# Second Harmonic Generation From Surfaces

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# Outline

- Nonlinear optic and second harmonic generation
- Surfaces
- How do we get the surface spectrum for SHG

# Response to a perturbation

**Perturbation** → **Response**

Electric field → Polarisation

**Linear Response** | **Nonlinear Response**

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

$\chi^{(1)}_{ij}$

- Absorption
- Refraction
- Birefringence

$\chi^{(2)}_{ijk}$

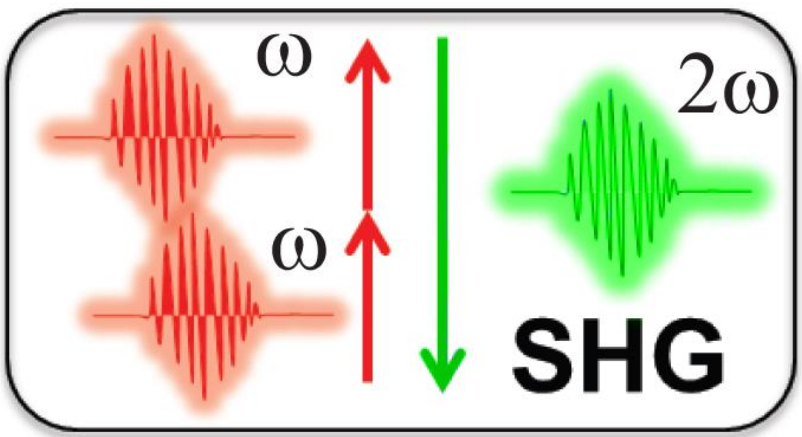
- Sum frequency Generation
- Pockels effect
- …

$\chi^{(3)}_{ijkl}$

- Kerr effect
- Four-wave mixing
- …

# Second harmonic generation

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

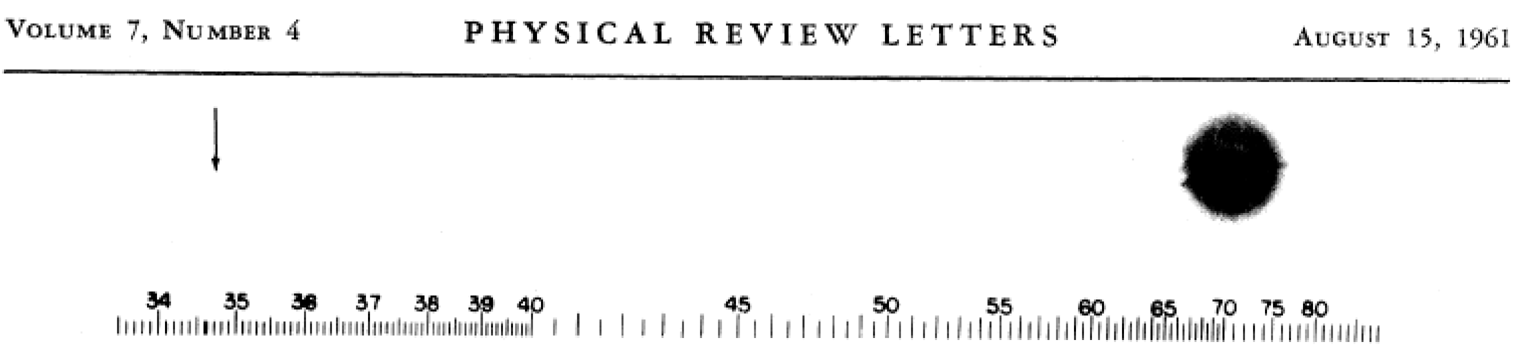



First nonlinear term

Centrosymmetric material : $\chi^{(2)} = 0$

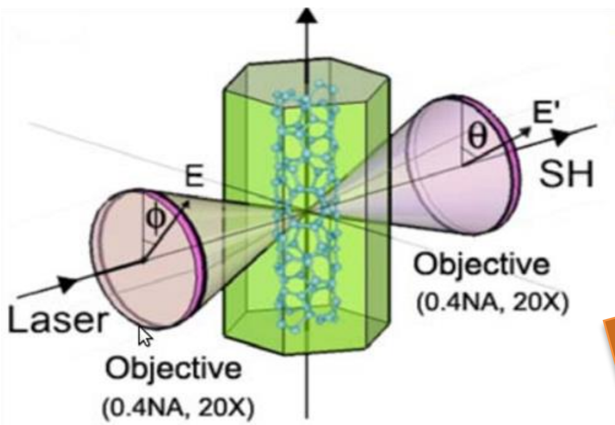
First nonlinear term : $\chi^{(3)}$

Non centrosymmetric material : $\chi^{(2)} \neq 0$

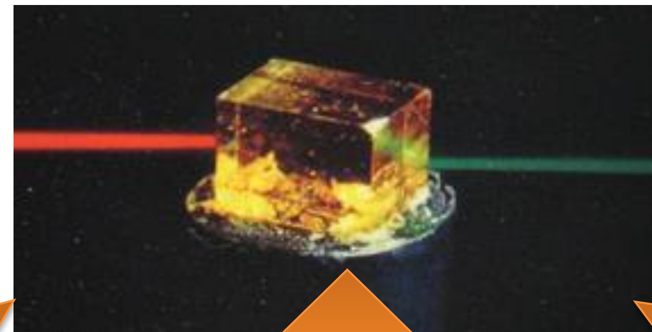


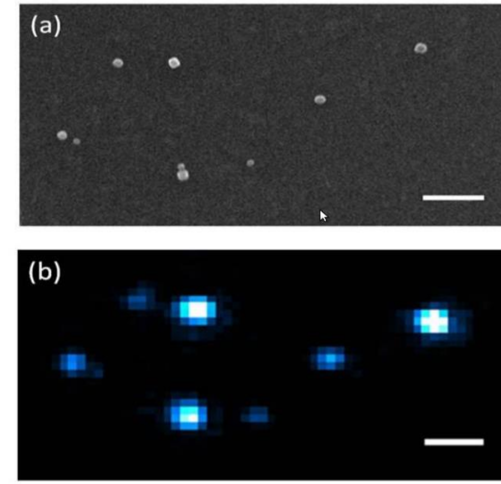

G. Frankel

# Applications of second harmonic generation (SHG)

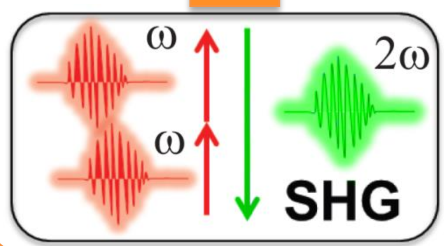


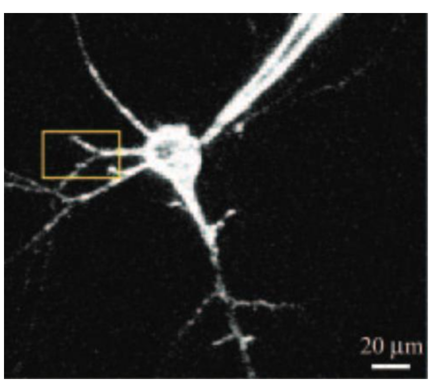

Nanotubes characterization
*(PRB 77 125428)*

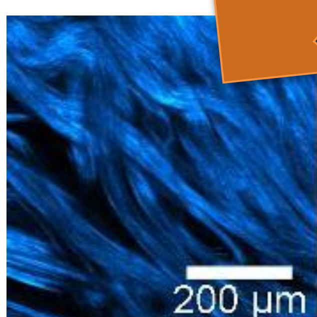




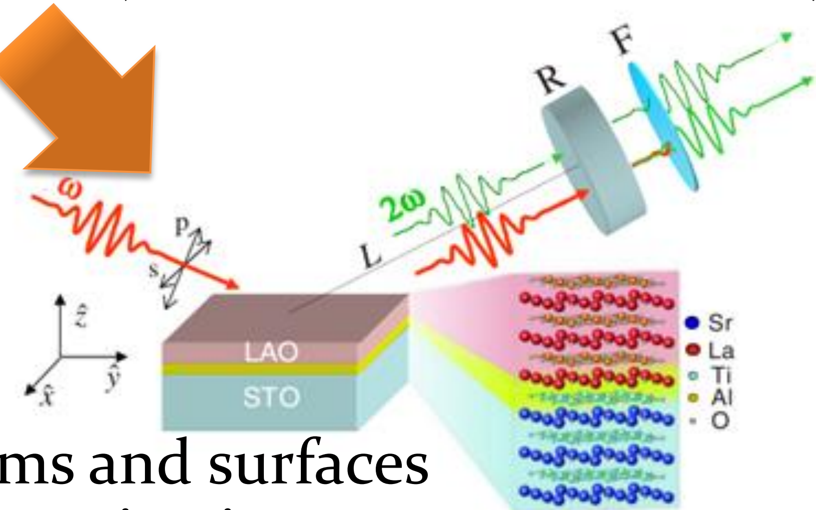

Nanoparticles imaging and microscopy
*( C-L Hsieh PhD thesis, Caltech 2011 )*




Biological tissues/neurons imaging
*(Biophys. J. 81 493; PNAS 103, 786)*




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

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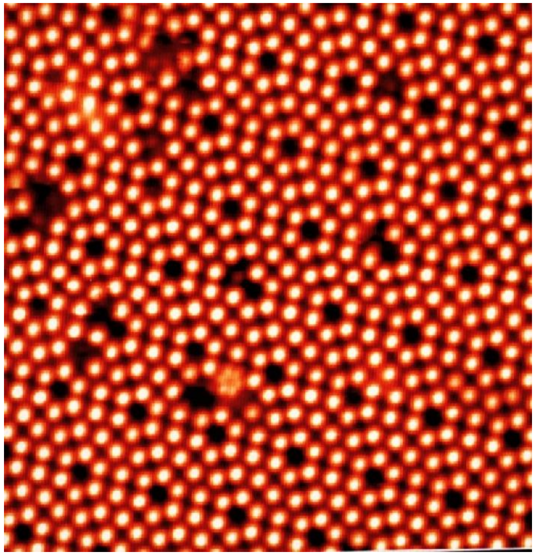
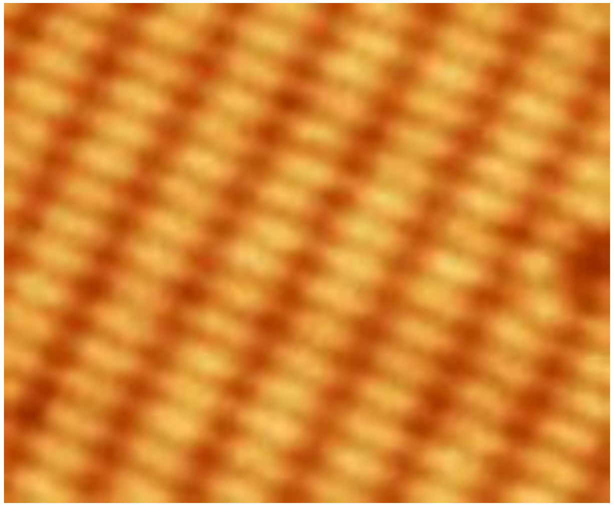
# Surfaces

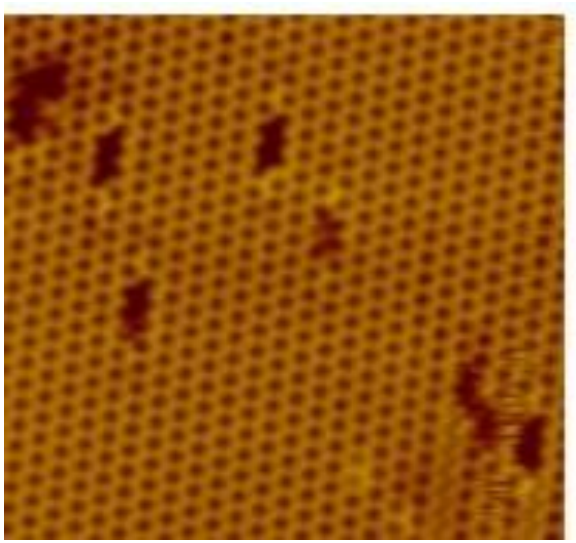
Different surfaces for the same material (e.g. Silicon)



Si(111) 7x7

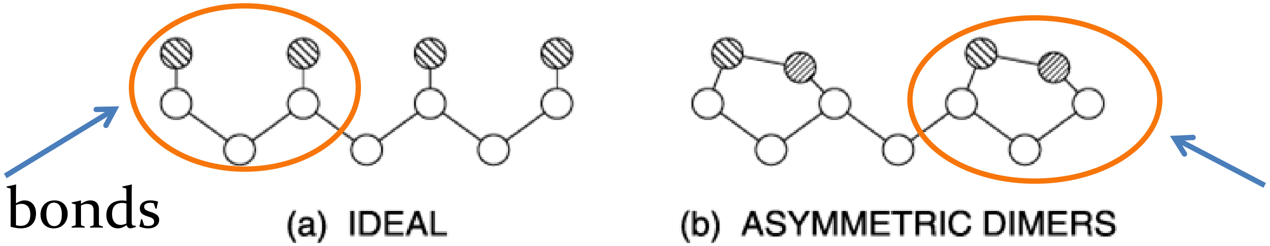


Si(001) 2x1



Si(001) 4x2

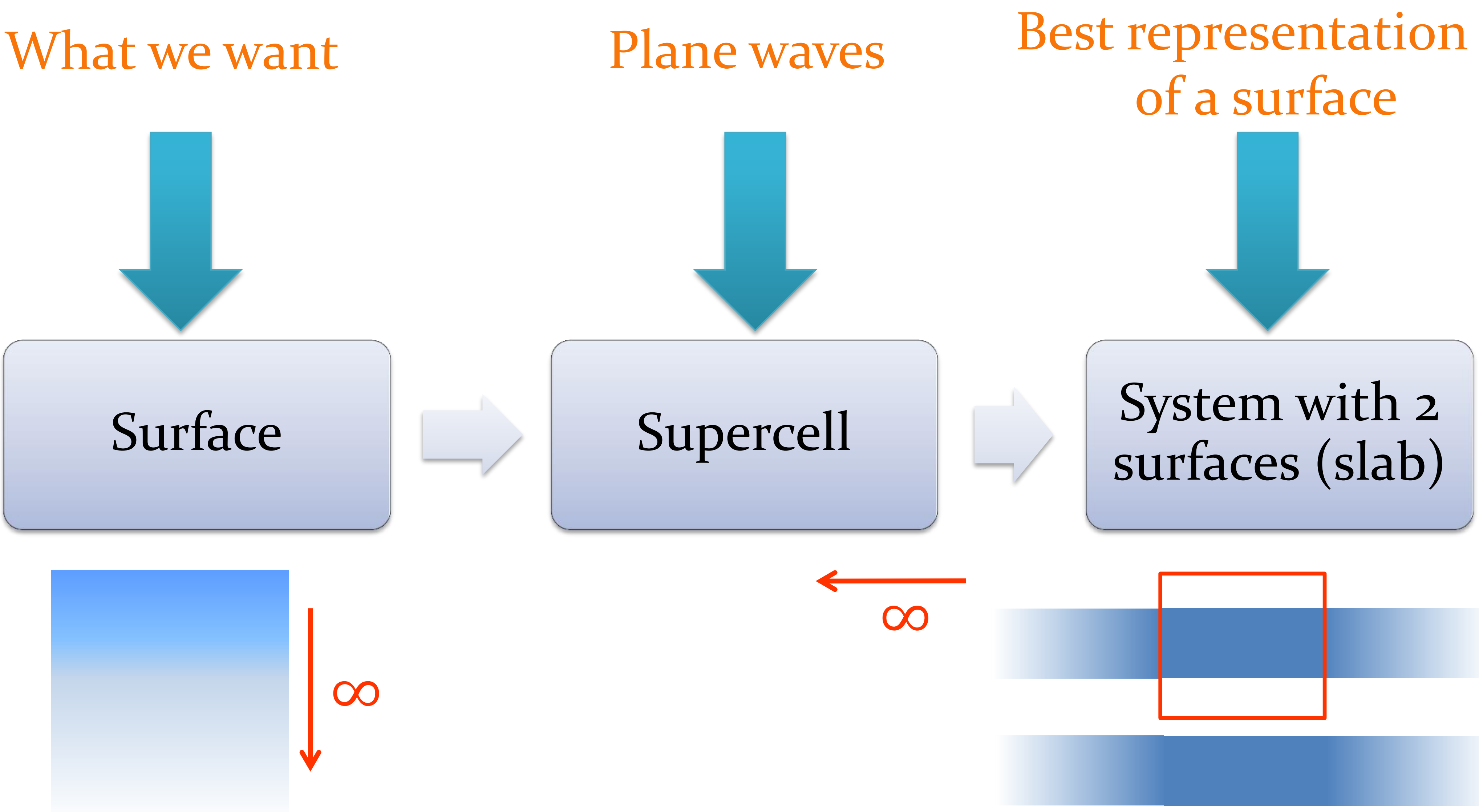
Surface = symmetry breaking



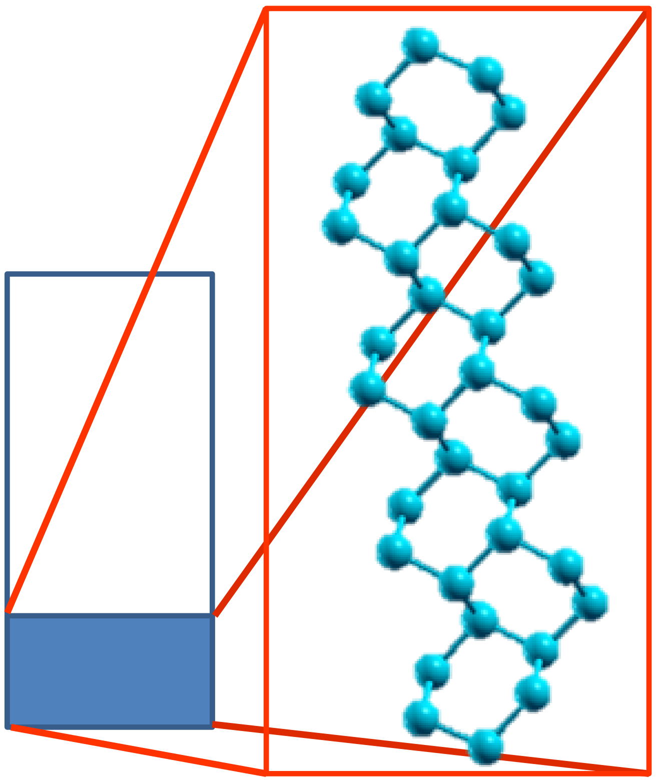

Dangling bonds

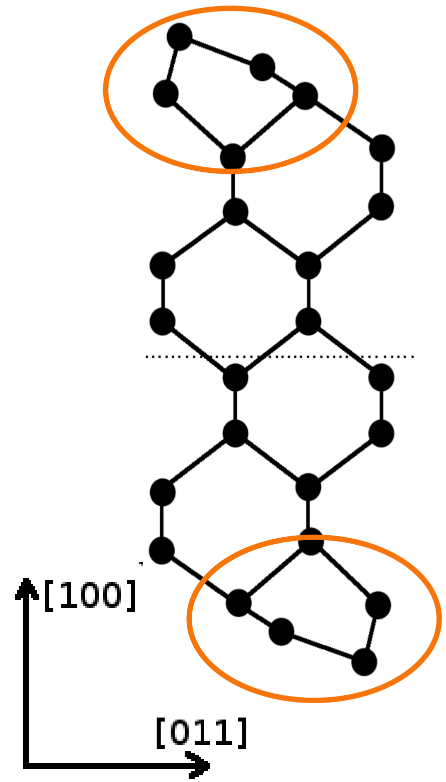
Asymmetric dimers

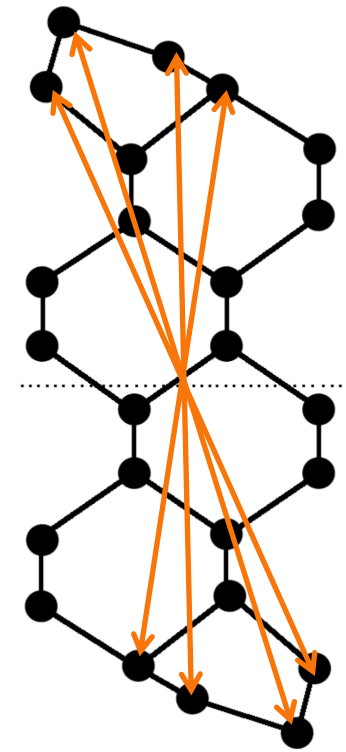
# Model of surface – Super-cells



# Model of surface – Super-cells





Construction of super-cell (atoms + vacuum)

System with 2 surfaces (slab)

**inversion symmetry**

$\chi^{(2)} = 0$

(artificial)

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# Second order response in Time-Dependent DFT

## Ground state (DFT)

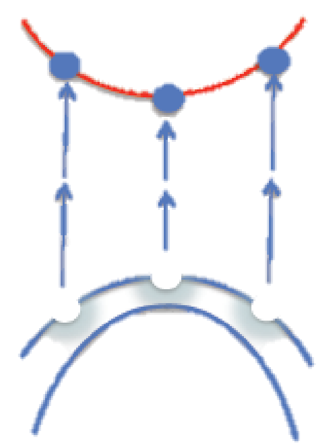
- Electronic structure : LDA functional
- ABINIT code

abinit

## Second order response

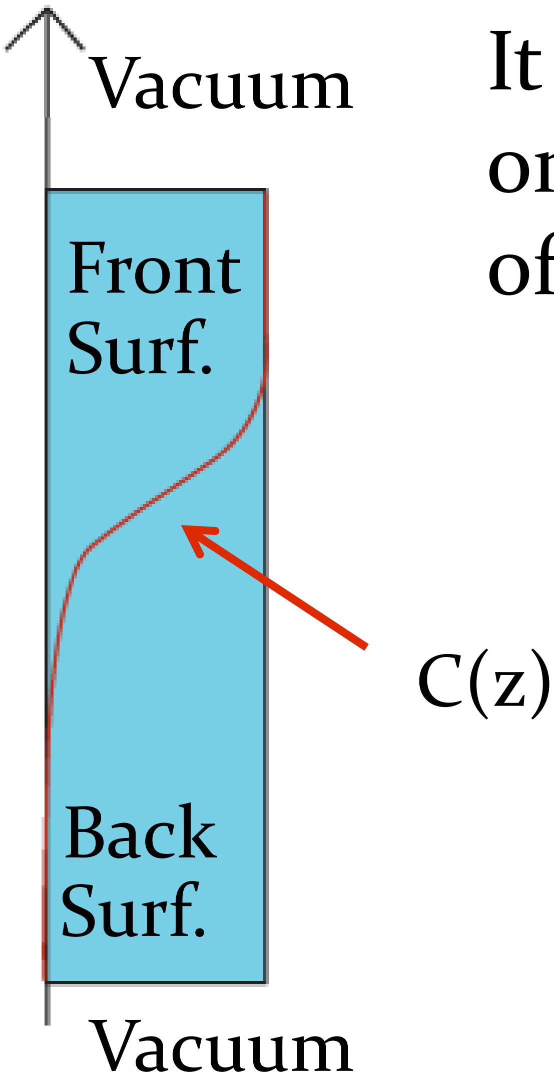
$$\chi^{(2)}_{abc}(-2\omega,\omega,\omega) = \frac{-ie3}{\hbar^2 m^3 \omega^3 V} \sum_{nml} \int d\vec{k} \, \frac{1}{E_m - E_n - 2\omega - 2i\eta}$$

$$\times \left[ f_{nl}(\vec{k}) \frac{p^a_{nm}(\vec{k}) \left\{ p^b_{ml}(\vec{k}) p^c_{\ln}(\vec{k}) \right\}}{E_l - E_n - \omega - i\eta} + f_{ml}(\vec{k}) \frac{p^a_{nm}(\vec{k}) \left\{ p^b_{ml}(\vec{k}) p^c_{\ln}(\vec{k}) \right\}}{E_m - E_l - \omega - i\eta} \right]$$



Independent Particles Approximation (IPA)

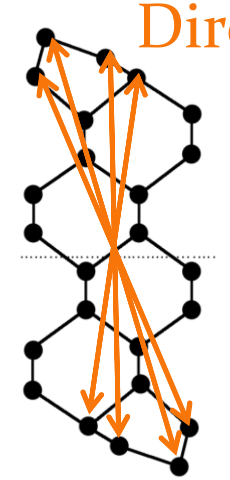
# Extraction of one surface signal




It is possible to extract the signal from only one surface, using a new operator $\tilde{p}$ instead of p[1]

$$\tilde{p} = \frac{1}{2}(pC(z) + C(z)p) \qquad p = i[H, r]$$

Direct Calculation



Inversion symmetry

$$\chi^{(2)} = 0$$

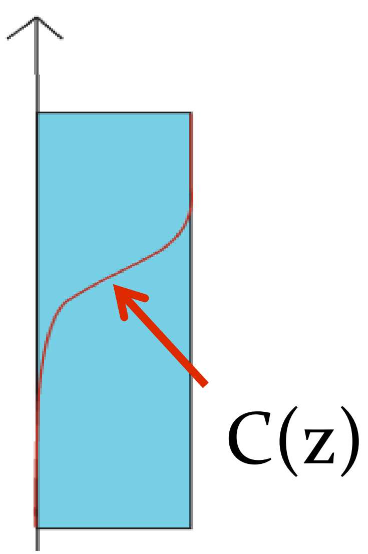
[1] L. Reining et al., Phys. Rev. B 50, 8411 (1994)

# Second-order response

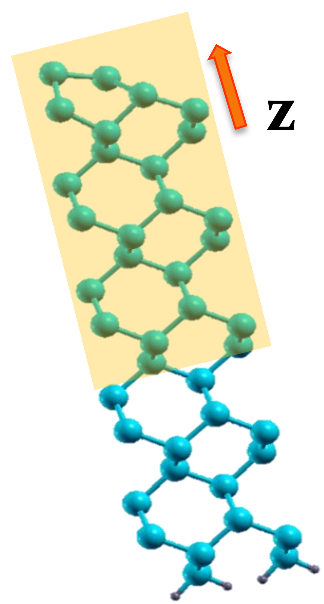
$$\chi^{(2)}_{abc}(-2\omega,\omega,\omega) = \frac{-ie^3}{\hbar^2 m^3 \omega^3 V} \sum_{nml} \int d\vec{k} \frac{1}{E_m - E_n - 2\omega - 2i\eta}$$

$$\times \left[ f_{nl}(\vec{k}) \frac{\tilde{p}^{a}_{nm}(\vec{k} \left\{ p^{b}_{ml}(\vec{k}) p^{c}_{ln}(\vec{k}) \right\}}{E_l - E_n - \omega - i\eta} + f_{ml}(\vec{k}) \frac{\tilde{p}^{a}_{nm}(\vec{k} \left\{ p^{b}_{ml}(\vec{k}) p^{c}_{ln}(\vec{k}) \right\}}{E_m - E_l - \omega - i\eta} \right]$$

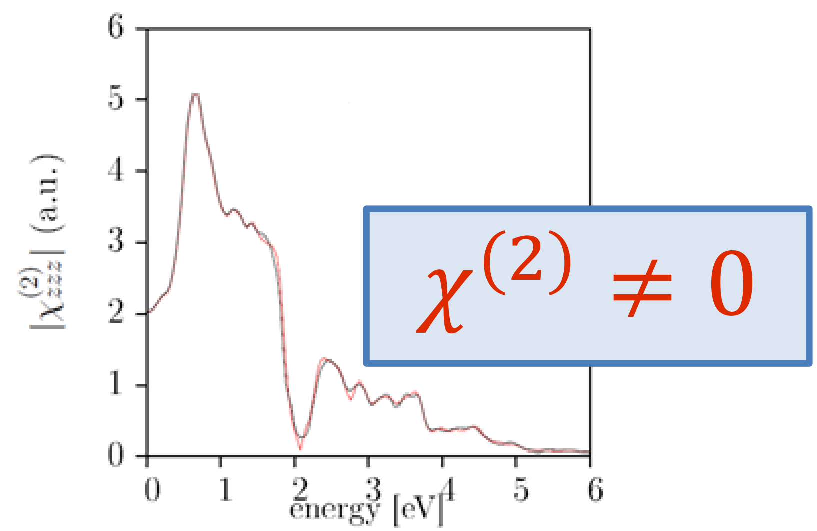
C(z) function




*ab initio* calculation

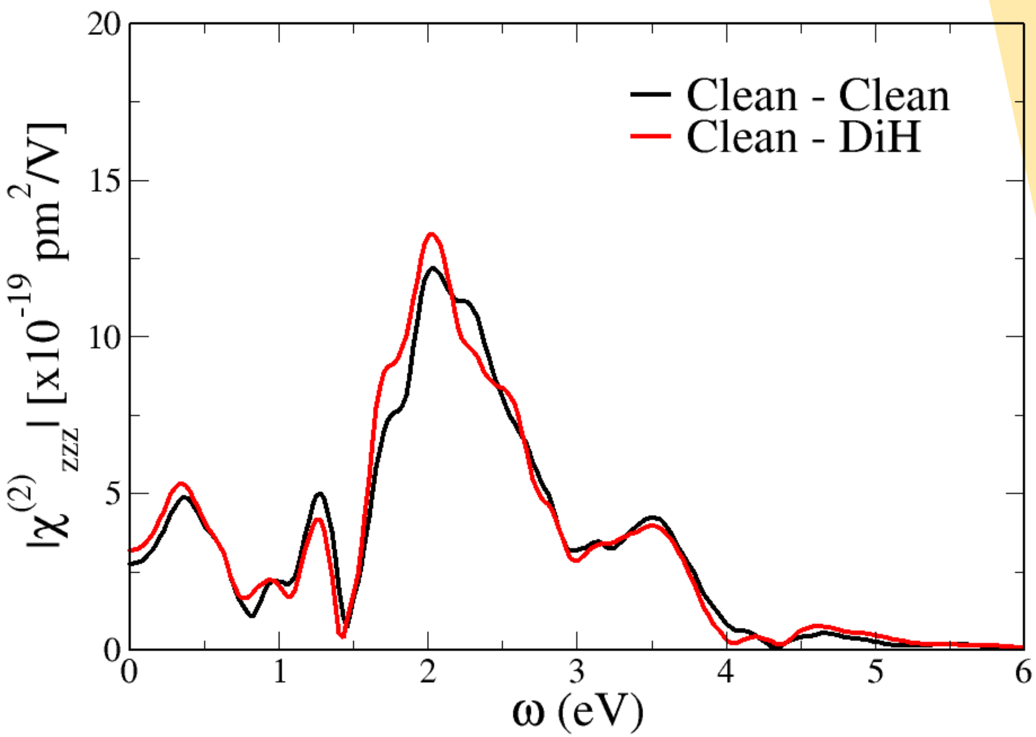


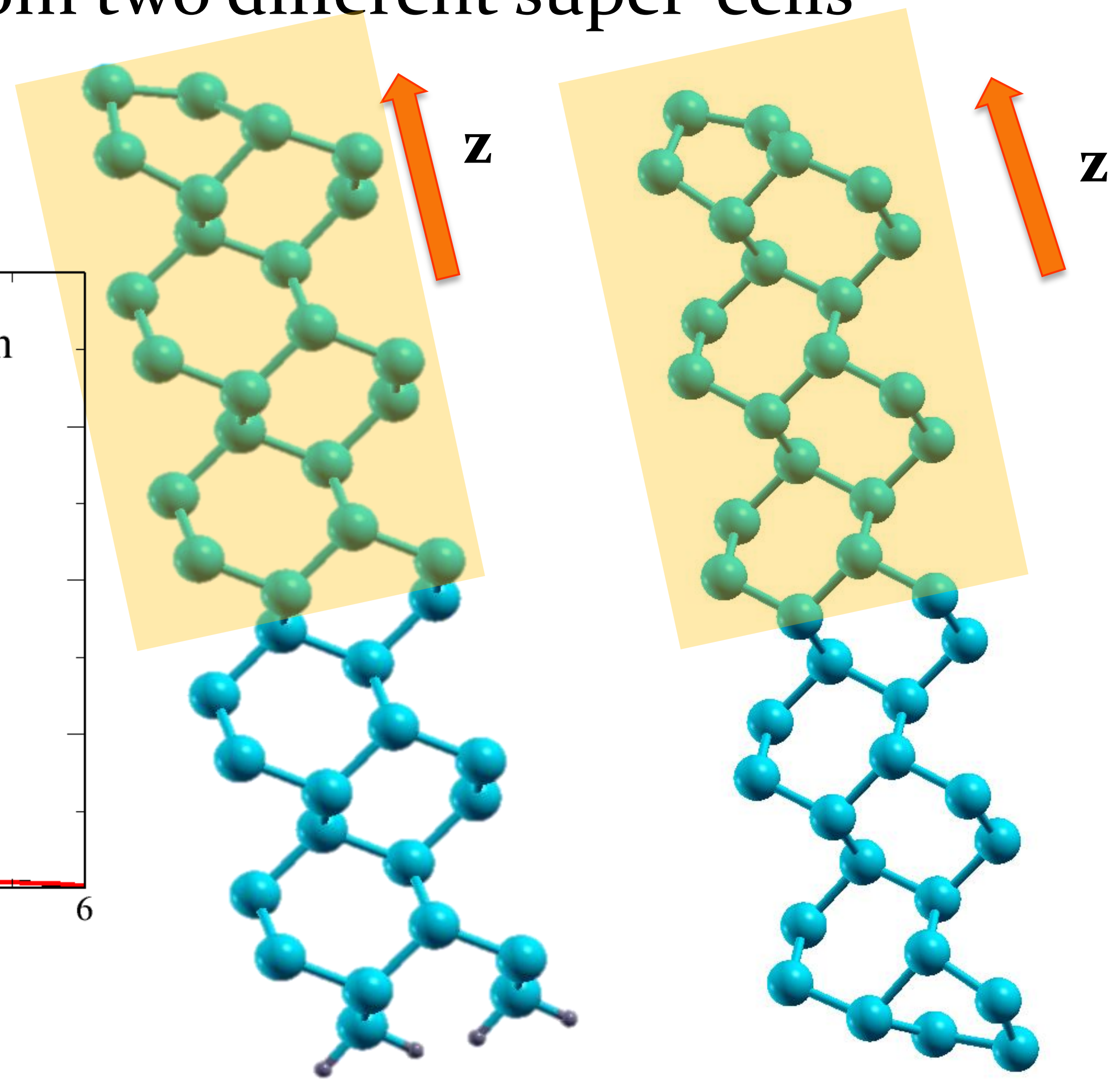

Extracted Signal



# Extraction from two super-cells

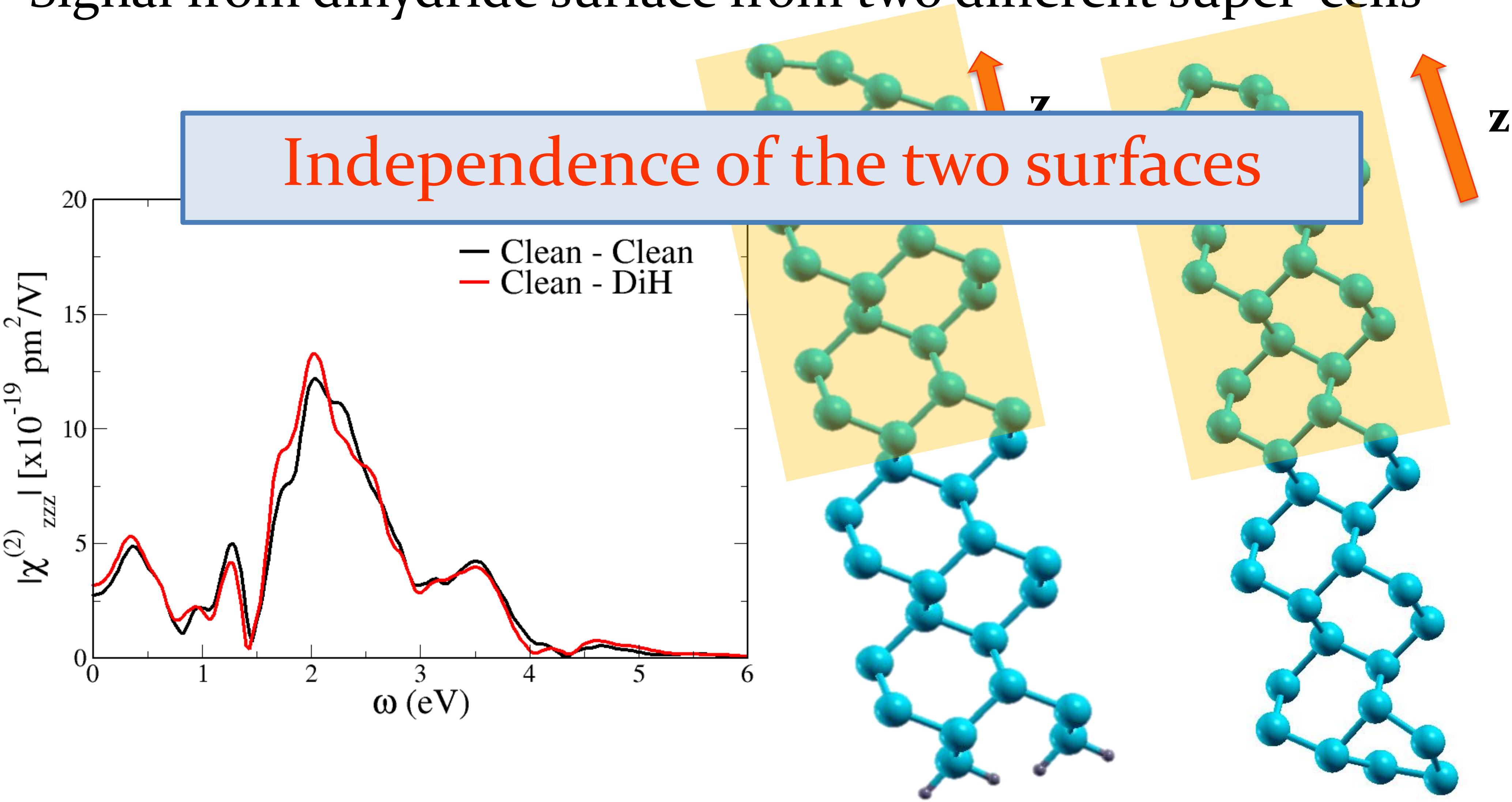
Signal from clean surface from two different super-cells



# Extraction from two super-cells

Signal from dihydride surface from two different super-cells

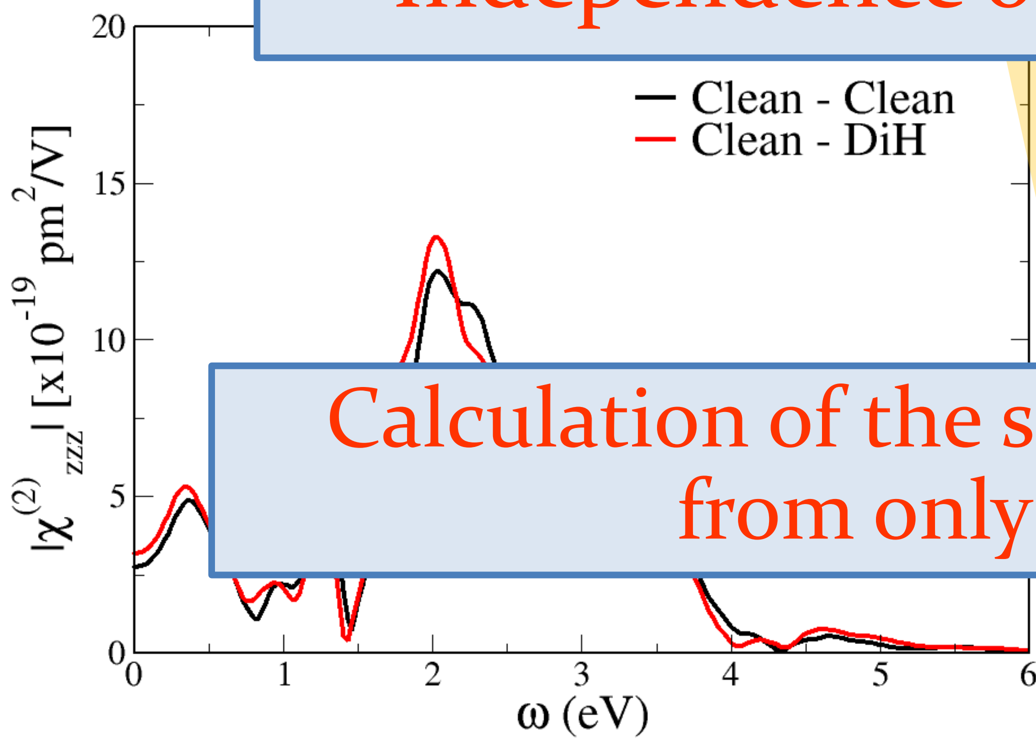



**Independence of the two surfaces**

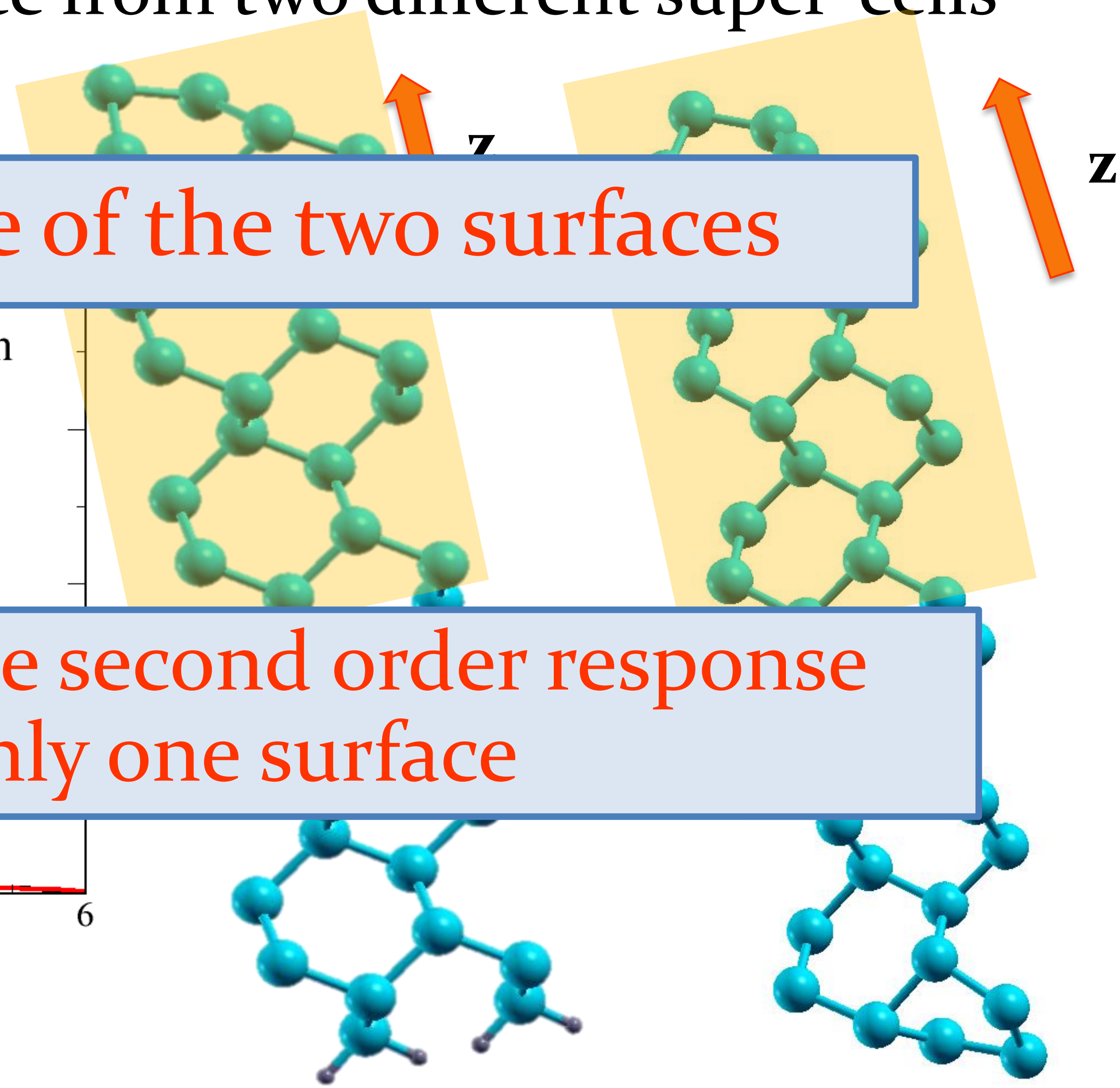
# Extraction from two super-cells

Signal from dihydride surface from two different super-cells

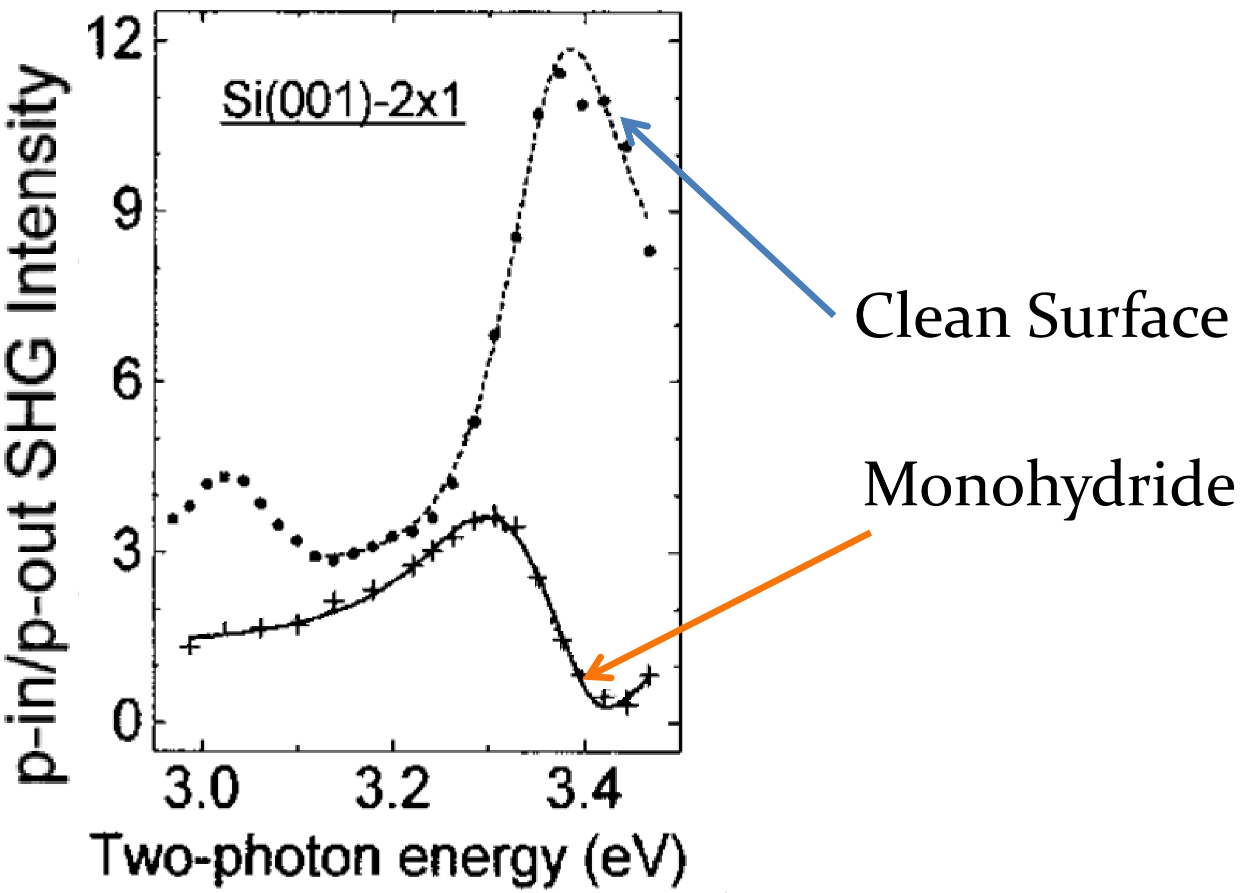
**Independence of the two surfaces**




**Calculation of the second order response from only one surface**



# Some results for Si(001)2x1




Adapted from
J. I. Dadap, *et al.*, Phys. Rev. B 56, 13367 (1997)

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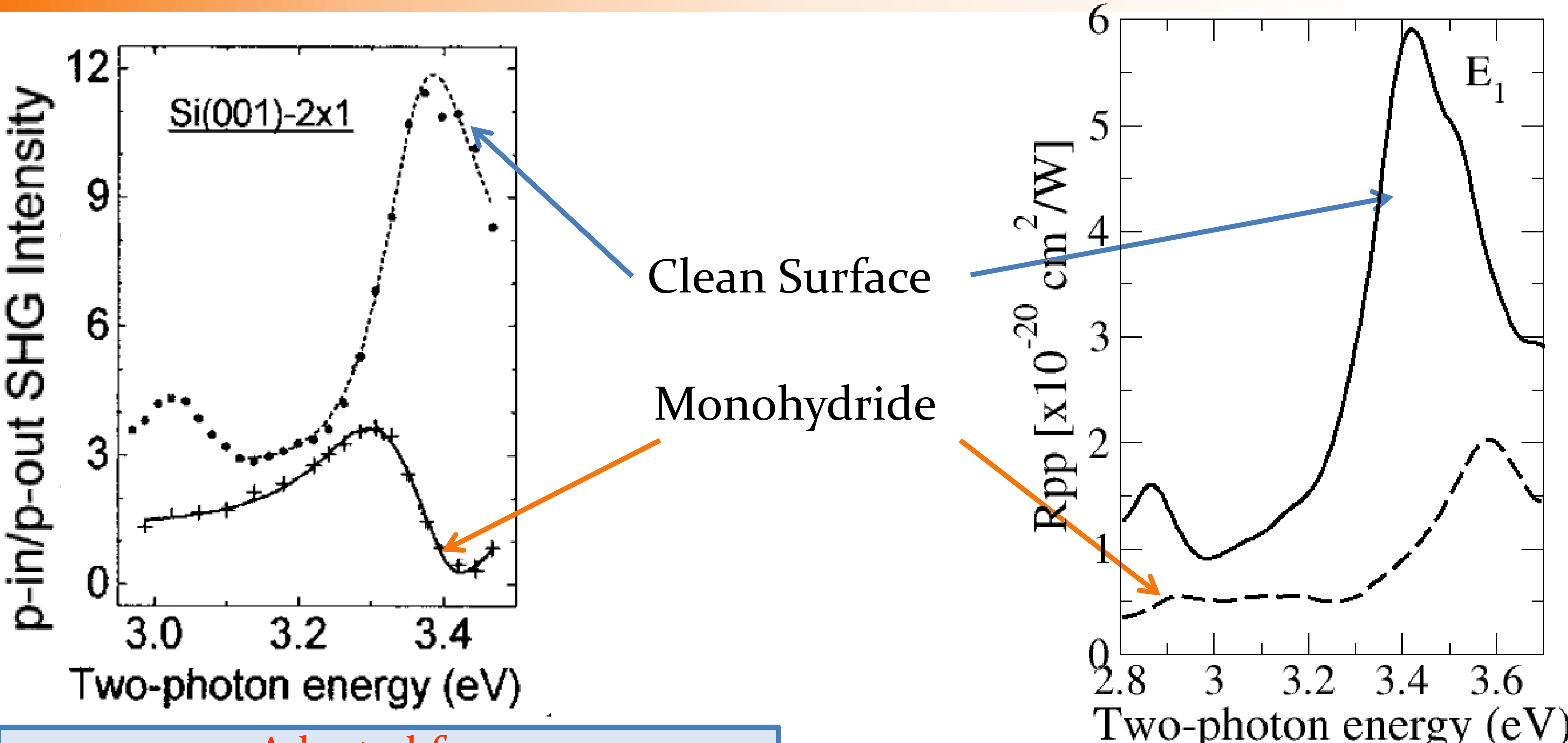


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*ab initio* calculations
40 Si atoms – 256 k-points

# Conclusion

## Conclusion

We have presented a scheme for extracting the response from one surface in a super-cell approach

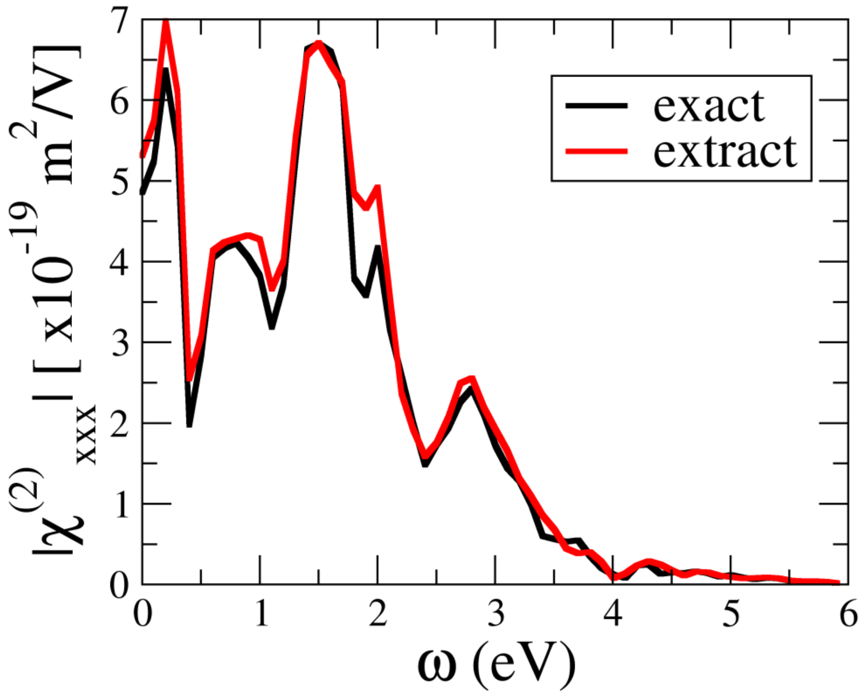
## Perspective

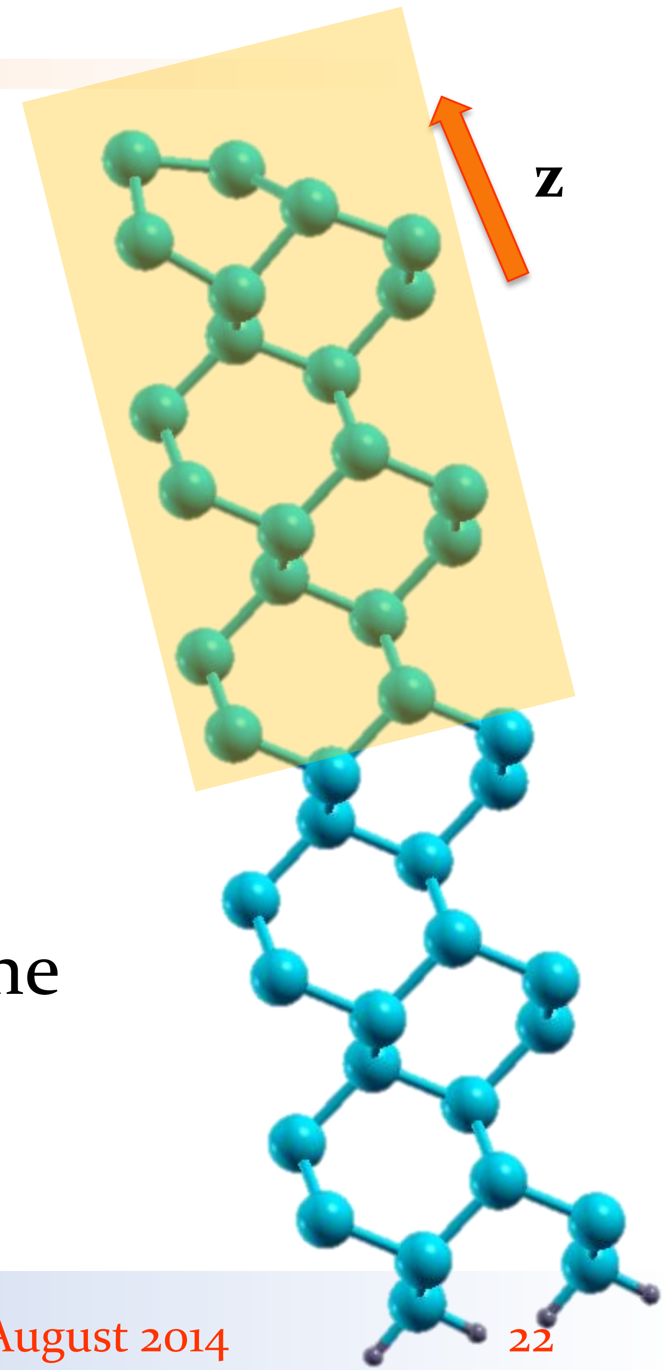
Beyond the Independent Particle Approximation

- Local-field effects
- Many body effects

# Thank you for your attention

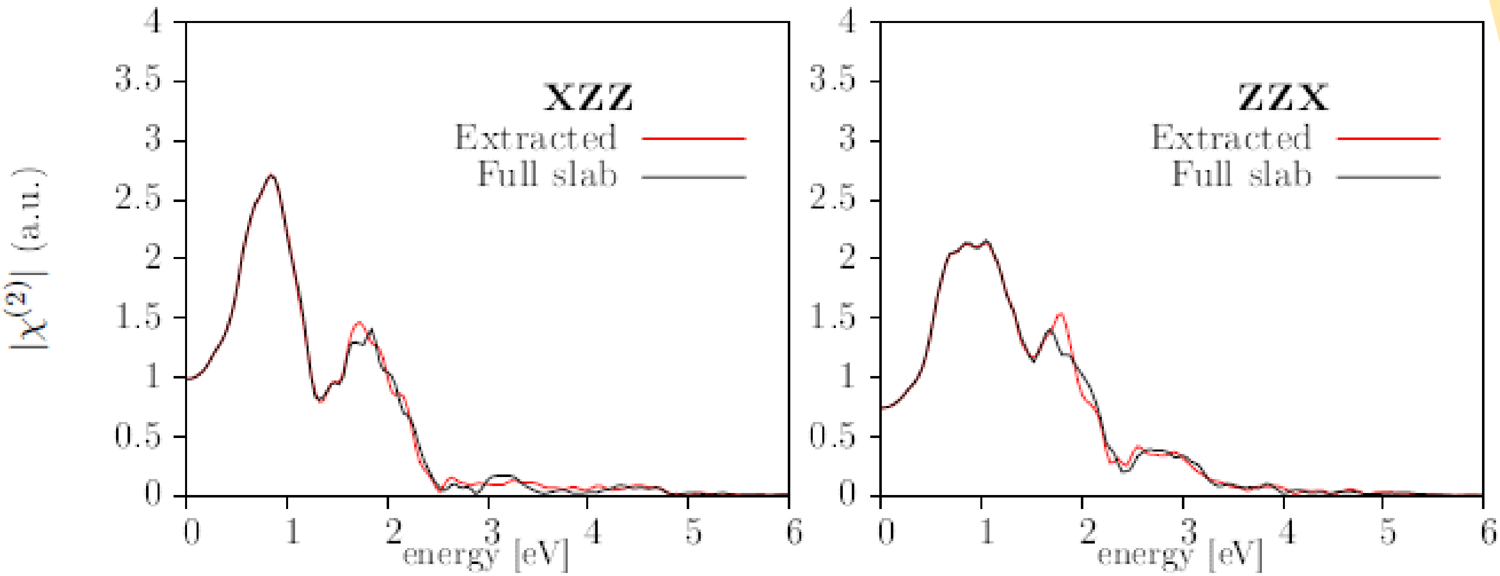
# Validation of the approach

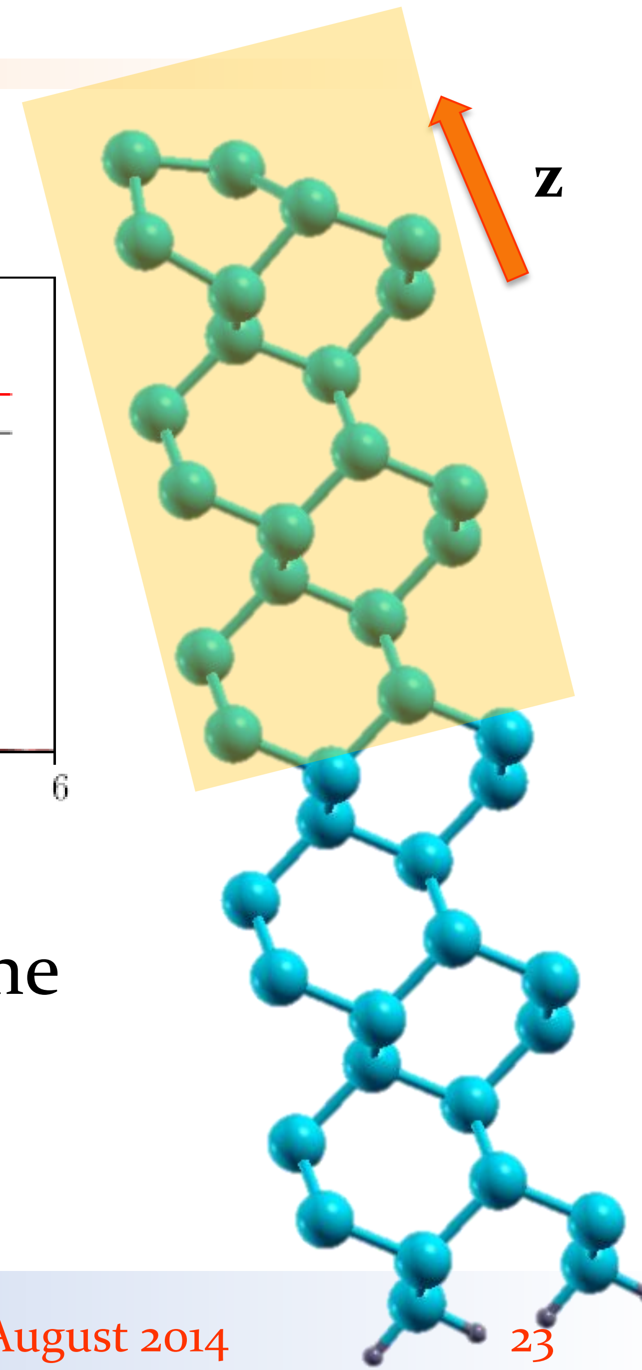



Comparison with exact results for some specific components of the tensor

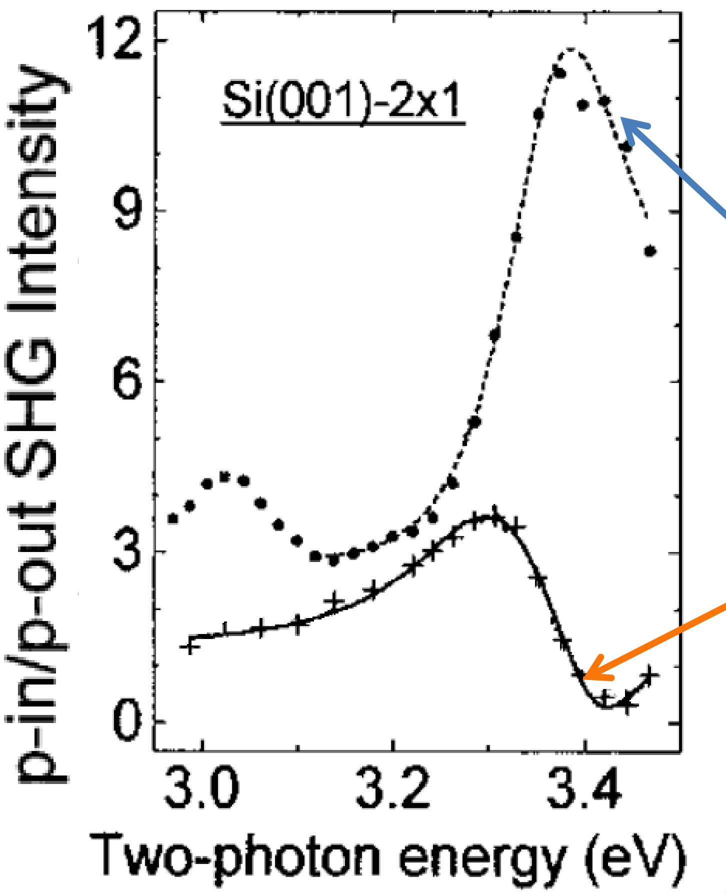
# Validation of the approach



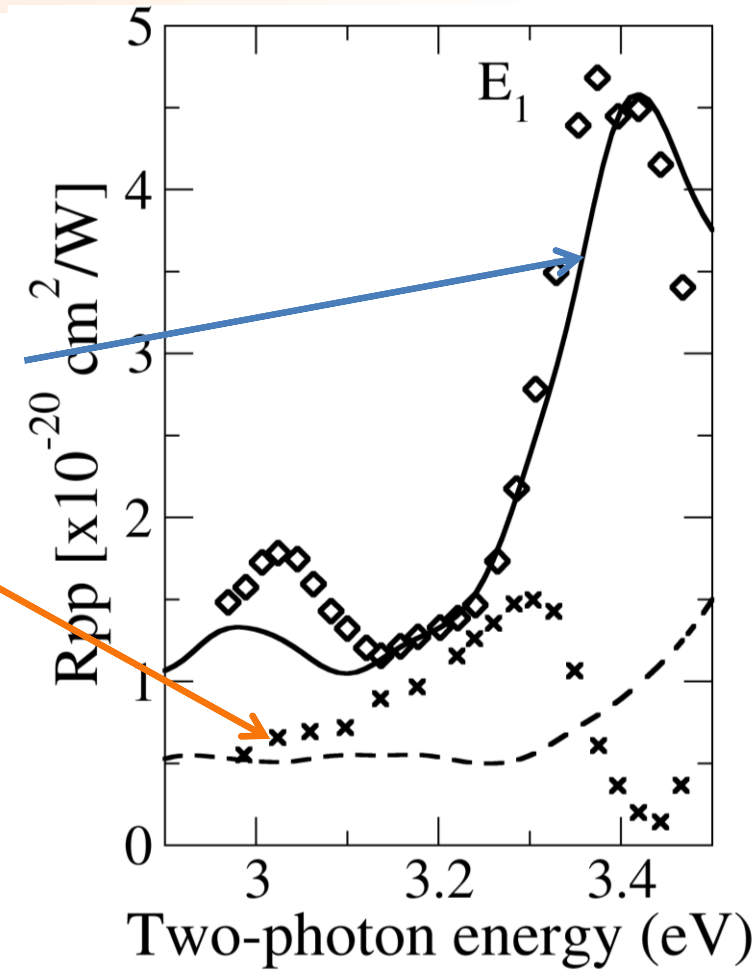

Comparison with exact results for some specific components of the tensor

# Some results for Si(001)2x1




Clean Surface

Monohydride

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