Non-linear optical properties of surfaces : Extraction of the signal

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Outline

- Non-linear optic and second harmonic generation
- Numerical simulation of optical properties
- Surface and super-cell
- Extraction of the signal

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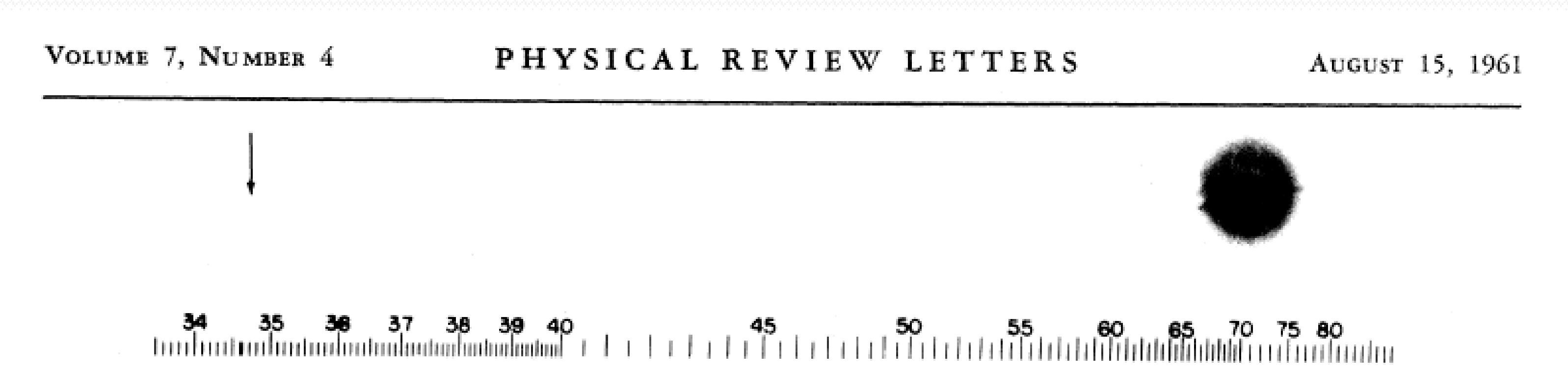
Response to a perturbation

Perturbation → Response

Electric field → Polarization

Linear response | Non linear response

$$P_i = \epsilon_0 \sum_j \chi^{(1)}_{ij} E_j + \epsilon_0 \sum_{jk} \chi^{(2)}_{ijk} E_j E_k + \epsilon_0 \sum_{jkl} \chi^{(3)}_{ijkl} E_j E_k E_l + \dots$$

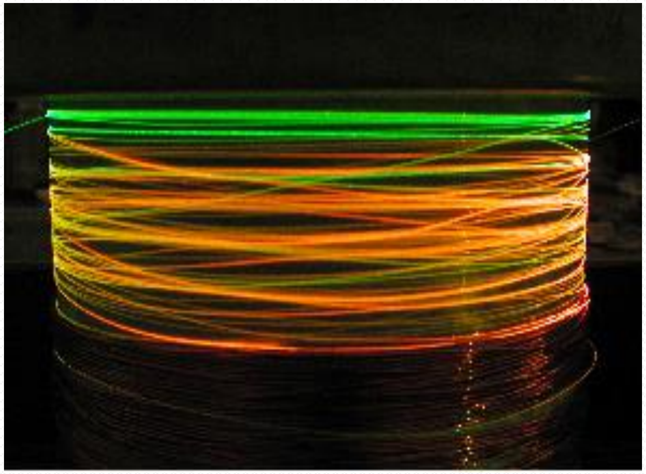


G. Frankel

Response to a perturbation

- When intensity is strong enough, we get non-linear effects in materials

$$P_i = \epsilon_0 \sum_j \chi_{ij}^{(1)} E_j + \epsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \epsilon_0 \sum_{jkl} \chi_{ijkl}^{(3)} E_j E_k E_l + \ldots$$



Raman effect in optical fiber[1]

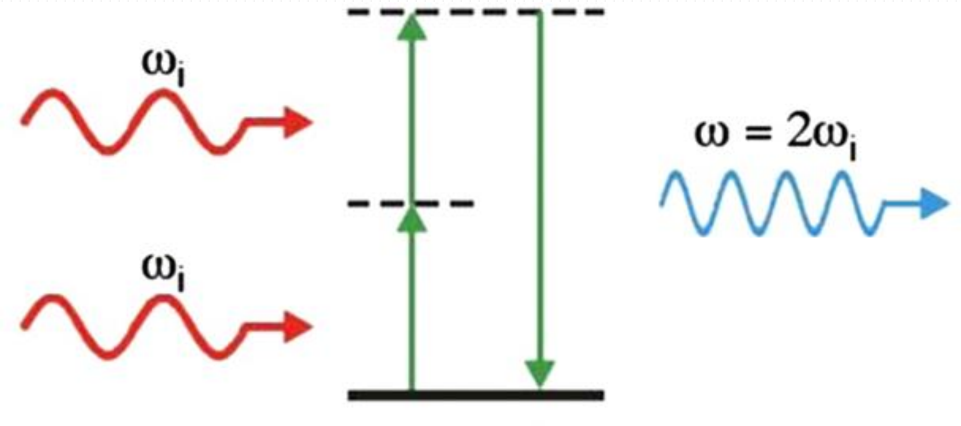
Harmonic generation [1]
(Parametric optical oscillator)

[1] www.optique-ingénieur.org/fr/cours/OPI_fr_M01_C01

Second harmonic generation

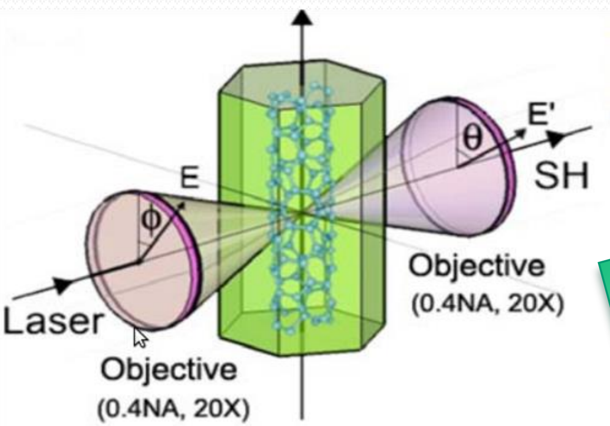
$$P_i = \epsilon_0 \sum_j \chi_{ij}^{(1)} E_j + \epsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j E_k + \epsilon_0 \sum_{jkl} \chi_{ijkl}^{(3)} E_j E_k E_l + \dots$$

First non-linear term



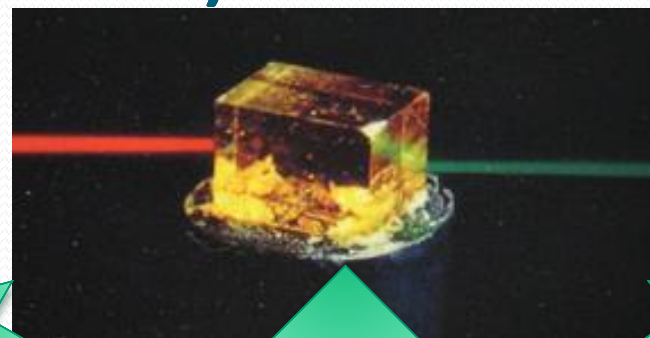
Centrosymetric material : $\chi^{(2)} = 0$ → First non-linear term : $\chi^{(3)}$

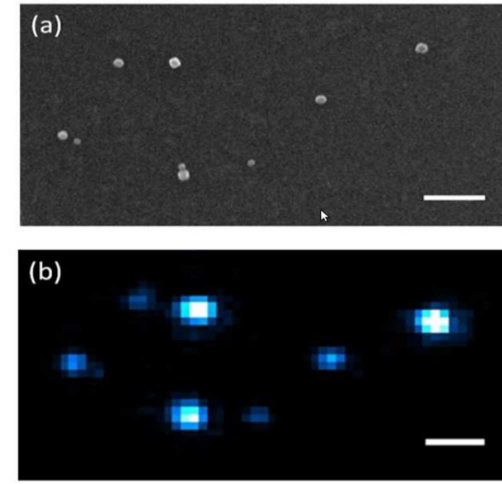
Applications of second harmonic generation (SHG)



Nanotubes characterization

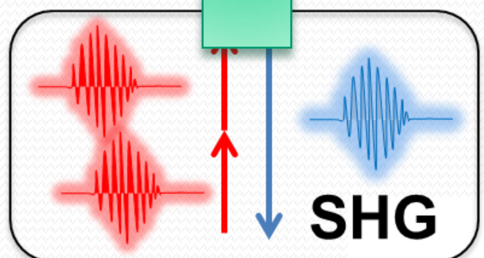
(PRB 77 125428)

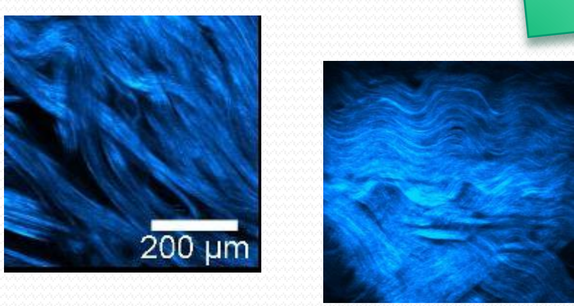




Nanoparticles imaging and microscopy

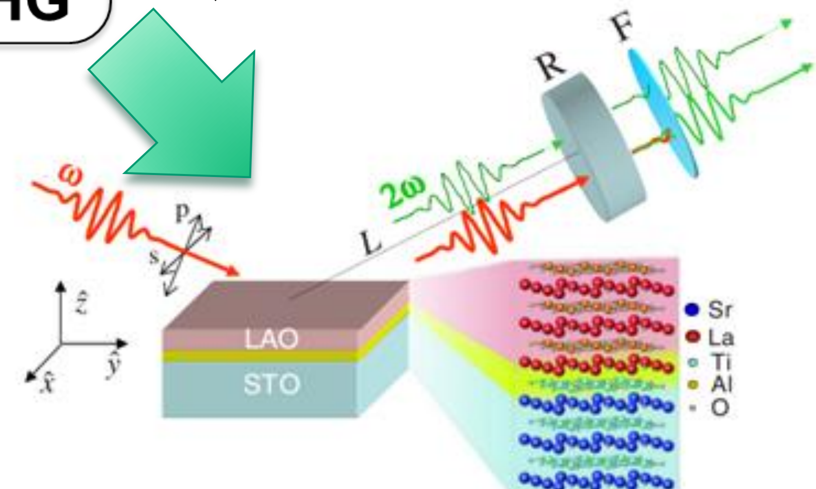
(C-L Hsieh PhD thesis, Caltech 2011)





Biological tissues imaging

(Biophys. J. 81 493)



Thin films and surfaces characterization *(PRB 89 075110)*

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State of art for second harmonic generation

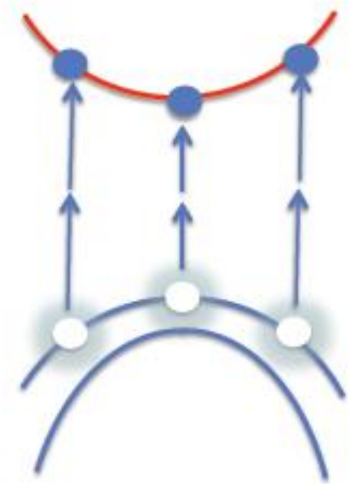
Bulk materials and interfaces

- Independent particles approximation (IPA) – end of 80's
- Calculation including local-field effect and excitonic effects (electron-hole) – TDDFT (2010) and Bethe-Salpeter Equation (2005)

Surfaces

- Some calculations in IPA – since 1994
- Limited to in plane component of $\chi^{(2)}$ - (problem of local fields)

Numerical simulation of optical properties



Linear response

$$\lim_{\mathbf{q}\to 0} \epsilon(\mathbf{q},\omega) = 1 - \frac{8\pi}{\Omega\omega^2} \sum_{n,n'} \sum_{\mathbf{k}}^{BZ} \frac{(f_{n,\mathbf{k}} - f_{n',\mathbf{k}})}{E_{n,\mathbf{k}} - E_{n',\mathbf{k}} + \omega + i\eta} |\hat{\mathbf{q}}\mathbf{p}_{n,n'}(\mathbf{k})|^2$$

2nd order response

$$\lim_{\mathbf{q}\mathbf{q_1}\mathbf{q_2}\to 0} \chi^{(2)}(\mathbf{q},\mathbf{q_1},\mathbf{q_2},\omega) = \frac{-i}{2\Omega\omega^3} \sum_{n,n',n'',\mathbf{k}} \frac{\hat{\mathbf{q}}\mathbf{p}_{n,n'}(\hat{\mathbf{q_2}}\mathbf{p}_{n',n''}\hat{\mathbf{q_1}}\mathbf{p}_{n'',n} + \hat{\mathbf{q_1}}\mathbf{v}_{n',n''}\hat{\mathbf{q_2}}\mathbf{v}_{n'',n})}{(E_{n,\mathbf{k}} - E_{n',\mathbf{k}} + 2\omega + 2i\eta)} \left[\frac{f_{nn''}}{E_{n,\mathbf{k}} - E_{n'',\mathbf{k}} + \omega + i\eta} + \frac{f_{n'n''}}{E_{n'',\mathbf{k}} - E_{n',\mathbf{k}} + \omega + i\eta} \right]$$

(**Independents Particles Approximation (IPA), Long wavelength limit**)

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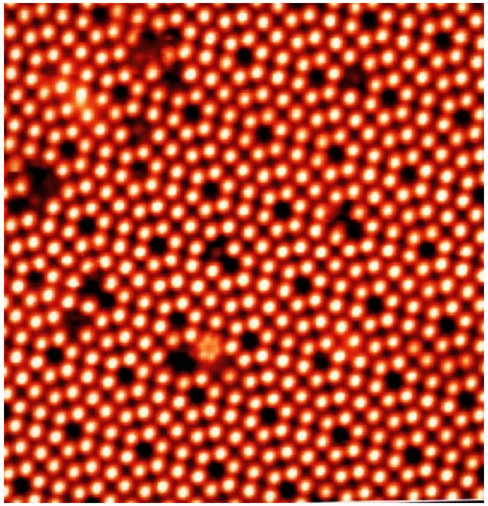
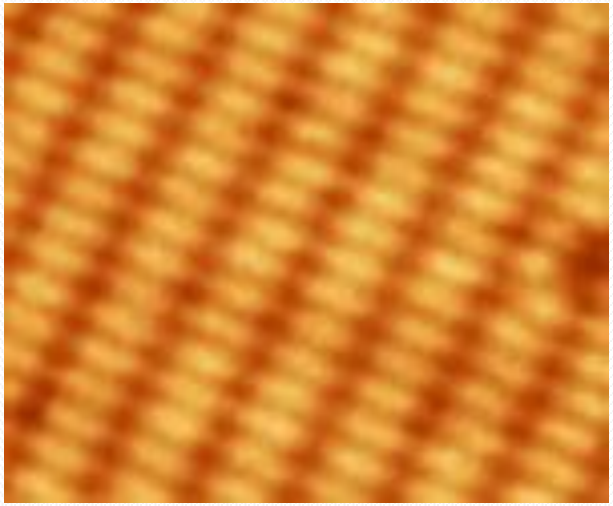
Surfaces

Different surfaces for the same material

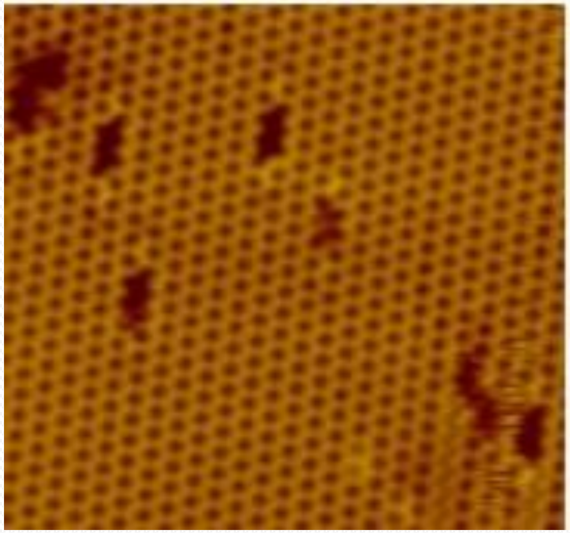
For example : silicium



Si(111) 7x7

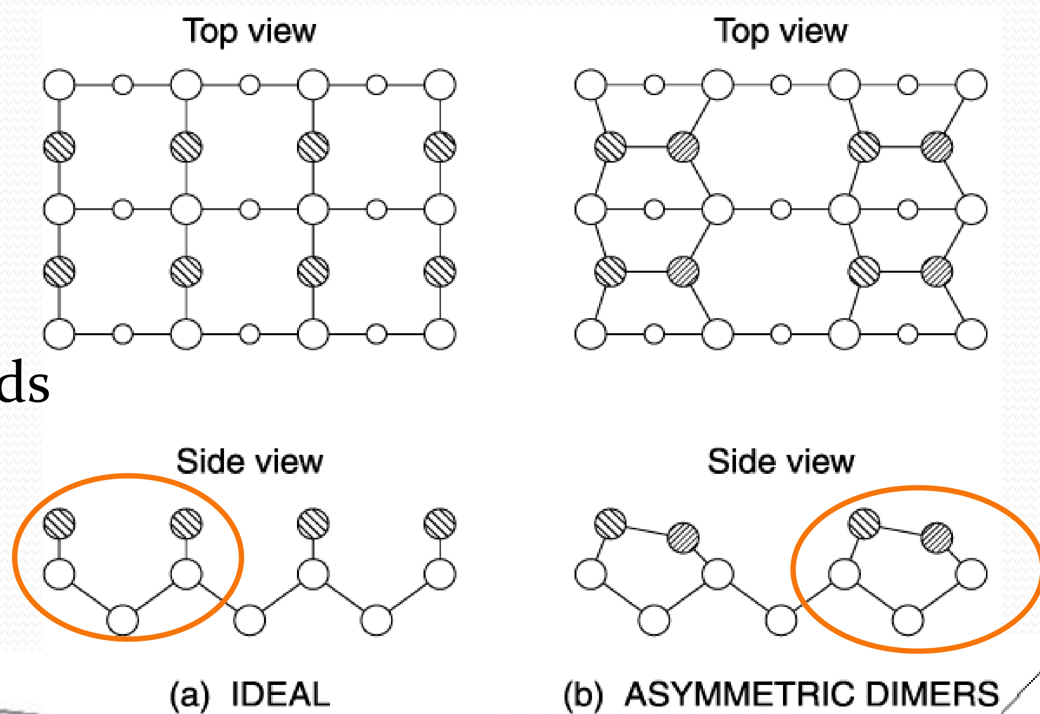


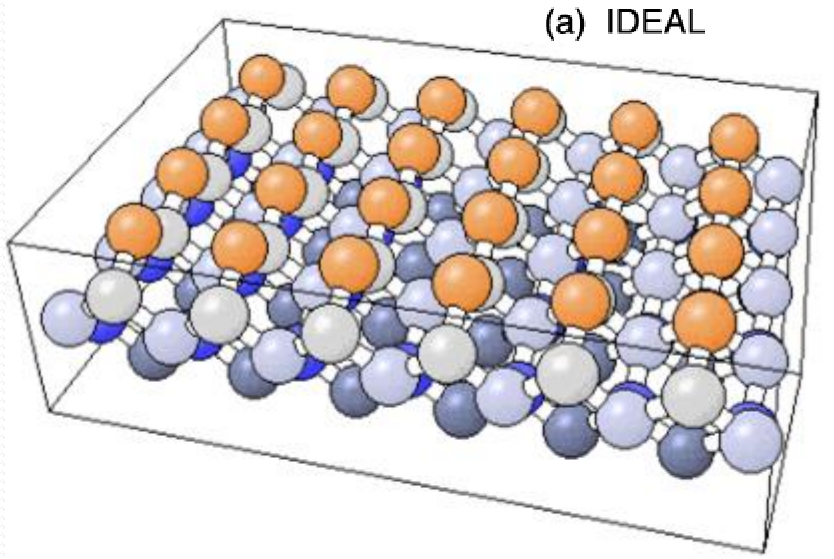
Si(001) 2x1

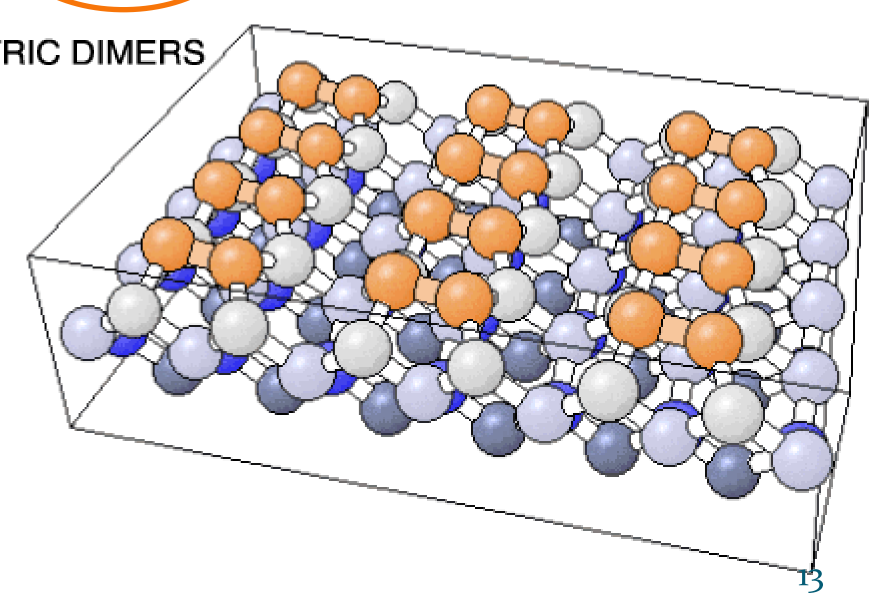


Si(001) 4x2

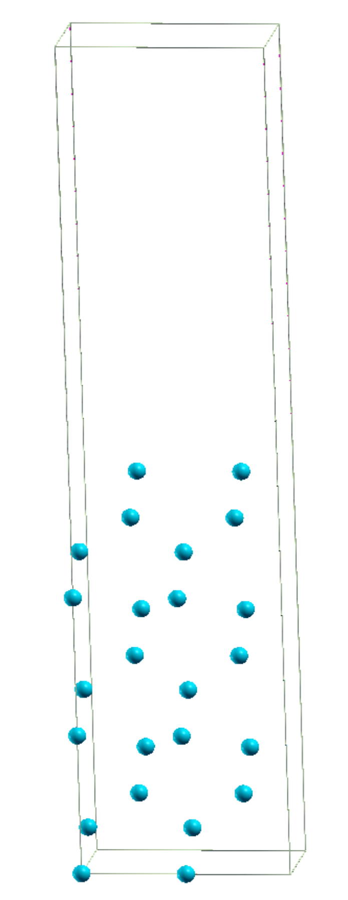
Example of surface reconstruction : Si(001)2x1







Model of surface – Super-cells



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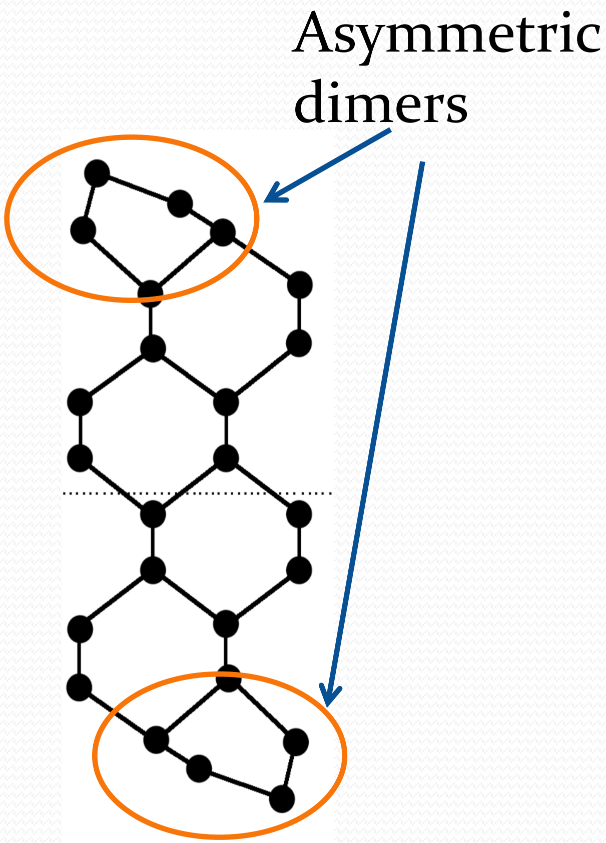
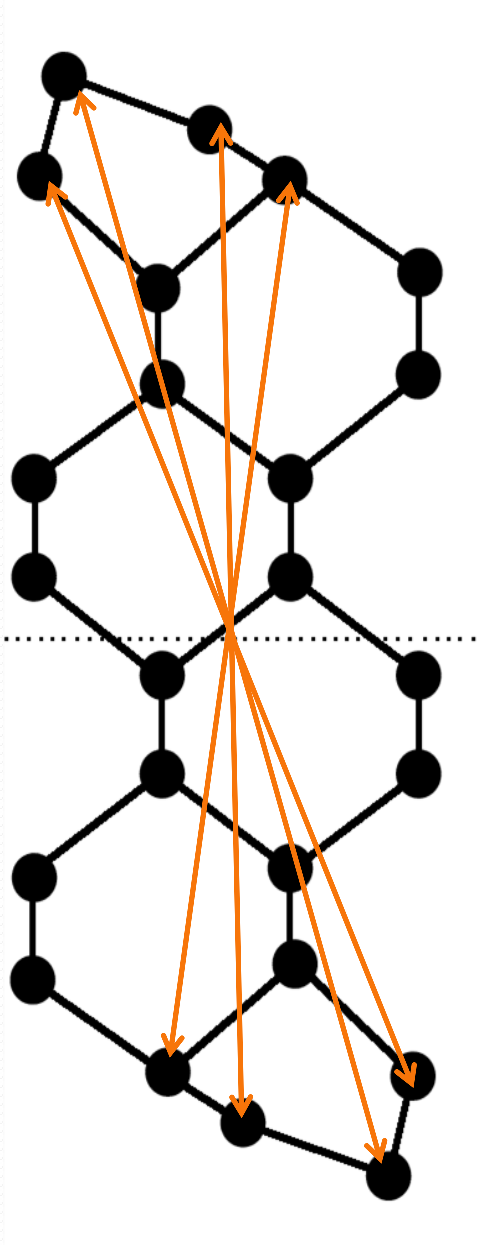


Construction of super-cell (atoms + vacuum)

Reconstruction of the surface

System with 2 surfaces

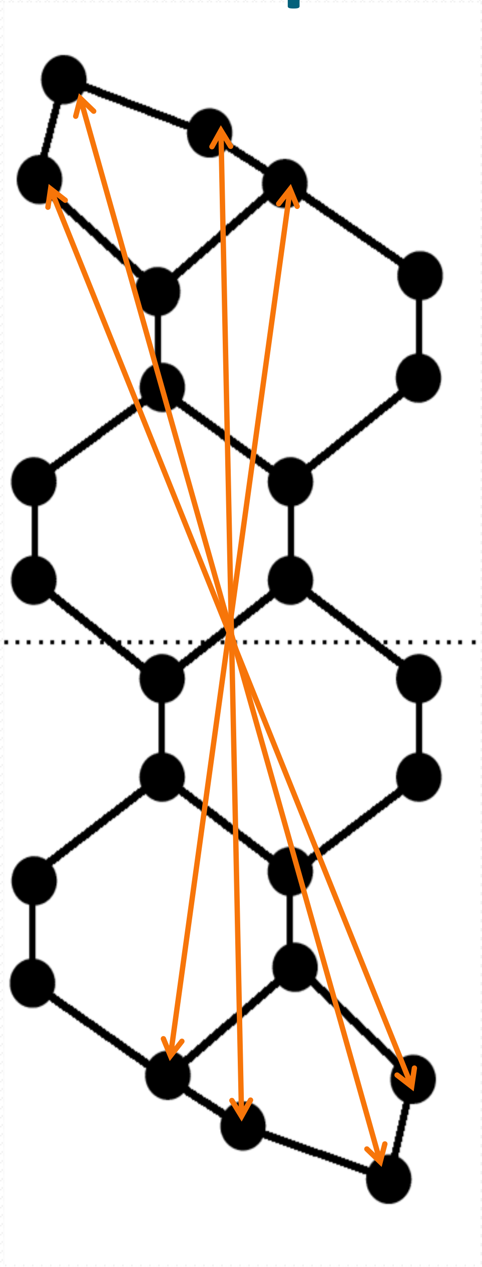
Second harmonic generation for silicon surface



The super-cell has **inversion symmetry**

So $$\chi_{super-cell}{}^{(2)} = 0$$

The super-cell problem



You need to use super-cell to model surfaces

But

Due to super-cell, you could not compute directly the second harmonic spectrum

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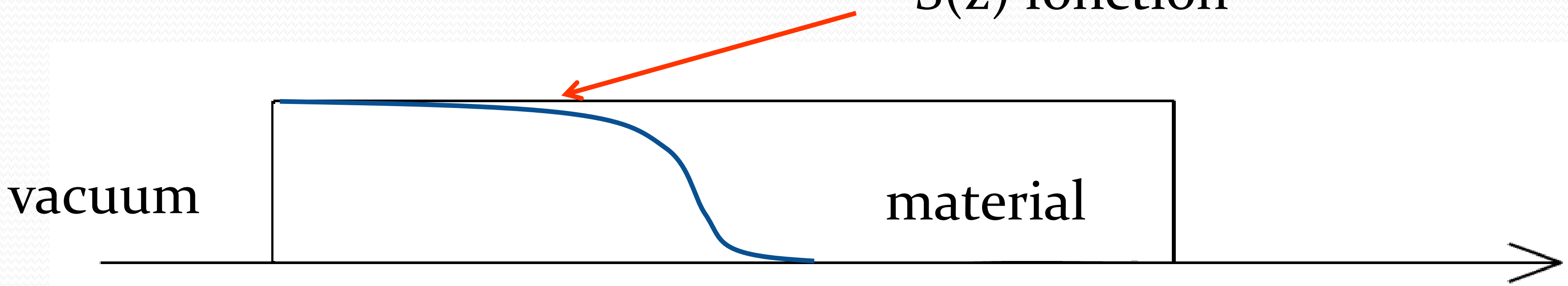
Extraction of one surface signal

It is possible to extract the signal using the $\tilde{p}$ instead of p [1] where

$$\tilde{p} = \frac{1}{2}(pS(z) + S(z)p) \qquad p = \frac{im}{\hbar}[H, r]$$

Where $\tilde{p}$ is introduced to screen the field inside the material.

S(z) fonction



Front surface

Back surface

[1] L. Reining *et al.*, Phys. Rev. B 50, 8411 (1994)

Extraction of one surface signal

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Where $\tilde{p}$ is introduced to screen the field inside the material.

Two approaches are possible :

-screen the two impinging fields at ω (Sz2) [1]

-screen the emitted field at 2ω (Sz1) [2]

[1] L. Reining *et al.*, Phys. Rev. B 50, 8411 (1994)

[2] B. Mendoza *et al.*, Phys. Rev. Lett. 81, 3781 (1998)

Extraction of one surface signal

Two approaches.

Are the two approaches equivalent?

Comparison of the two approaches

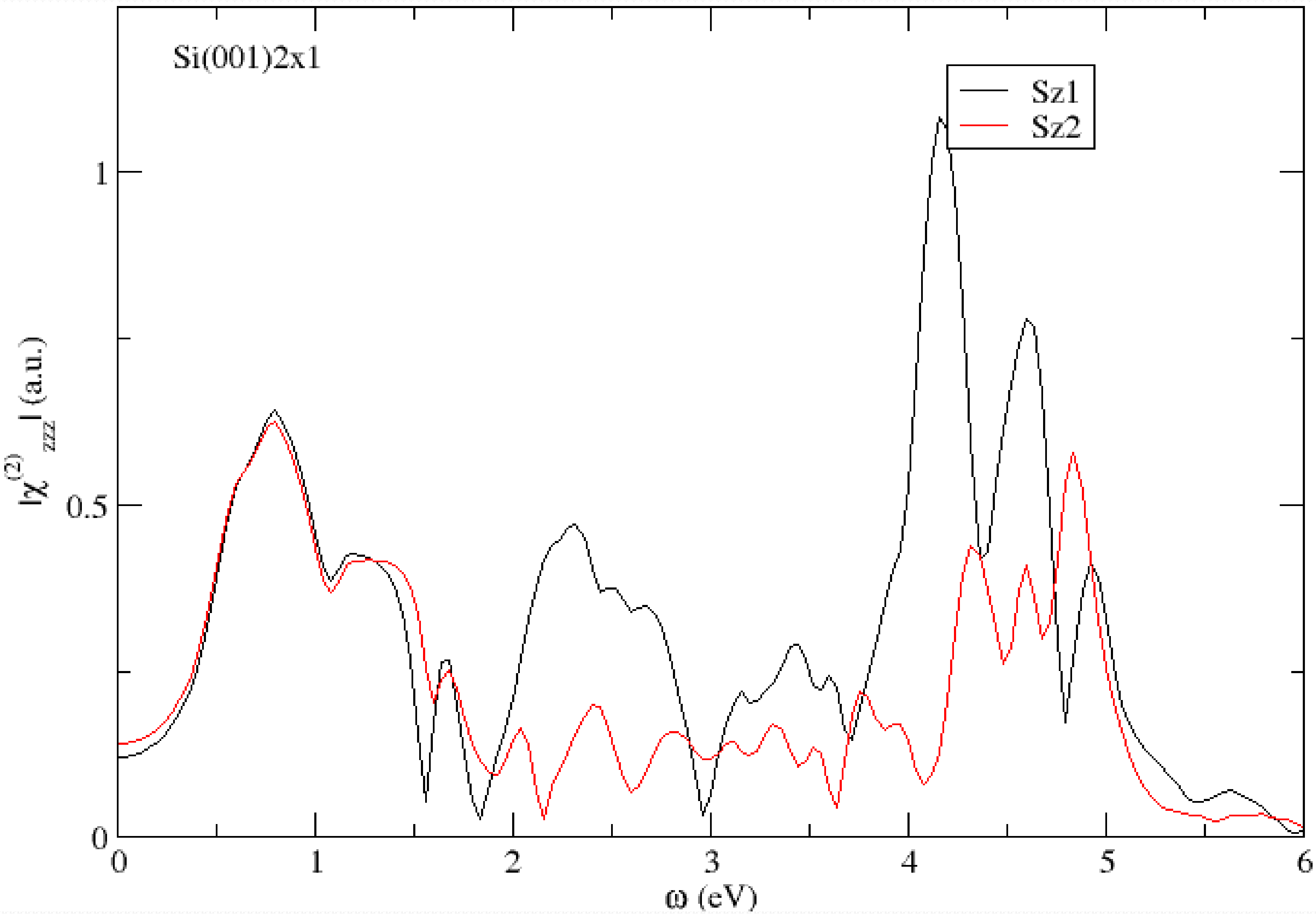
Lets compare the two approaches on an interesting component (e.g. zzz component)

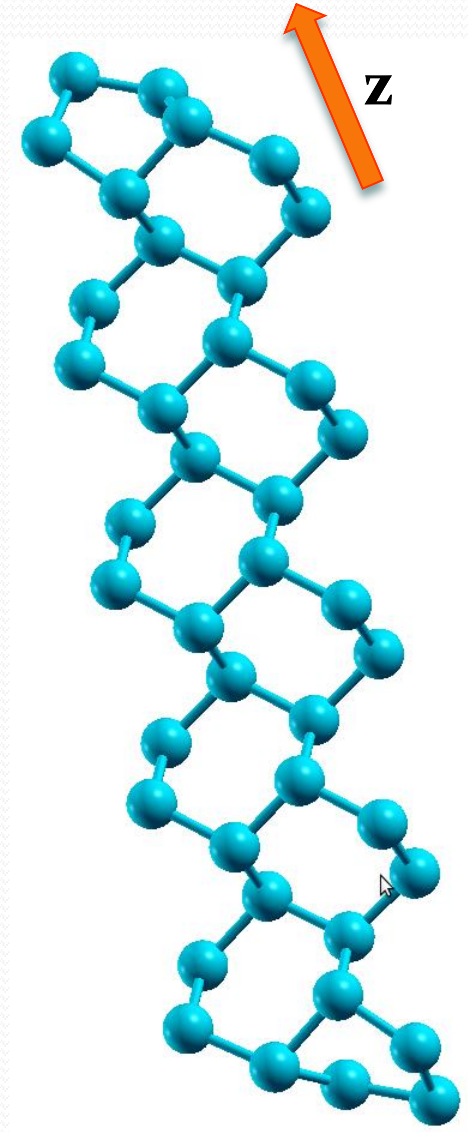
Implementation in Tight-Binding for two reasons :

- Layer-by-layer analysis in tight-binding straightforward
- Rapidity of the code

Comparison of the two approaches

Let's compare the two approaches on an interesting component (e.g. zzz component)

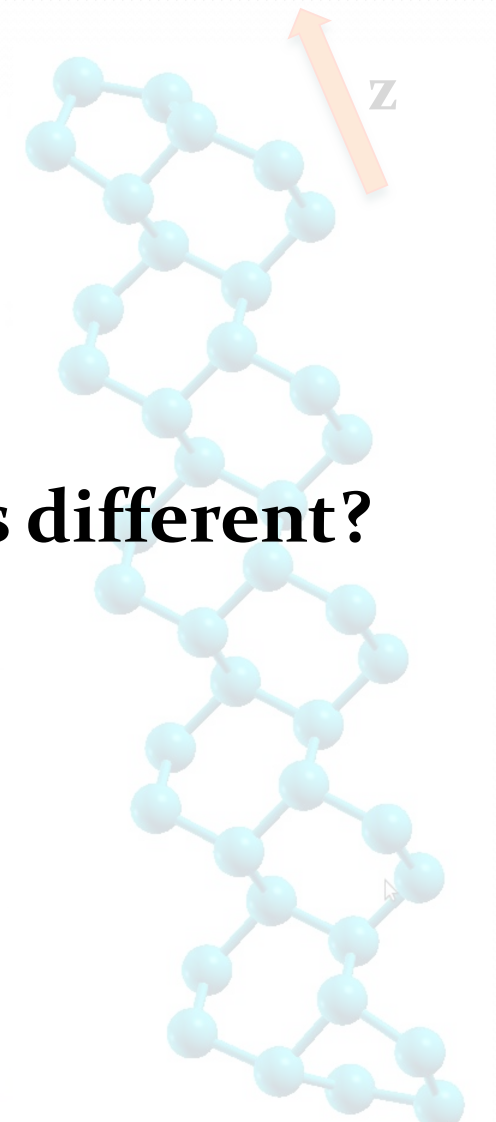




Comparison of the two approaches

The two approaches give different results

Question : Why are the two approaches different?



Comparison of the two approaches

Why the two approaches can give different results ?

Possible reasons discarded :

- Convergence in number of atoms (tested up to 240 atoms)
- Convergence in k-point
- Numerical errors (tested with 3 different formula)

Extraction of one surface signal

Some components are non-zero only by reconstruction

Non-reconstructed surface (always present) :

xxz; yyz; zxx; zyy; zzz

Asymmetric dimers (reconstructed) :

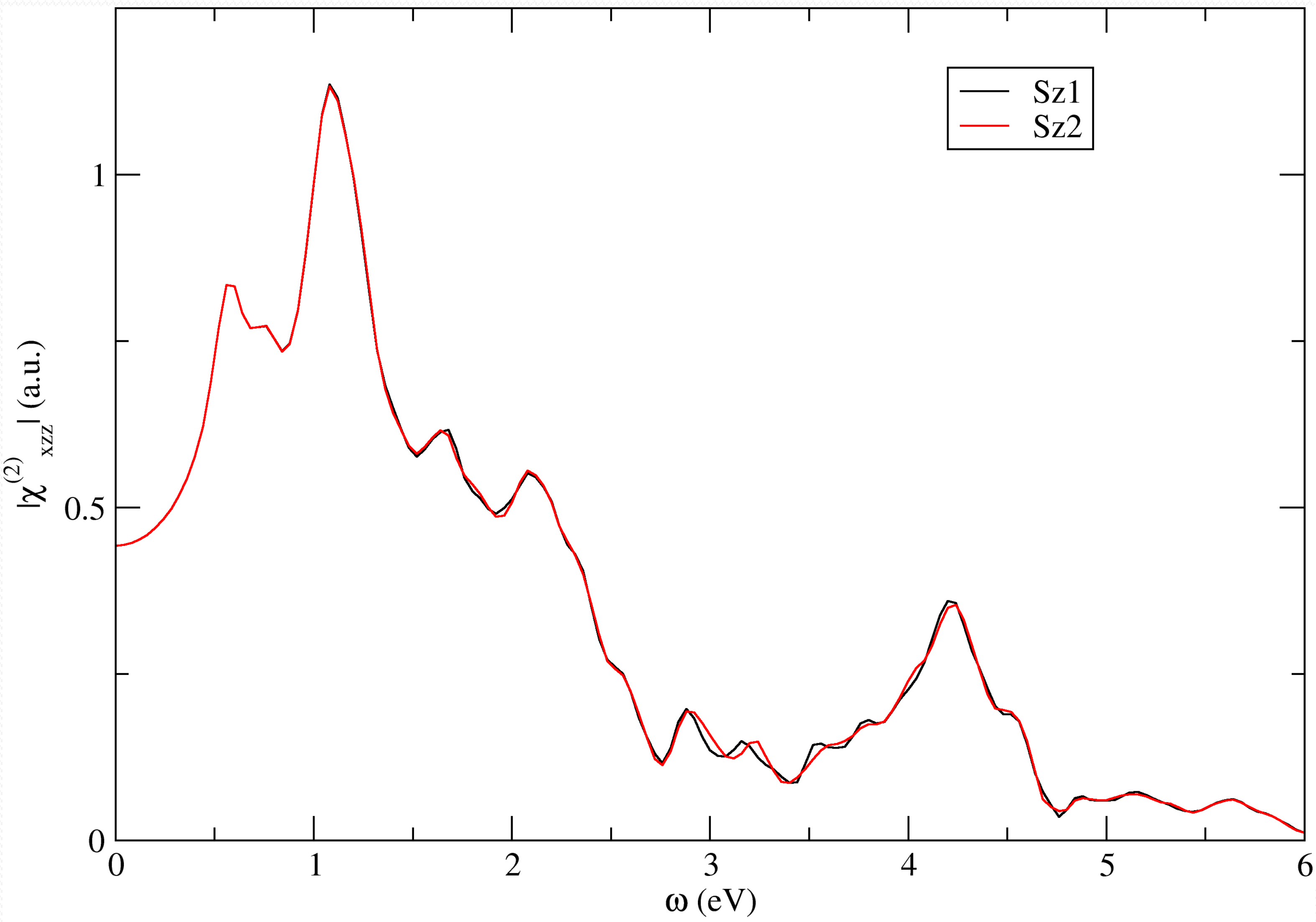
yyx; xyy; yyz; zyy; xxx; zxx; xxz; xzz; zzx; zzz

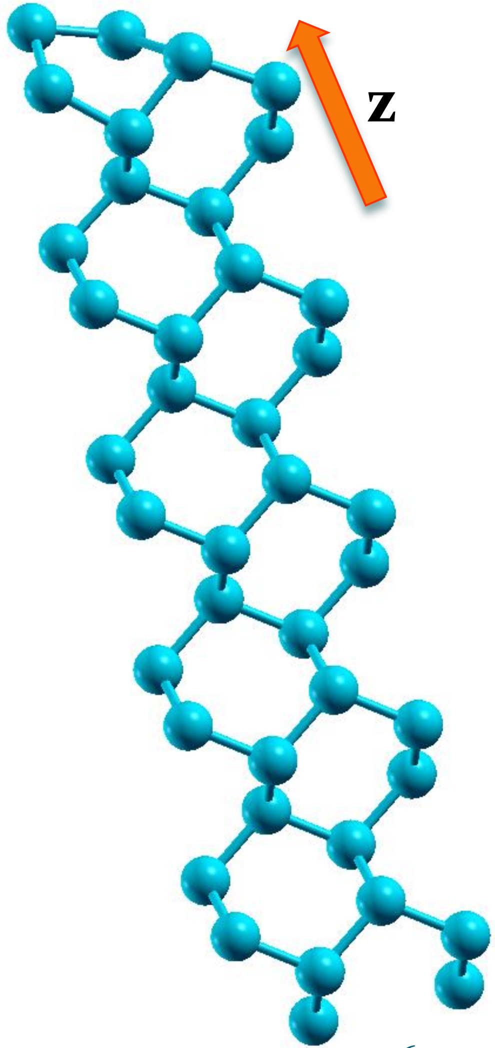
We can test also the two approaches on these new components

New components : *yyx; xxy; xxx; xzz; zzx*

Comparison of the two approaches

We compare the signal for the reconstructed half-slab

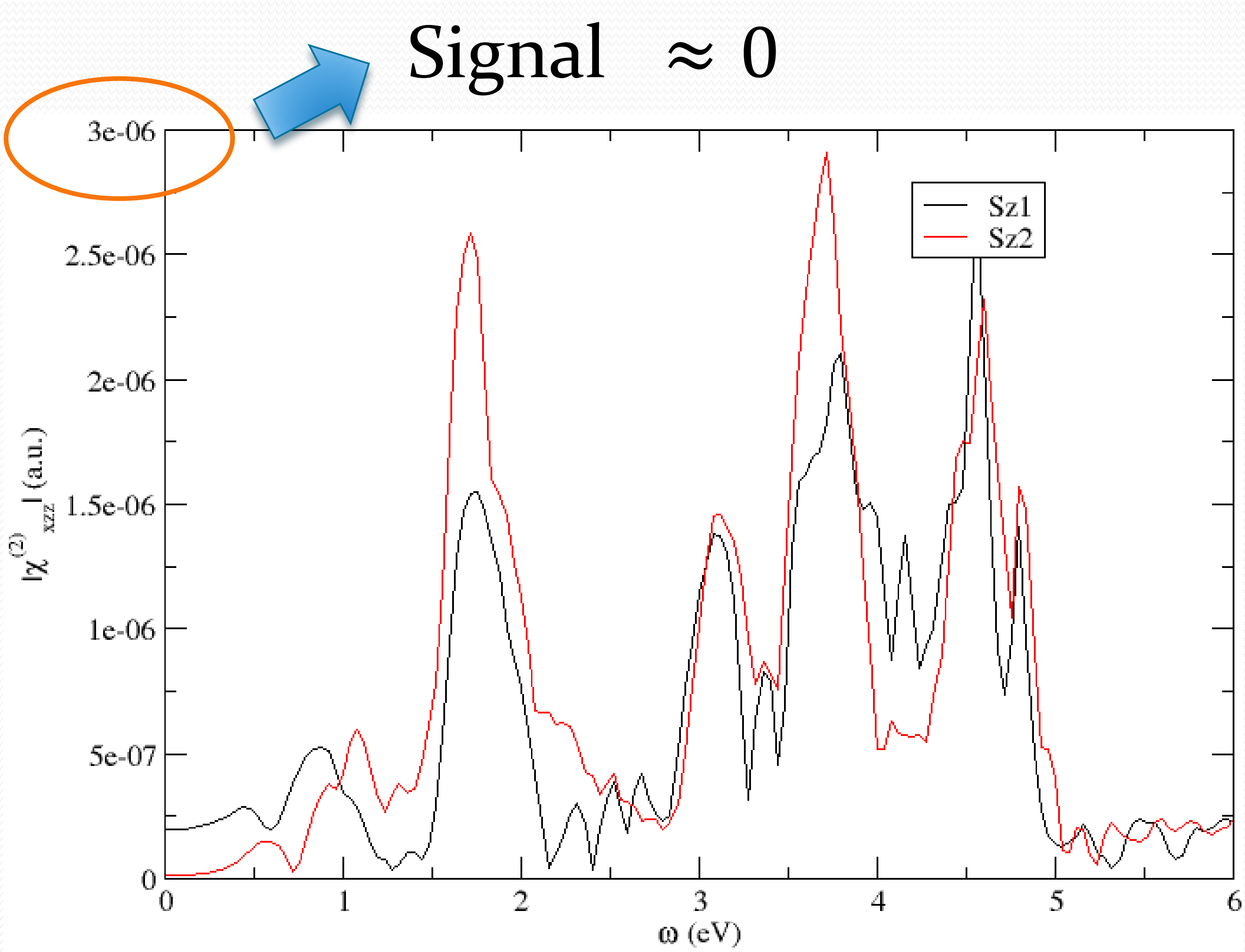


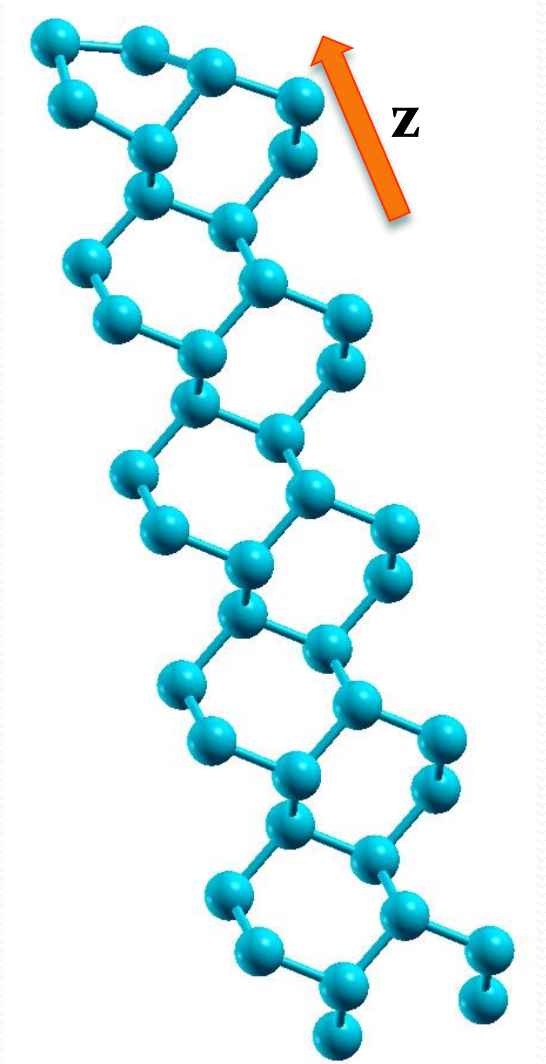


Comparison of the two approaches

We compare the signal for the non-reconstructed half-slab

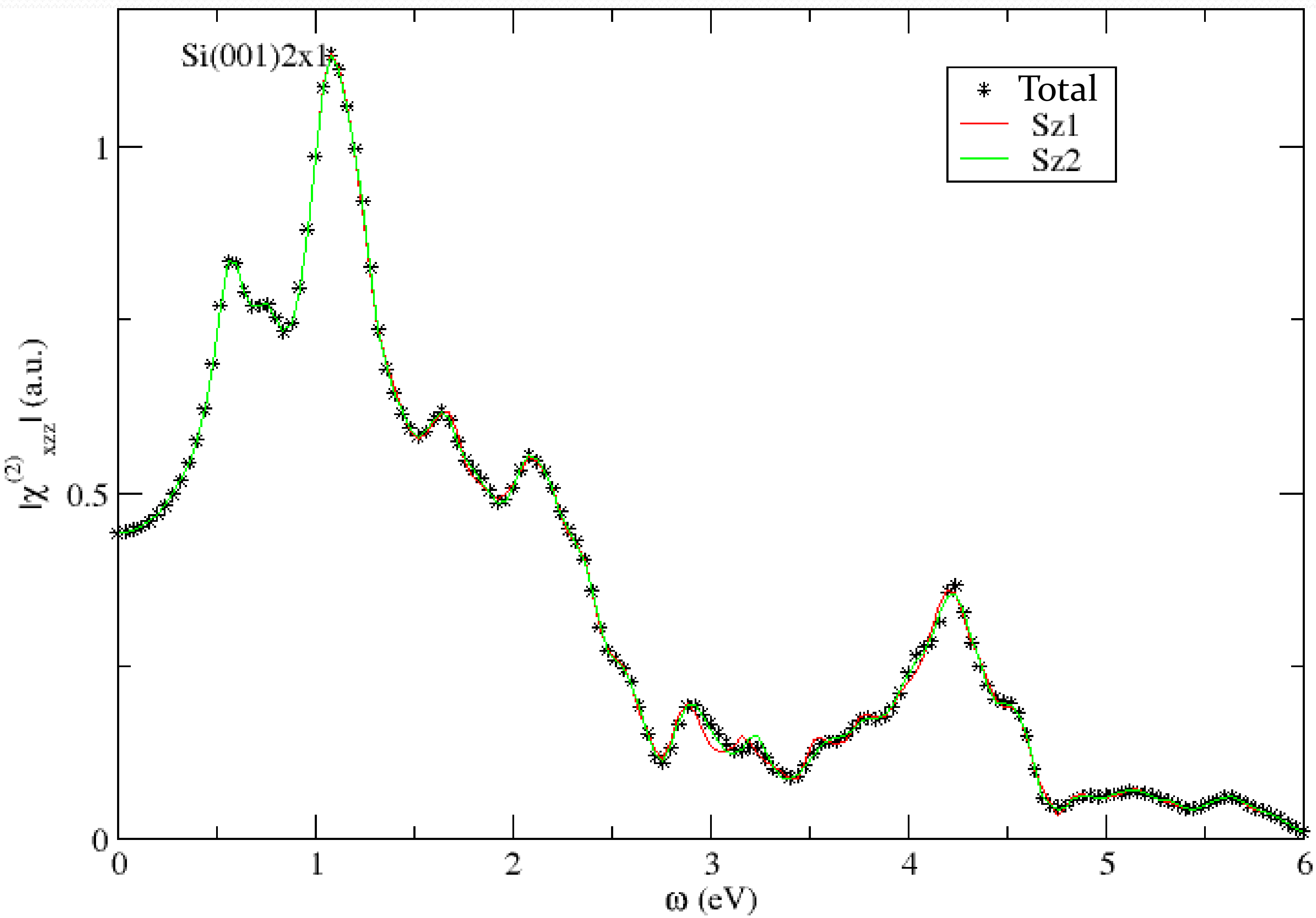
Signal ≈ 0

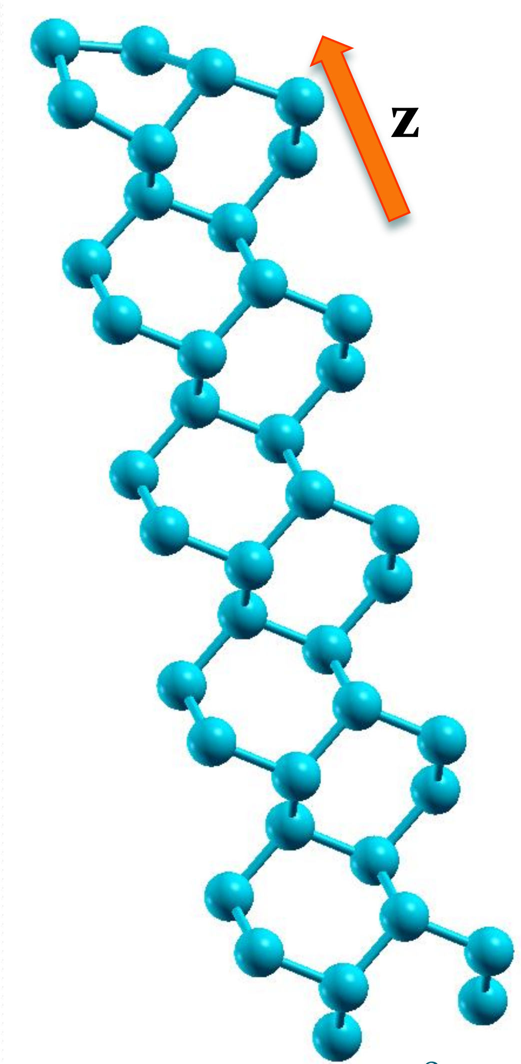




Comparison of the two approaches

We compare the signal of the half-slab to the total super-cell signal





Comparison of the two approaches

- Everything seems to be like

$$\chi^{(2)}{}_{super-cell} = \chi_1{}^{(2)} - \chi_2{}^{(2)}$$

- When $\chi_2{}^{(2)} = 0$, we recover a semi-infinite crystal and in that case the two approaches give the same result

- What is happening with the *zzz* component?

Conclusion and Future work

Conclusion

- Two approaches for extracting the signal are possible
- The two approaches give the same result in some cases and that result seems correct

Work in progress

- Explain the differences between the two approaches

Future work

- *ab initio* calculations
- Local-field effects

Thank you for your attention