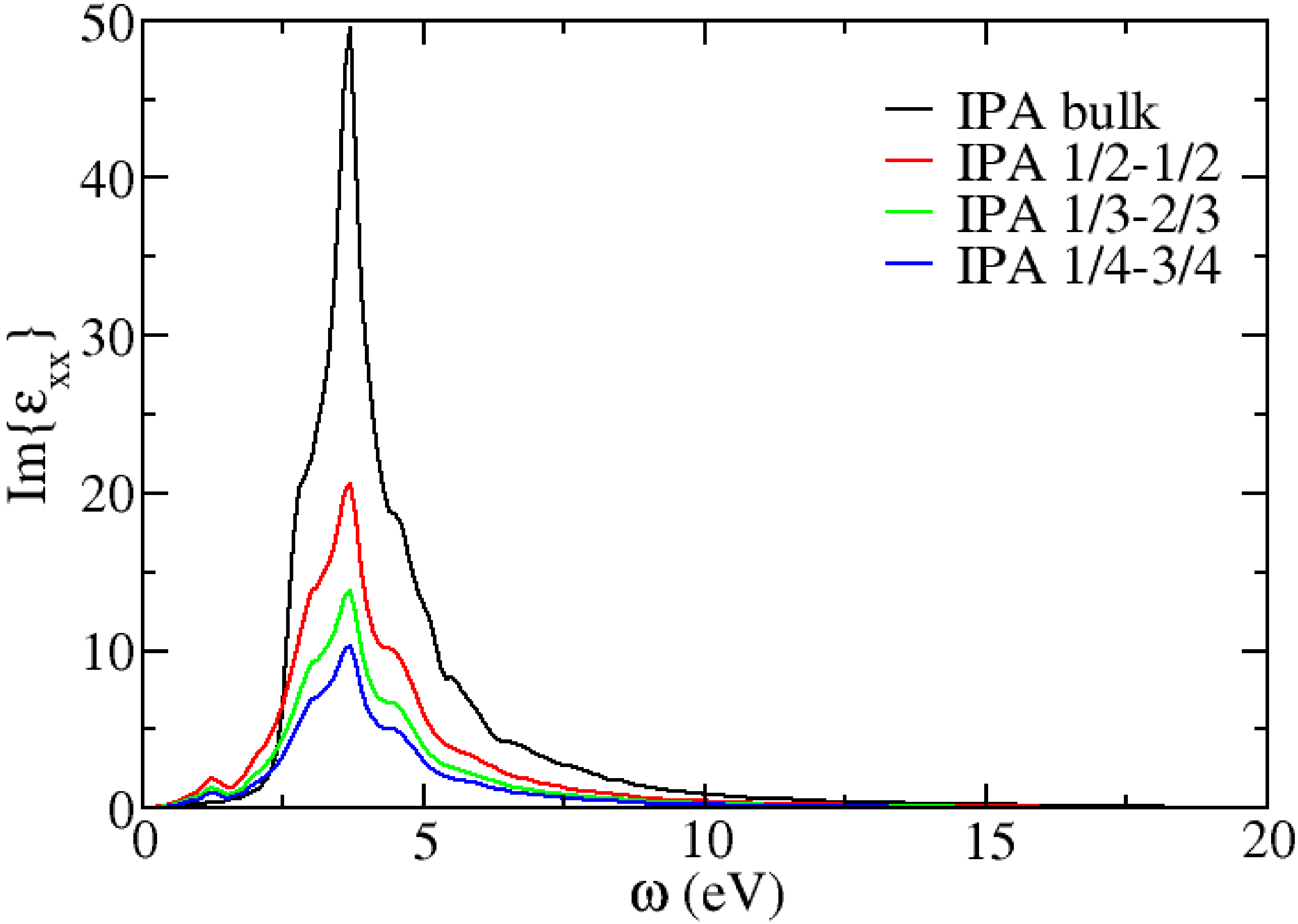
Analysis of the effect of the vacuum on the IPA and RPA spectra for 3 systems :





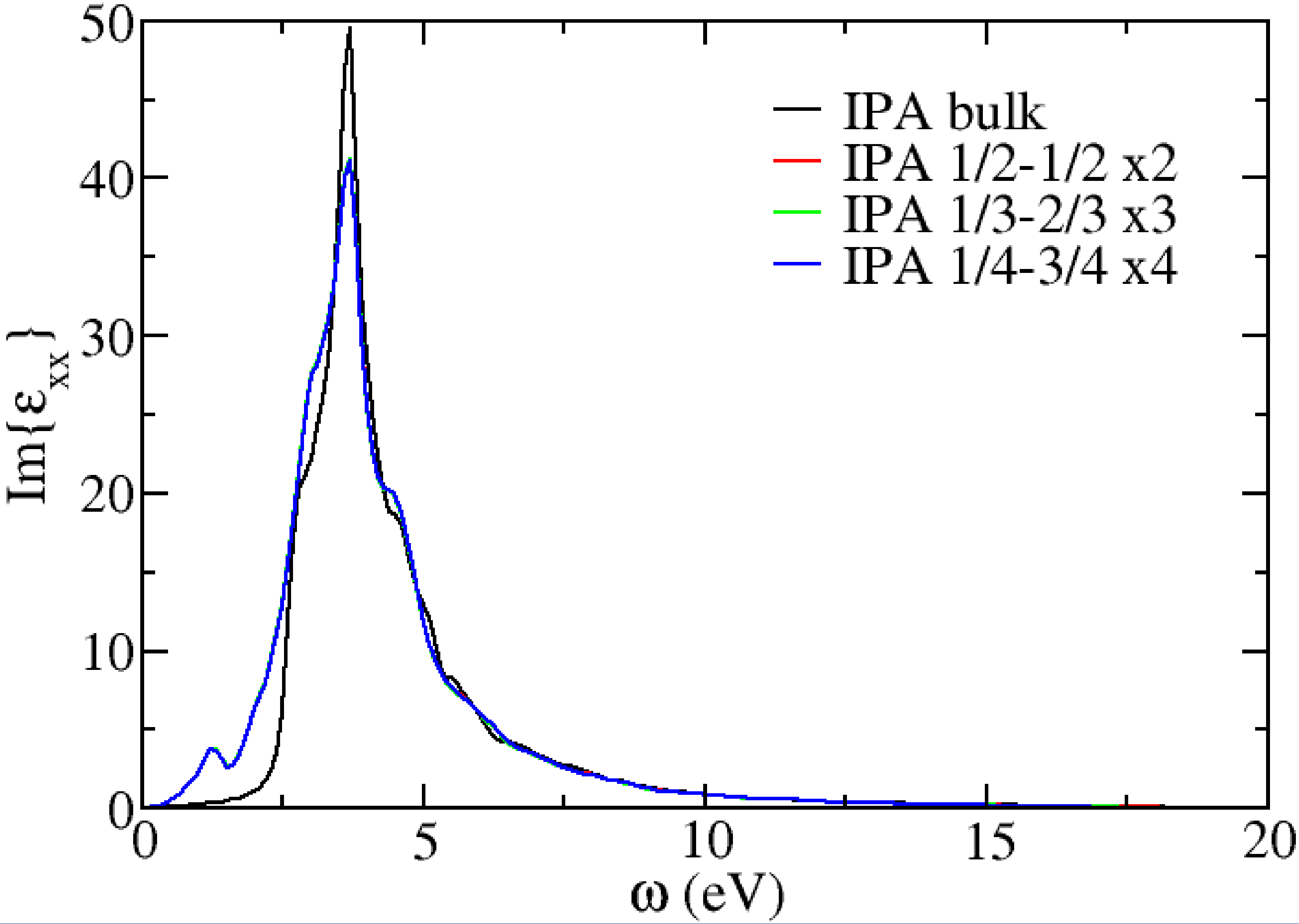
IPA calculations

In-plane calculations : ε_{xx}



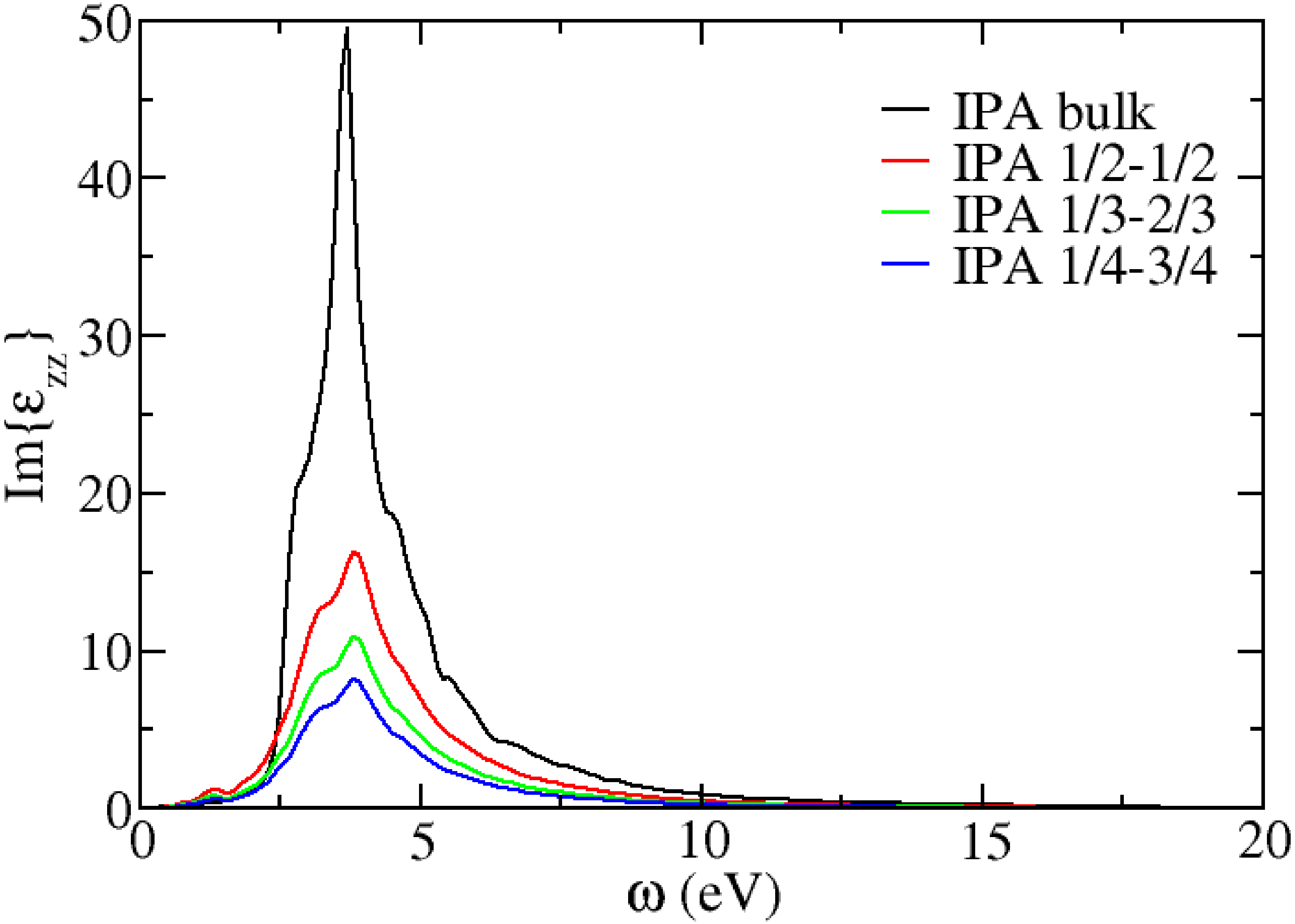
IPA calculations

Renormalized in-plane calculations : ε_{xx}



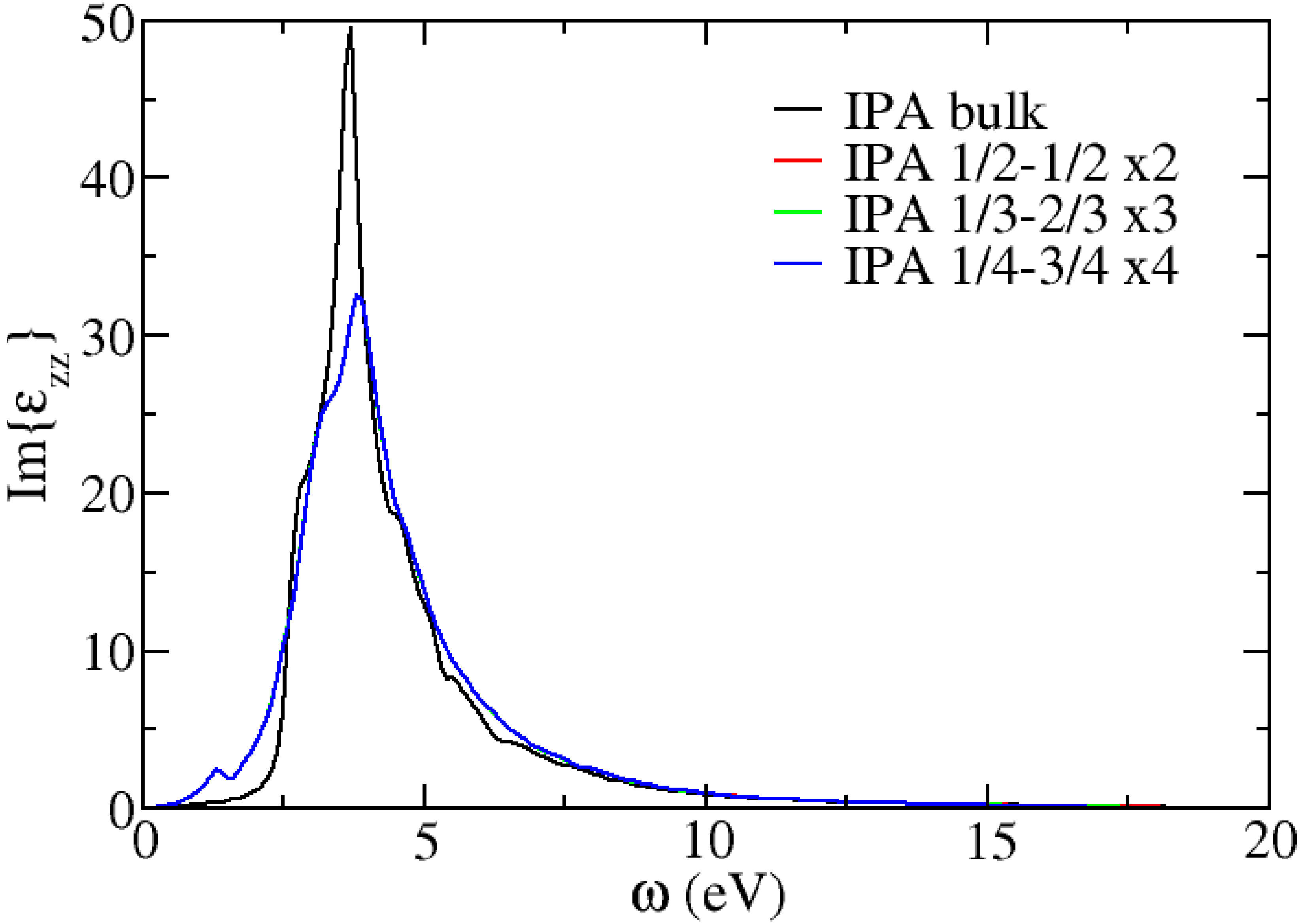
IPA calculations

Out-of-plane : ε_{zz}



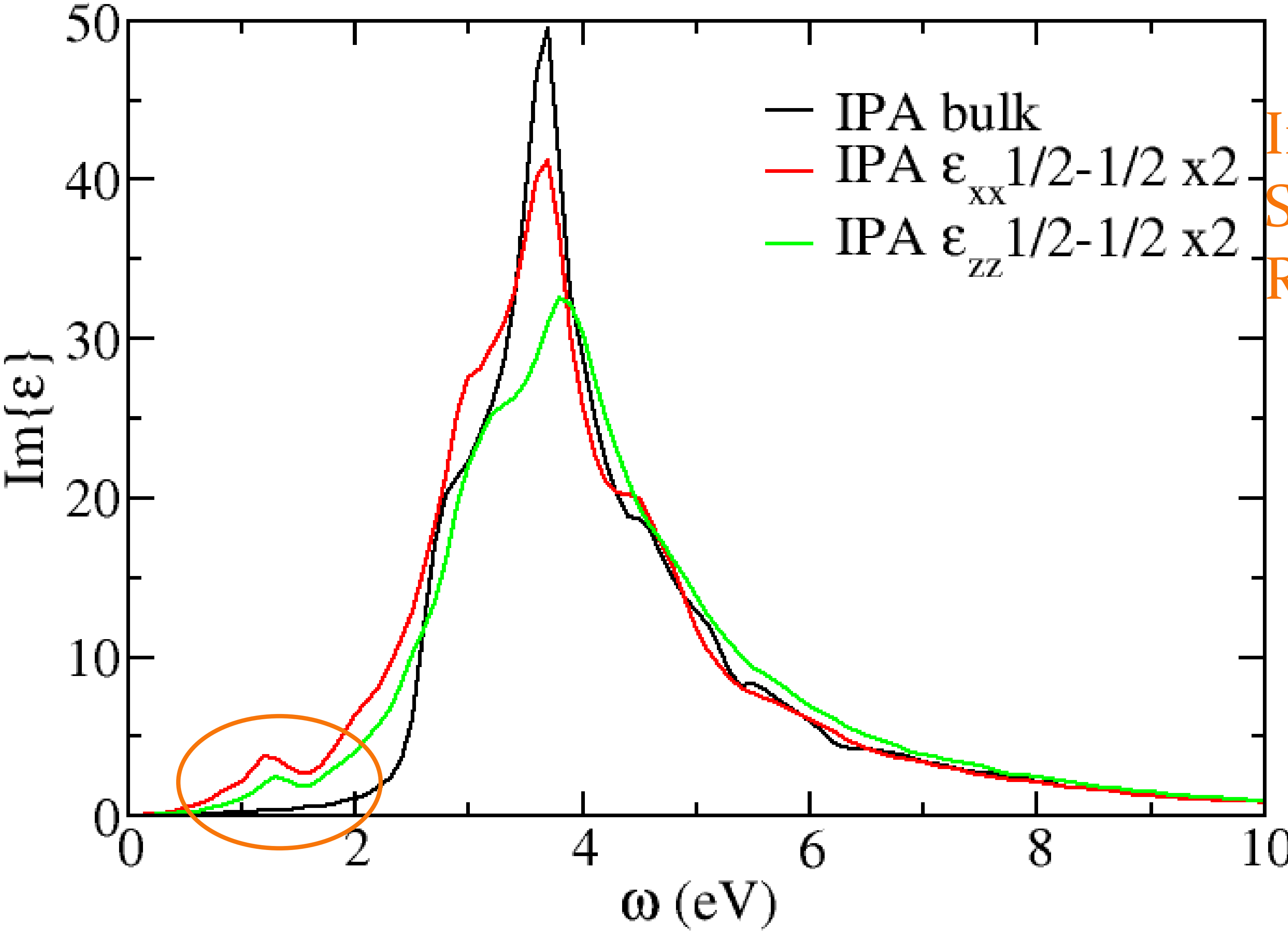
IPA calculations

Renormalized out-of-plane : ε_{zz}



IPA calculations

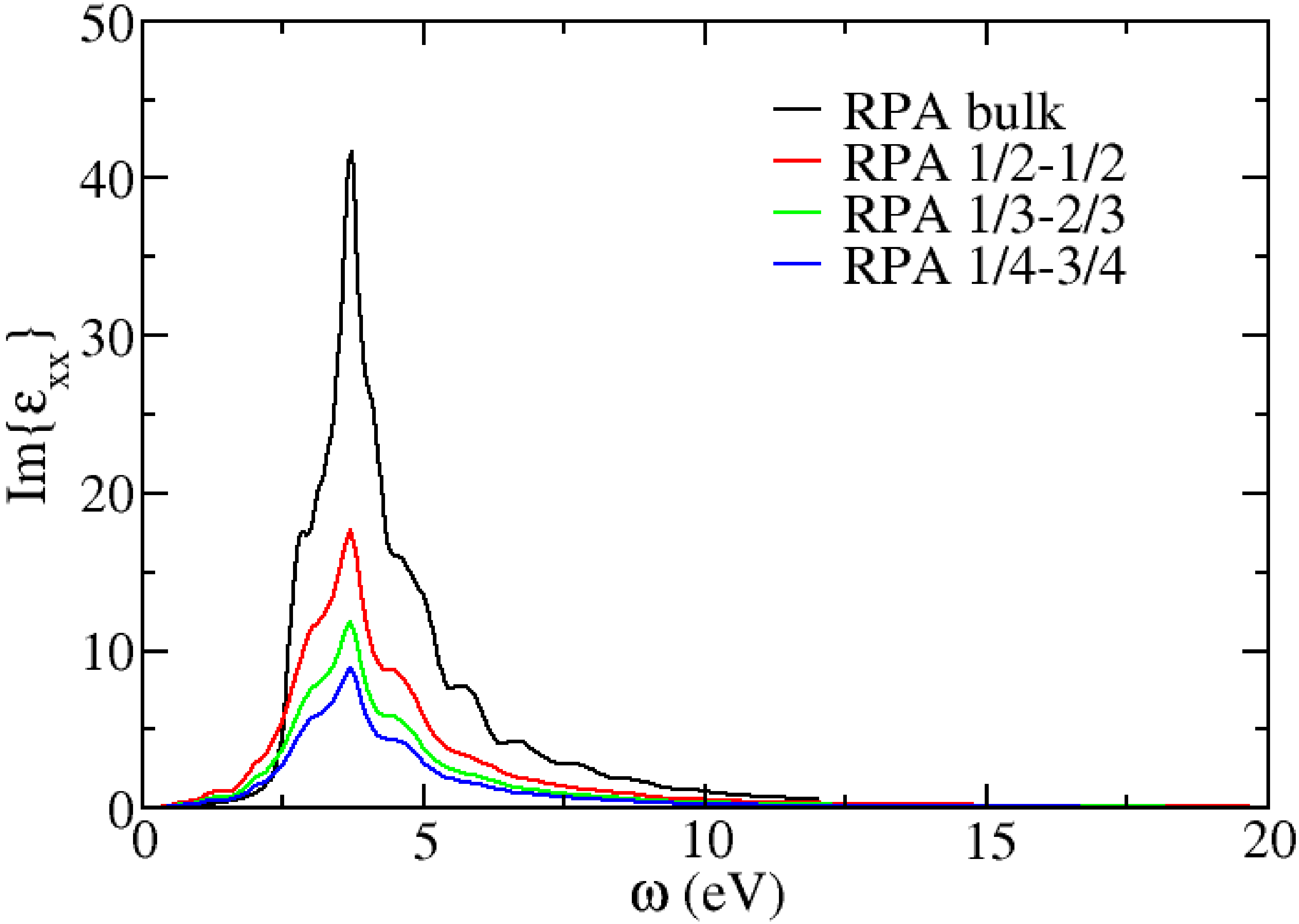
Renormalized spectra (to slab volume)



Include :
Surface states
Reconstruction

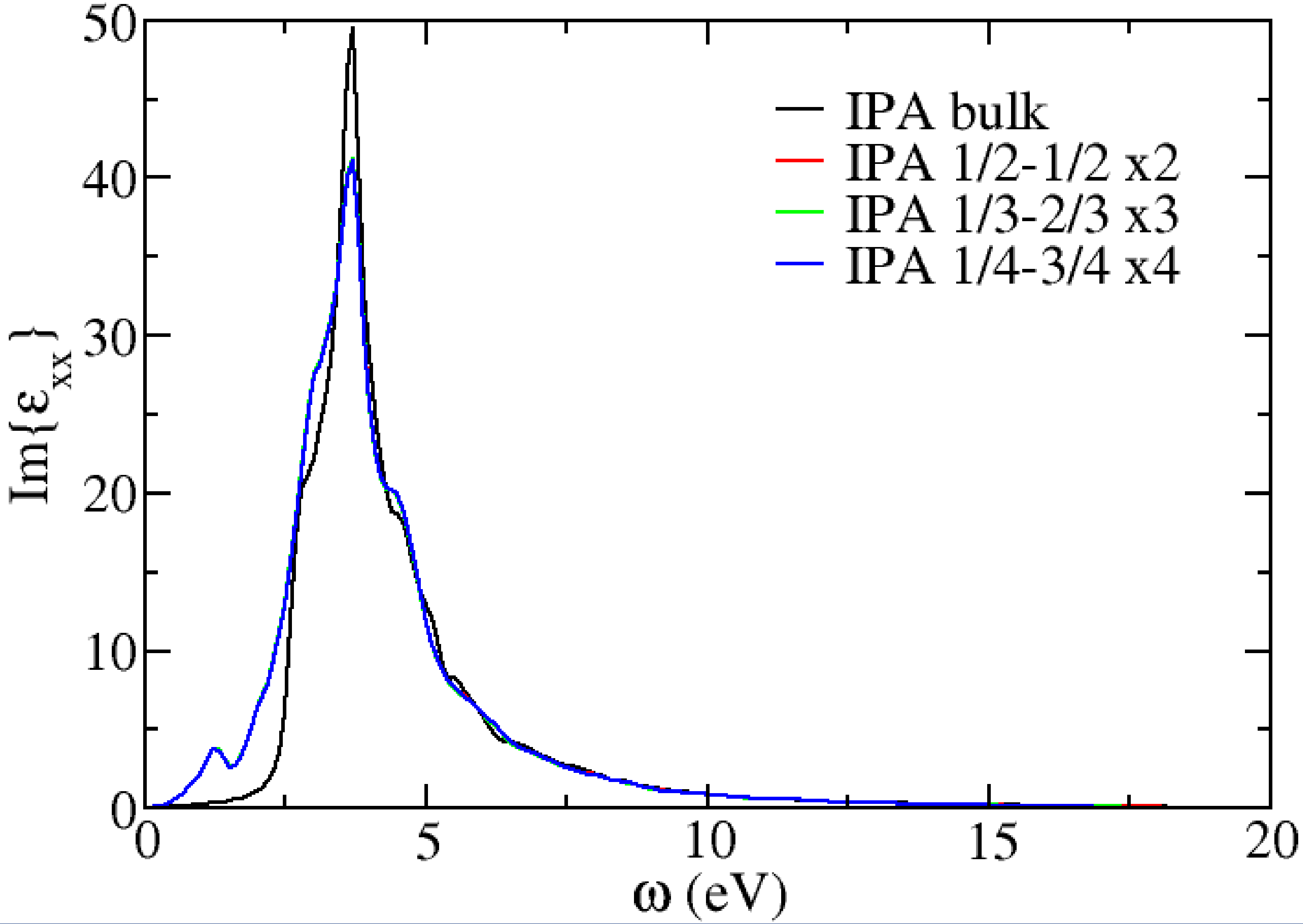
RPA calculations in TDDFT

In-plane calculations : ε_{xx}



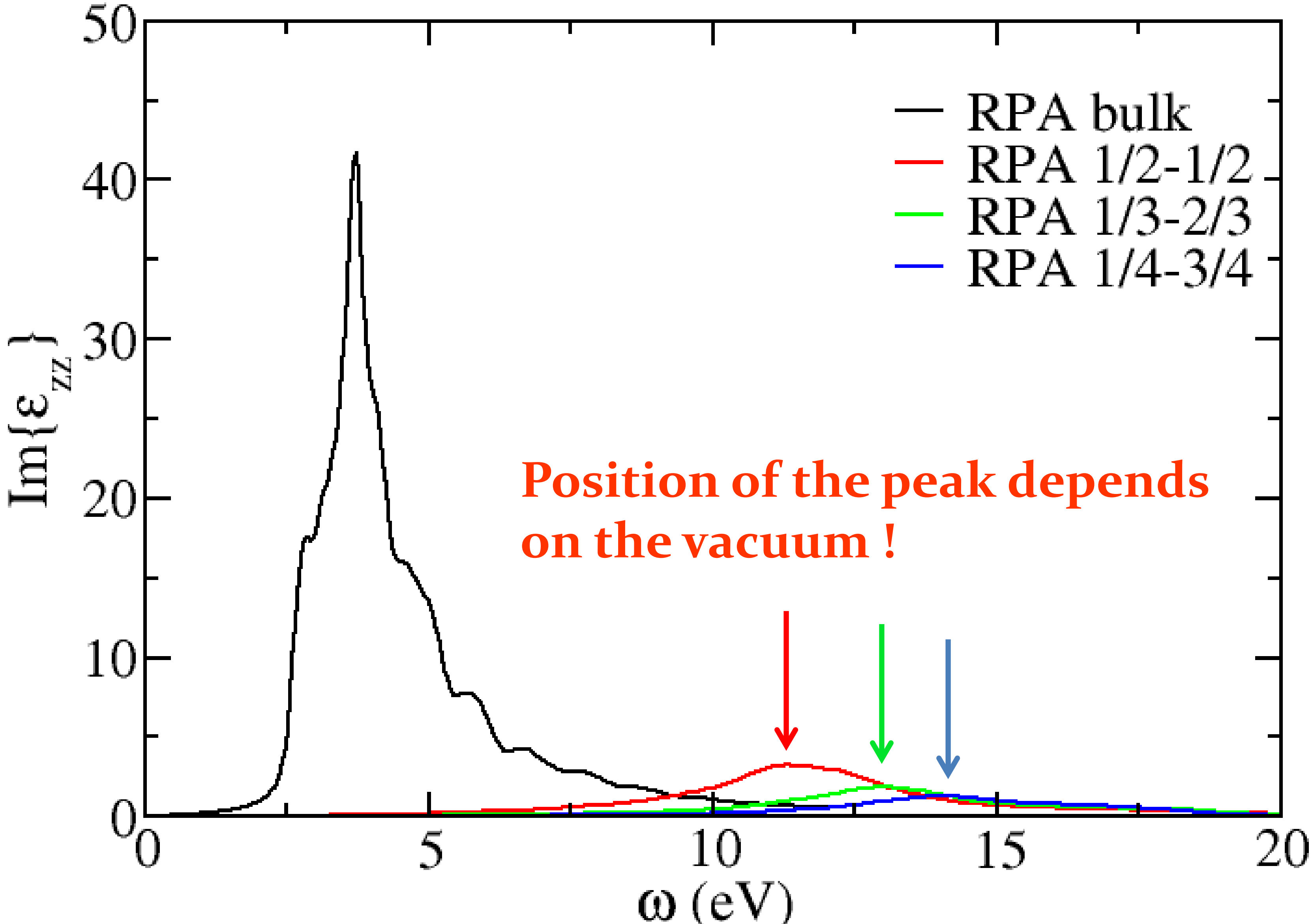
RPA calculations in TDDFT

Renormalized in-plane calculations : ε_{xx}



RPA calculations in TDDFT

Out-of-plane : ε_{zz}



Result of the analysis

IPA : Can be renormalized to the volume of the slab

RPA

in-plane → Small LFE

Behave as IPA

out-of-plane → Strong LFE

Position of the peak depends on the size of the vacuum

Response of the slab ≠ supercell

Abs. Vs EELS

$$Abs = -v_0 Im\{\chi_{00}\}$$

$$EELS = -v_0 Im\left\{\frac{\chi_{00}}{1 - v_0\chi_{00}}\right\}$$

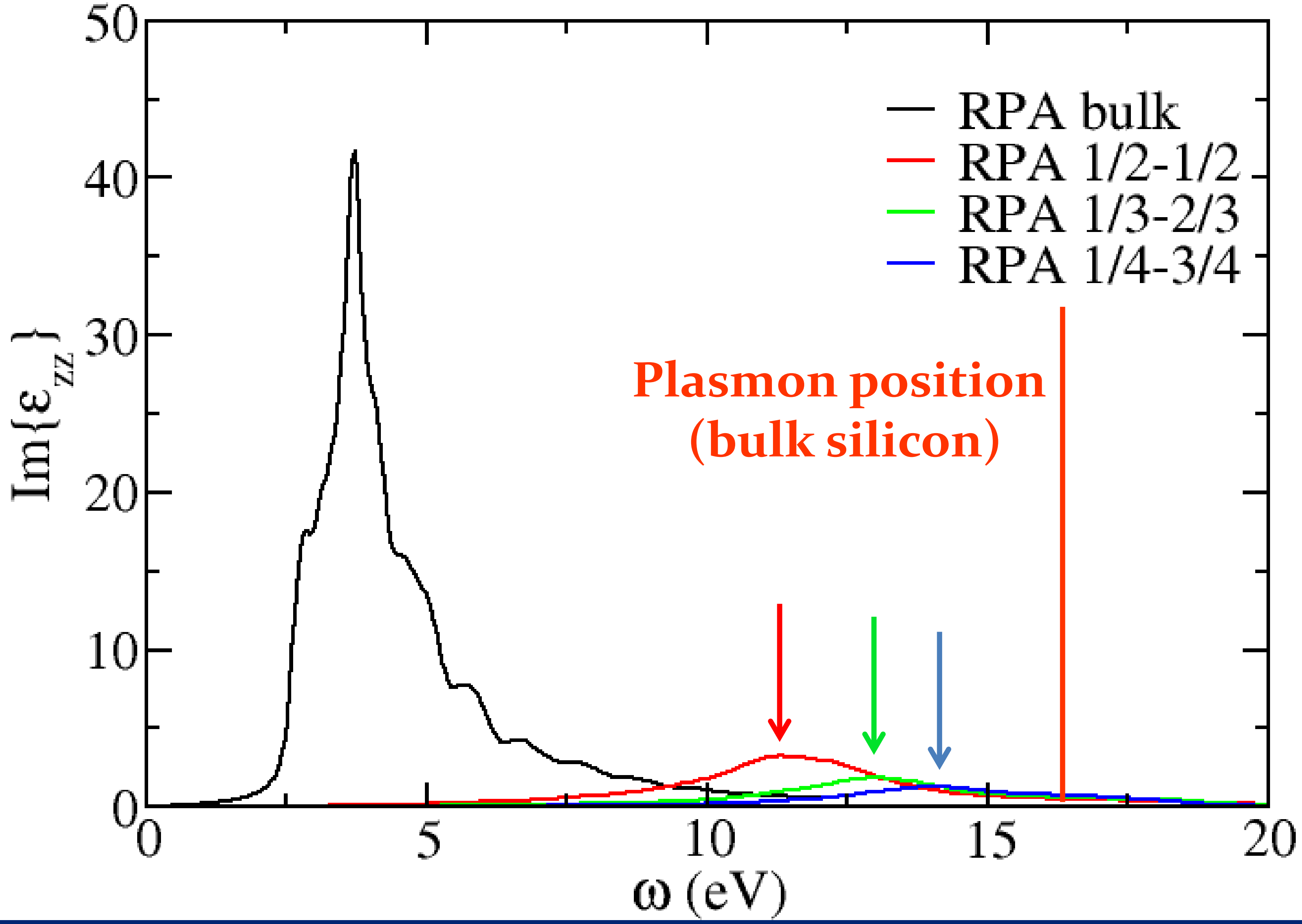
$$v_0\chi_{00} \;\; \alpha \;\; \frac{1}{V}$$

When $V \rightarrow \infty, \frac{Abs}{EELS} \rightarrow 1$

ε_{zz} converges to the plasmon of silicon

RPA calculations in TDDFT

Out-of-plane : ε_{zz}



Where does normalization come from?

- In momentum space, $\chi^{(0)}$ is explicitly normalized to the volume

$$\chi^{(0)}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \frac{2}{V}\sum_{i,j}(f_i - f_j)\frac{\langle\phi_j|e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\phi_i\rangle\langle\phi_i|e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}}|\phi_j\rangle}{E_i - E_j - \omega - i\eta}$$

Explains the behavior of IPA calculations

Where does normalization come from?

- In momentum space, $\chi^{(0)}$ is explicitly normalized to the volume
- In real space, $\chi^{(0)}$ is not normalized to the volume

$$\chi^{(0)}(\mathbf{r},\mathbf{r}',\omega) = 2\sum_{i,j}(f_i - f_j)\frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{E_i - E_j - \omega - i\eta}$$

Computing Local Field Effects in real space could solve the problem of normalization

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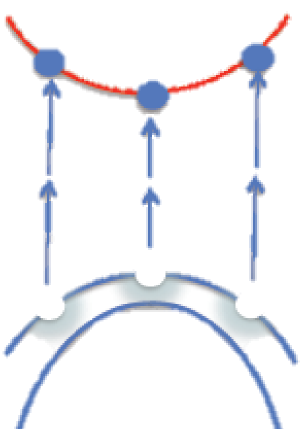
Optical properties in Real Space

$$\chi^{(0)}(\mathbf{r},\mathbf{r}',\omega) = 2\sum_{i,j}(f_i - f_j)\frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{E_i - E_j - \omega - i\eta}$$

Independent Particles (IPA)

$$\epsilon(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r},\mathbf{r}') - \int d\mathbf{r}'' V(\mathbf{r},\mathbf{r}'')\chi_0(\mathbf{r}", \mathbf{r}')$$



(No Local Field Effects)

Random Phase Approximation (RPA)

$$\chi(\mathbf{r},\mathbf{r}') = \chi^{(0)}(\mathbf{r},\mathbf{r}') + \int\int \chi^{(0)}\mathbf{r},\mathbf{r}_1)v(\mathbf{r}_1 - \mathbf{r}_2)\chi(\mathbf{r}_2,\mathbf{r}')$$

+

$$\epsilon^{-1}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}'' V(\mathbf{r},\mathbf{r}'')\chi(\mathbf{r}", \mathbf{r}')$$

(Local Field Effects included)

Tiago, *et al.* PRB 73, 205334 (2006)
Ogut, *et al.* PRL 90, 127401 (2003)

Real Space and supercell

The slab is periodic in x and y-directions.
We can define a 2D Fourier Transform

$$(x, y, z) \rightarrow \left(q_x + G_x, q_y + G_y, z\right) = (q_{||} + G_{||}, z)$$

Approximation : One can neglect in-plane LFE

$$G_{||} = 0$$

$$(x, y, z) \rightarrow (q_{||}, z)$$

Silkin, *et al.* PRL 93, 176801 (2004)

This eases calculation for surfaces

Real Space and supercell

Dyson-like equation becomes

$$\chi(z, z'; \mathbf{q}_{||}) = \chi^{(0)}(z, z'; \mathbf{q}_{||}) + \int \chi^{(0)}(z, z_1; \mathbf{q}_{||}) v(z_1, z_2; \mathbf{q}_{||}) \chi(z_2, z'; \mathbf{q}_{||})$$

with *v*, 2D-Fourier transform of the Coulomb potential given by

$$v(z, z'; \mathbf{q}_{||}) = 2\pi \frac{e^{-q_{||}|z-z'|}}{q_{||}}$$

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Roadmap for computing ε

$\chi^{(0)}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$

DP code

Real Space code

$\chi^{(0)}(z,z';\mathbf{q}_{||})$

1D Dyson-like equation

$\chi(z,z';\mathbf{q}_{||})$

Macroscopic Average

$\epsilon_M^{IPA}(\mathbf{q},\omega)$

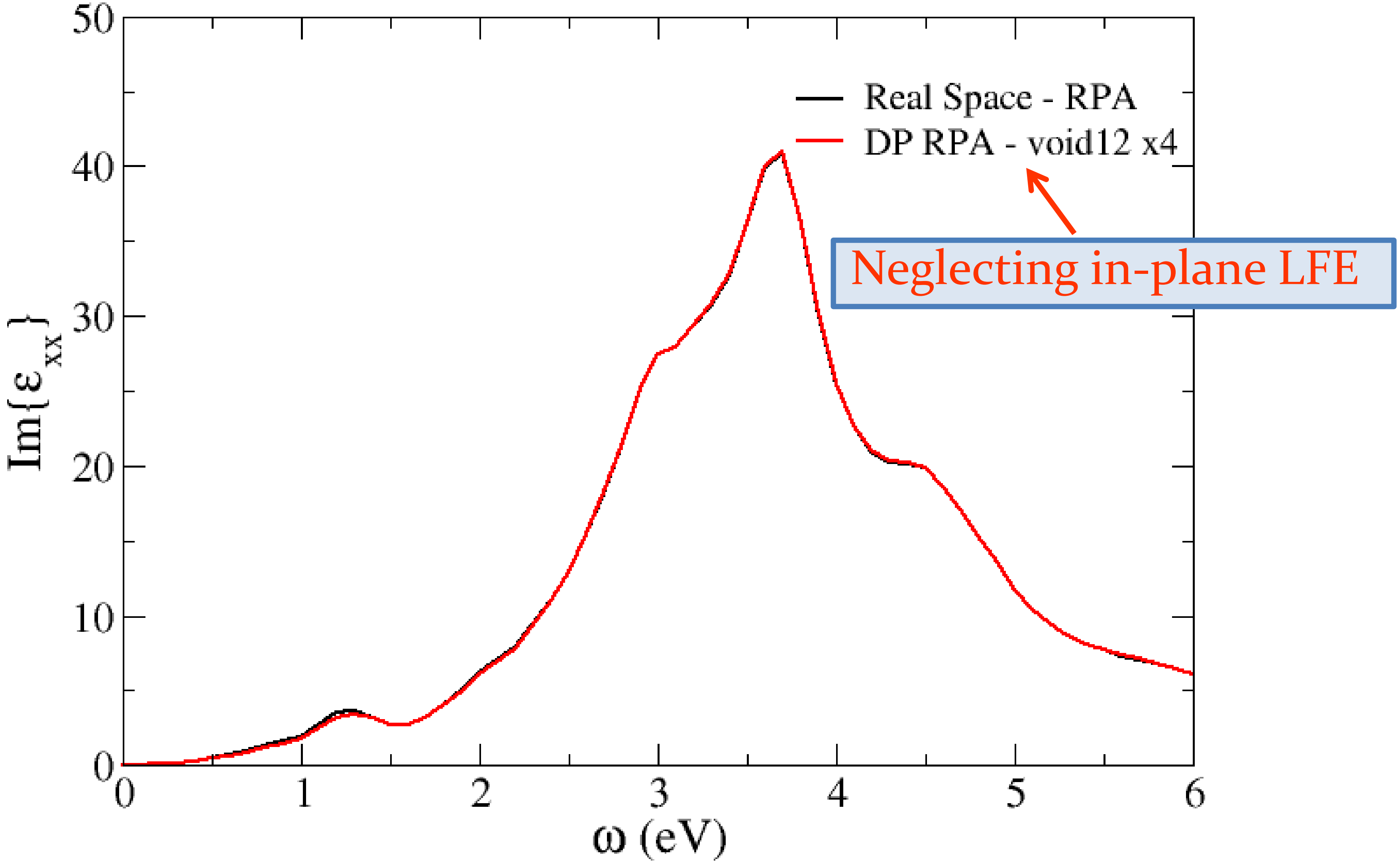
$\epsilon_M^{RPA}(\mathbf{q},\omega)$

Computational Details

- 32 atoms
- 8x16x1 shifted k-point grid
- 800 G_z vectors $\rightarrow\ \Delta z \approx 0.2$ Bohr
- $q_{||} = 10^{-3}$ [reduced coordinates]

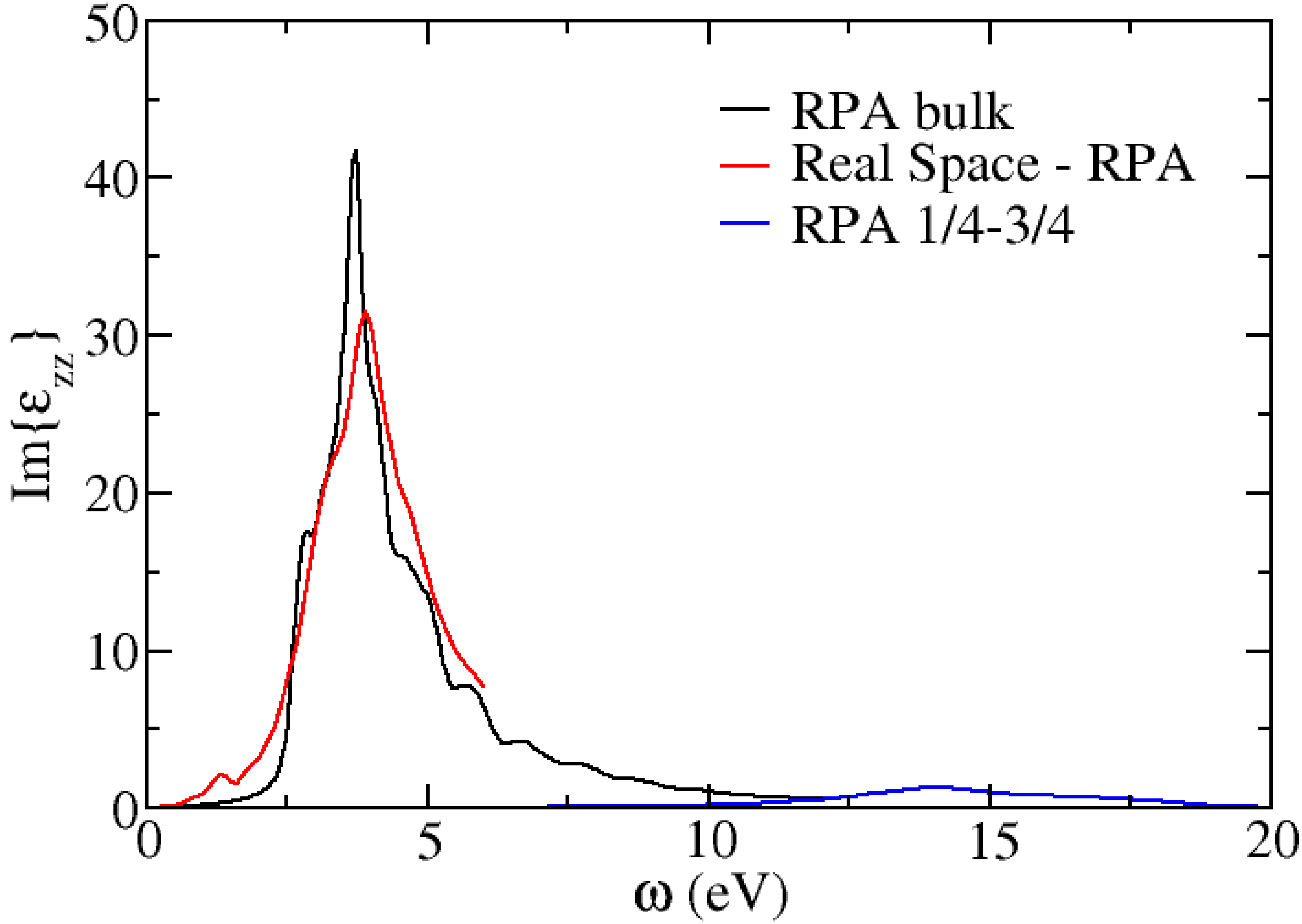
Application to surfaces

Validation : In-plane RPA calculation



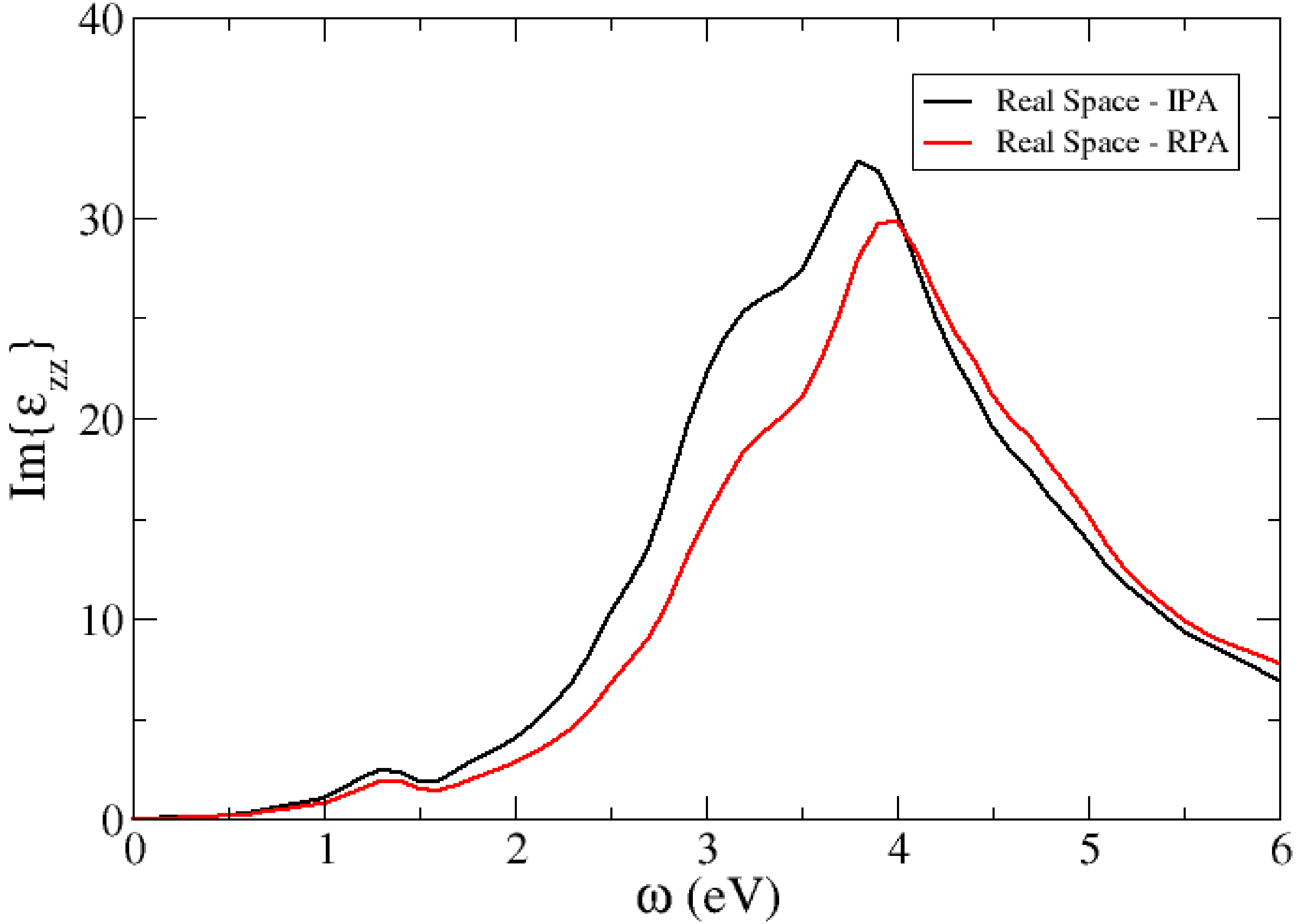
Local Field effects from real space

Out-of-plane IPA/RPA calculations



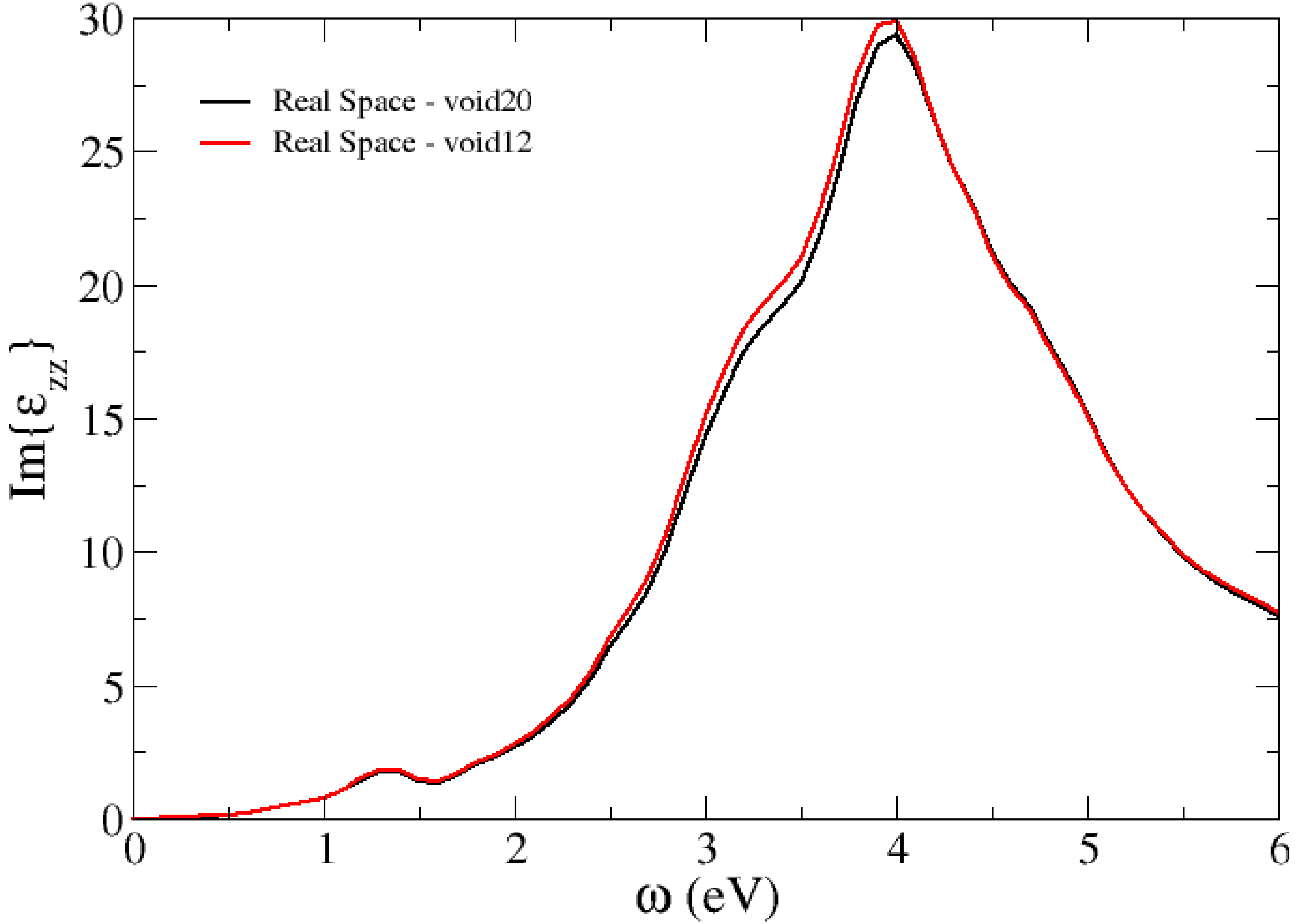
Local Field effects from real space

Out-of-plane IPA/RPA comparison



Out-of-plane component and vacuum

Independence from the amount of vacuum



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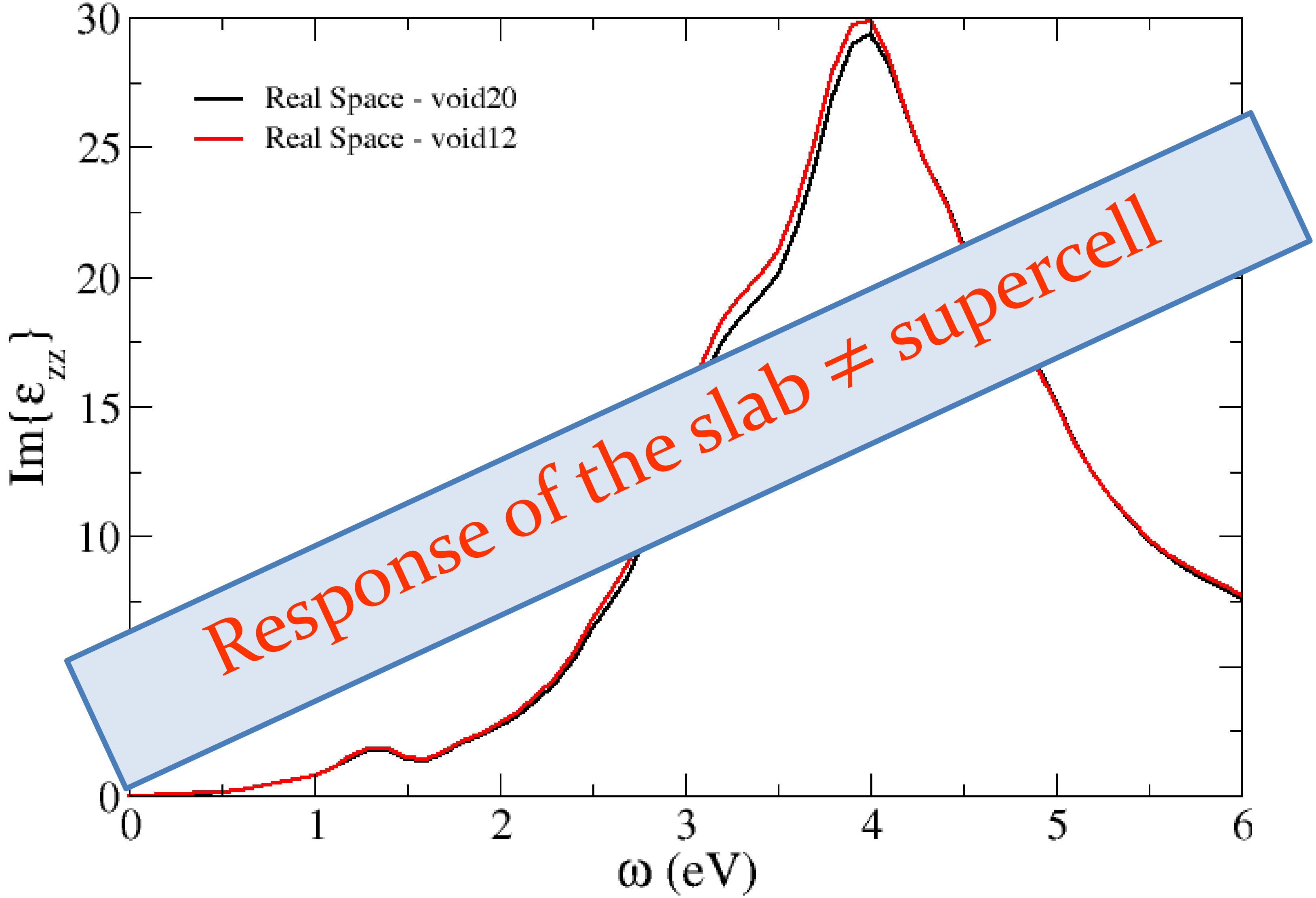

Conclusion and Future work

Conclusion

- 1D real space treatment of LFE
- Out-of plane RPA response

Work in progress

- Formulation in momentum space and without approximation
- Second Harmonic Generation from surfaces in RPA

Thank you for your attention

Application to surfaces

Coulomb potential in our case of interest :

$$v(z, z'; \mathbf{q}_{||}) = 2\pi \frac{e^{-q_{||}|z-z''|}}{q_{||}}$$

Divergent at $q_{||} = 0$

Question : How to compute ε_{zz} with a $q_{||}$?

ε is a tensor

The dielectric function is a tensor, independently of the level of approximation used in its calculation

For instance, choosing $\vec{q} = q\vec{e}_x$,

$$\vec{q}\overleftrightarrow{\varepsilon}\vec{q} = q^2\varepsilon_{xx}.$$

And if $\vec{q} = q_x\vec{e}_x + q_z\vec{e}_z$,

$$\vec{q}\overleftrightarrow{\varepsilon}\vec{q} = {q_x}^2\varepsilon_{xx} + {q_z}^2\varepsilon_{zz} + 2q_xq_z\varepsilon_{xz}.$$

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Can be computed due to a non-zero $q_{||}$

Contains ε_{zz}

Obtaining ε_{zz} in our model

From simple algebra one can obtain ε_{zz} from the combination of 3 calculations :

- $\vec{q} = q\vec{e}_x$
- $\vec{q} = q_x\vec{e}_x + q_z\vec{e}_z$
- $\vec{q} = q_x\vec{e}_x - q_z\vec{e}_z$