# *Ab initio* local field effects for surface second-harmonic generation

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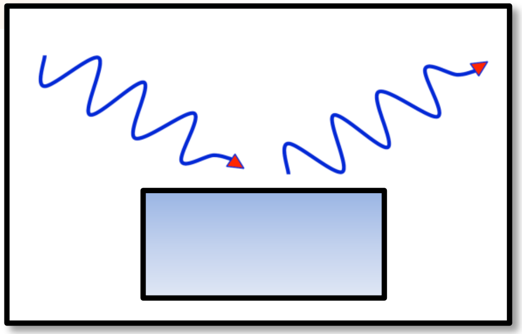
# Response to a perturbation

Perturbation → Response

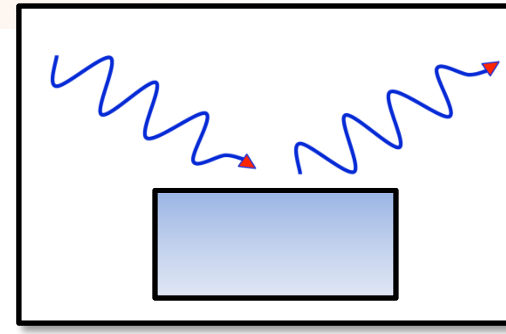
Electric field → Polarisation



Linear Response | Nonlinear Response

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

# Response to a perturbation



Perturbation → Response

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

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

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

- Absorption
- Refraction
- Loss function

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

- Second-harmonic generation
- Pockels effect
- ...

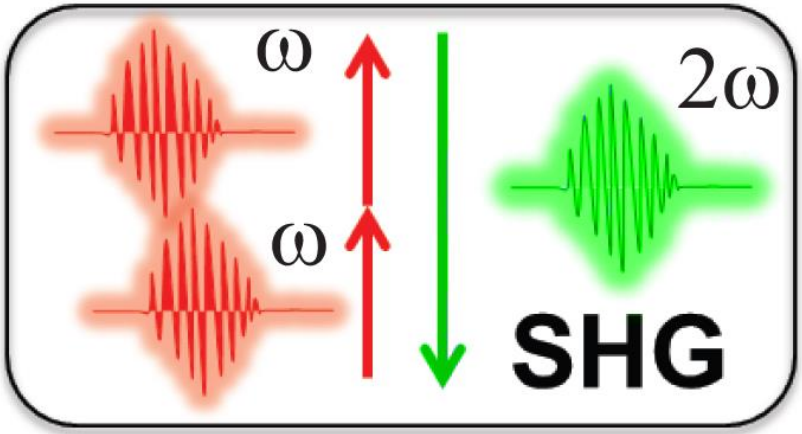
$\chi^{(3)}_{ijkl}$

- Kerr effect
- Four-wave mixing
- ...

# Second harmonic generation

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

First nonlinear term



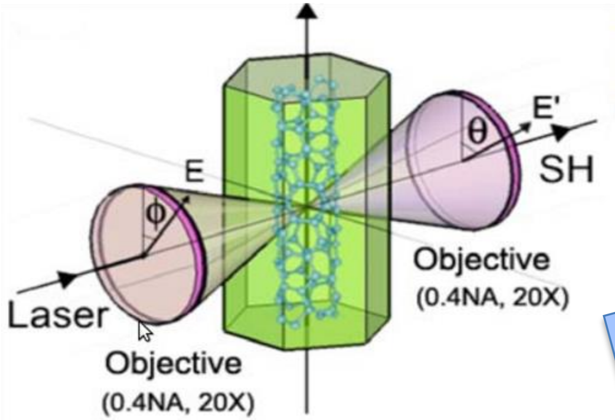

Dipole approximation

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

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

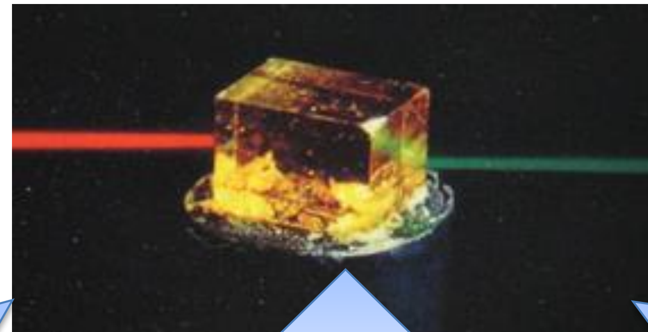
Non centrosymmetric material : $\chi^{(2)} \neq 0$

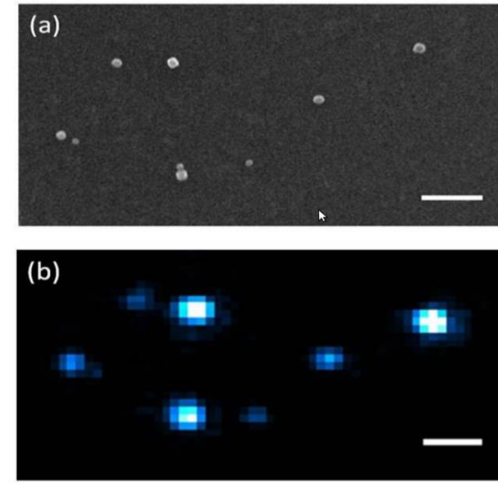
# Applications of second harmonic generation (SHG)




Nanotubes characterization

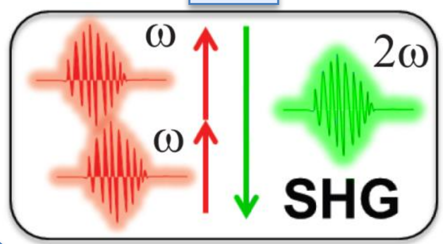
*(PRB 77 125428)*

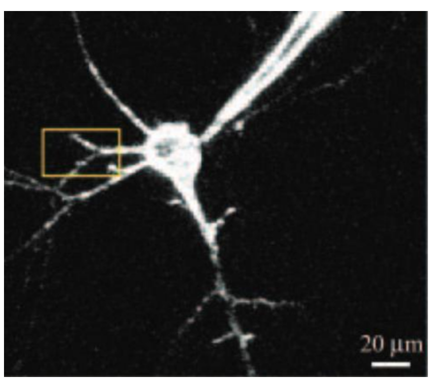


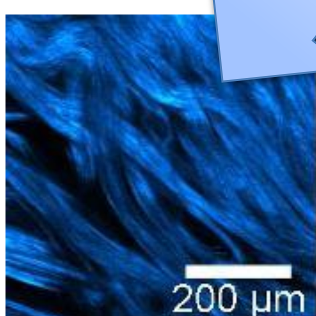



Nanoparticles imaging and microscopy

*( C-L Hsieh PhD thesis, Caltech 2011 )*

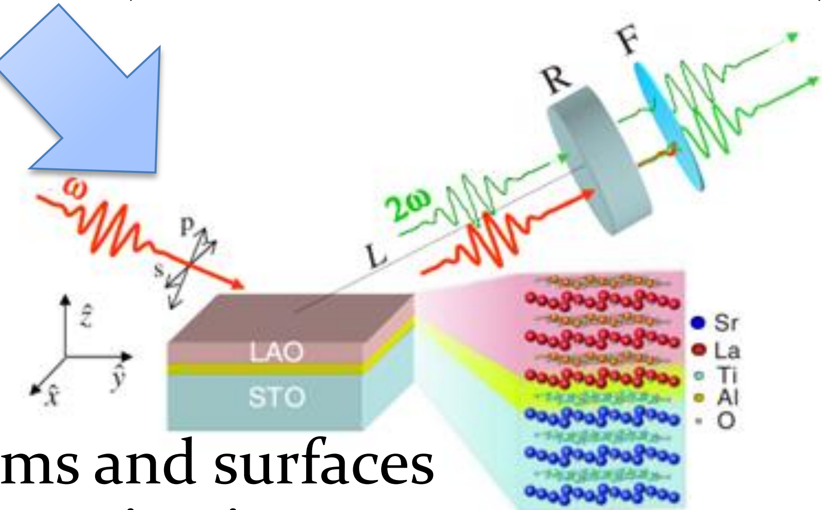



Biological tissues/neurons imaging

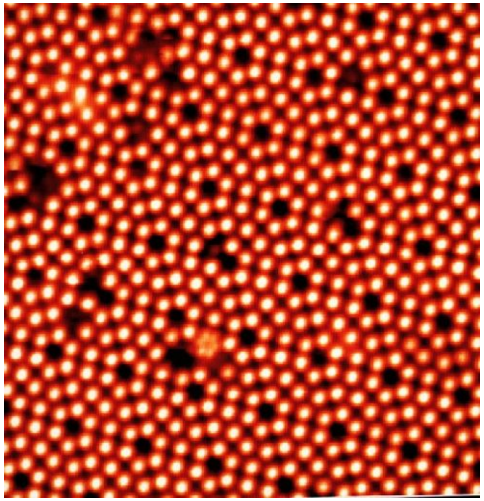
*(Biophys. J. 81 493; PNAS 103, 786)*



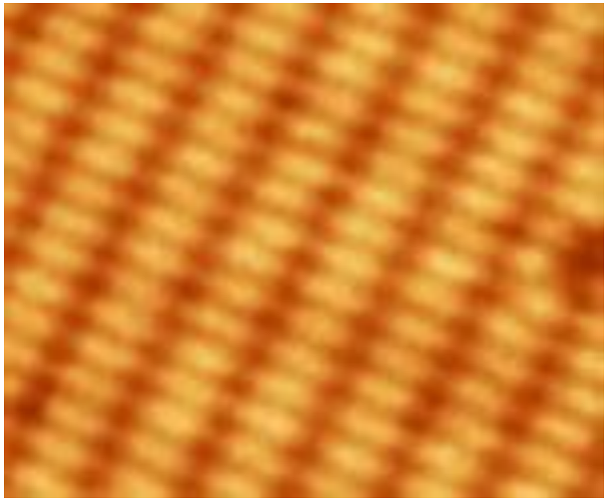

Thin films and surfaces characterization *(PRB 89 075110)*

# Surfaces

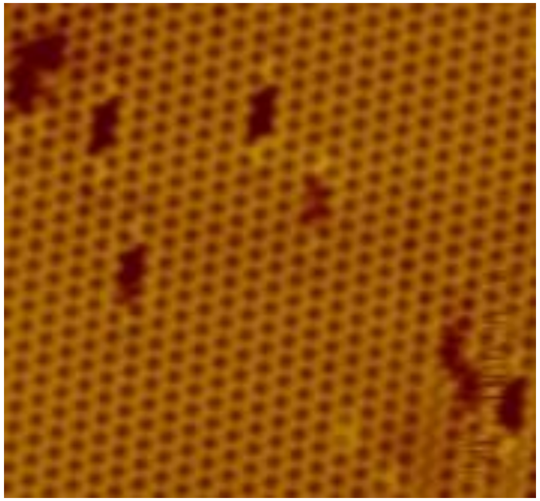
Different surfaces for the same material (e.g. Silicon)



Si(111) 7x7



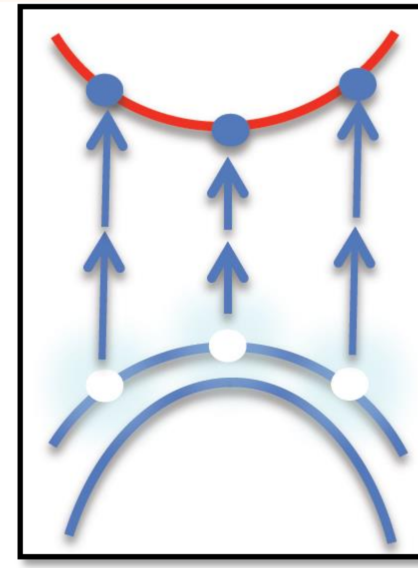
Si(001) 2x1



Si(001) 4x2

**Surface = symmetry breaking**

# How do we get the spectrum for SHG



## Second-order response

### Independent Particles Approximation

*All the electrons make independent transitions*

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

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

2light

# Local field effects

Total perturbation

=

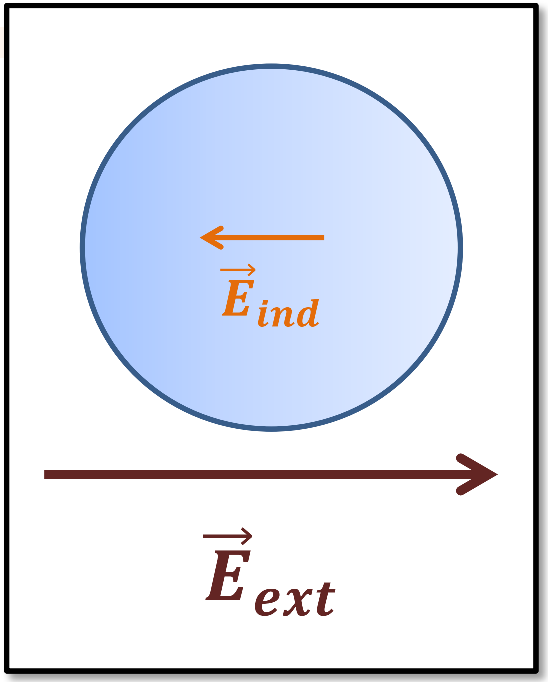
External perturbation

*Macroscopic external field*

+

Local fields

*Microscopic fluctuations of the electric field on the nanoscale*




**Local field effects:**

**Difference between the microscopic and macroscopic responses**

# Macroscopic response and local field effects in TDDFT

## Linear and Second-order Response Function in the framework of TDDFT

Time-Dependent Density Functional Theory

1st order

$$\left[1-\chi_0^{(1)}\left(v+\boxed{f_{xc}}\right)\right]\chi^{(1)}=\chi_0^{(1)}$$

$$\boxed{f_{xc}=\frac{\partial V_{xc}}{\partial\rho}}$$

Linear response

# Macroscopic response and local field effects in TDDFT

## Linear and Second-order Response Function in the framework of TDDFT

Time-Dependent Density Functional Theory

1st order

$$\left[1-\chi_0^{(1)}(v+f_{xc})\right]\chi^{(1)}=\chi_0^{(1)}$$

$$f_{xc}=\frac{\partial V_{xc}}{\partial\rho}$$

2nd order

$$[1-\chi_0^{(1)}(2\omega)f_{uxc}(2\omega)]\chi^{(2)}(2\omega,\omega)=\chi_0^{(2)}(2\omega,\omega)\left[1+f_{uxc}(\omega)\chi^{(1)(\omega)}\right]^2$$
$$+\chi_0^{(1)}(\omega)g_{xc}(\omega)\chi^{(1)}(\omega)\chi^{(1)}(\omega)$$

Linear response

$$g_{xc}=\frac{\partial^2 V_{xc}}{\partial\rho\partial\rho}$$

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Second-harmonic generation

# Second-order response
# State-of-the-art

## Bulk materials and interfaces

- Independent particles - end of 1980's
- Local field and excitonic effects - TDDFT (2010) and Bethe-Salpeter equation (2005)

## Surfaces

- Some calculations in independent particles - since 1994
- Effect of nonlocal operators ( "scissors" but wrong formula) – since 2001
- Effect of nonlocal operators ("scissors" and pseudo-potential) – [1] 2015

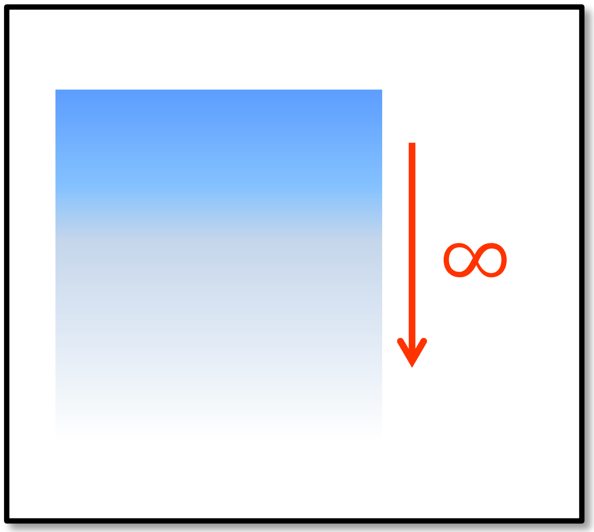
[1] S. Anderson, **N. T-D**, B. Mendoza and V. Véniard, PRB 91, 07530 (2015)

# Model of surface – Super-cells

## Surfaces

- Periodic in 2 directions
- Aperiodic in one direction

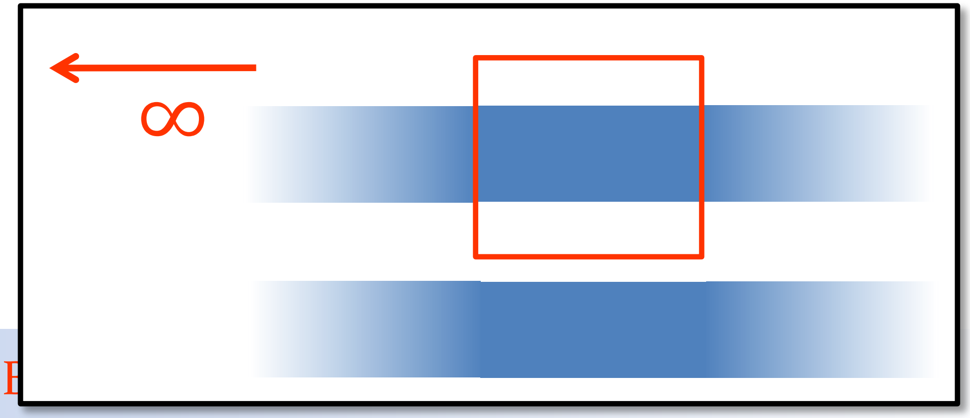
*Semi-infinite material*



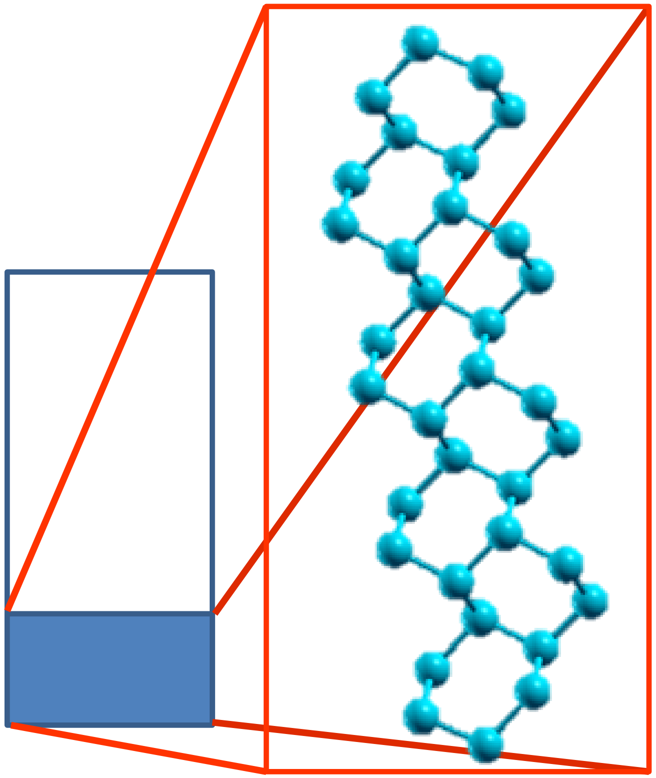

Periodic ⇨ Plane-waves

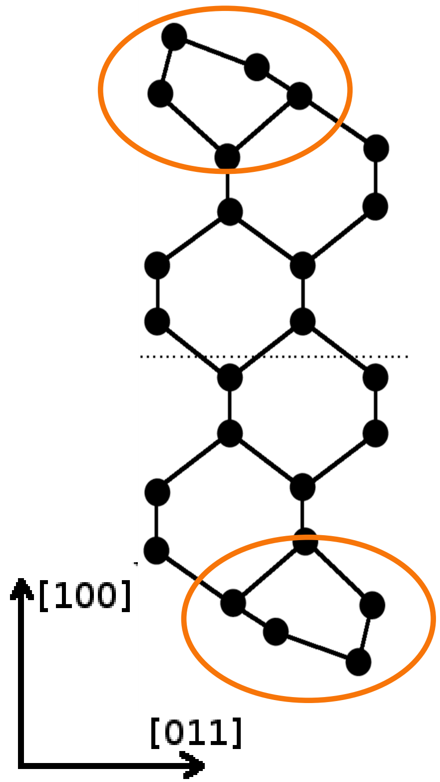
Aperiodic ⇨ Supercells (atoms + vacuum)

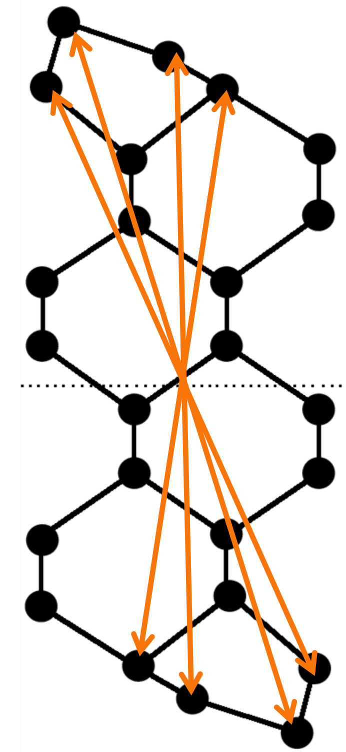
*System with 2 surfaces (slab)*



# Model of surface – Super-cell





Construction of super-cell (atoms + vacuum)

System with 2 surfaces (slab)

**inversion symmetry**

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

(artificial)

# Surface second-order response in Time-Dependent DFT

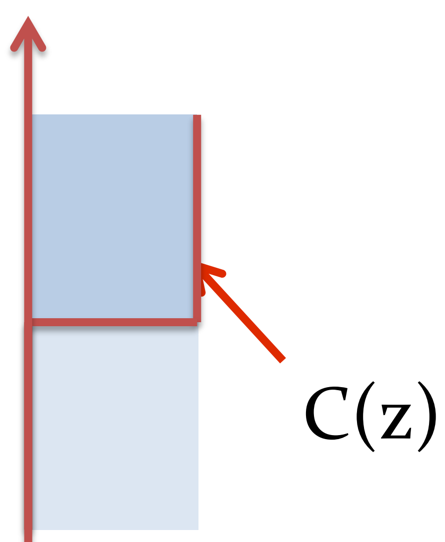
$$\chi^{(2)}_{abc}(-2\omega,\omega,\omega) = \frac{-ie^3}{\hbar^2 m^3 \omega^3 V} \sum_{nml} \int d\vec{k} \frac{1}{E_m - E_n - 2\omega - 2i\eta}$$

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

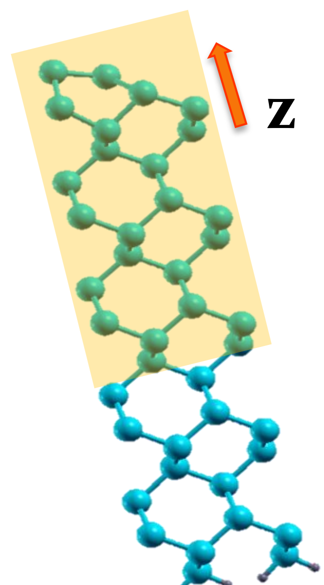
$$\tilde{p} = \frac{1}{2}(pC(z) + C(z)p)$$

$$p = i[H, r]$$

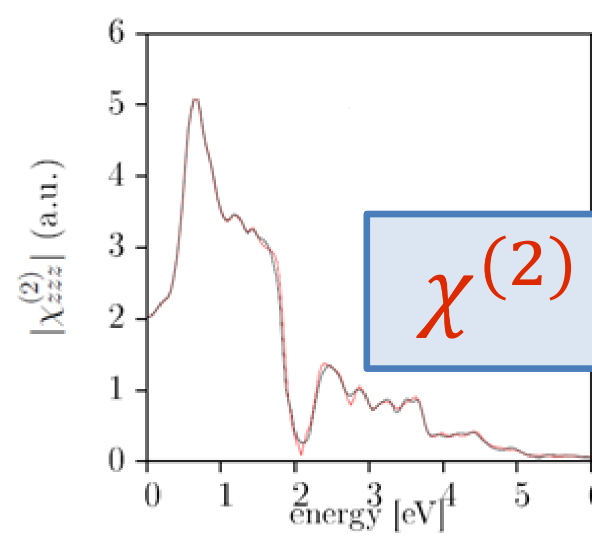
C(z) function




*ab initio* calculation




Extracted Signal




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

S. Anderson, **N. T-D**, B. Mendoza and V. Véniard, PRB 91, 07530 (2015)

# Macroscopic response and local field effects

## Macroscopic surface response

$$\chi_M^{(2)S}(\mathbf{q},\mathbf{q_1},\mathbf{q_2},\omega_1,\omega_2) = \frac{-i}{2|\mathbf{q}||\mathbf{q_1}||\mathbf{q_2}|}\chi^S_{\rho\rho\rho}(\mathbf{q},\mathbf{q_1},\mathbf{q_2},\omega_1,\omega_2)$$
$$\epsilon_M^S(\mathbf{q},\omega)\epsilon_M(\mathbf{q_1},\omega_1)\epsilon_M(\mathbf{q_2},\omega_2)$$

## 2nd order Dyson equation

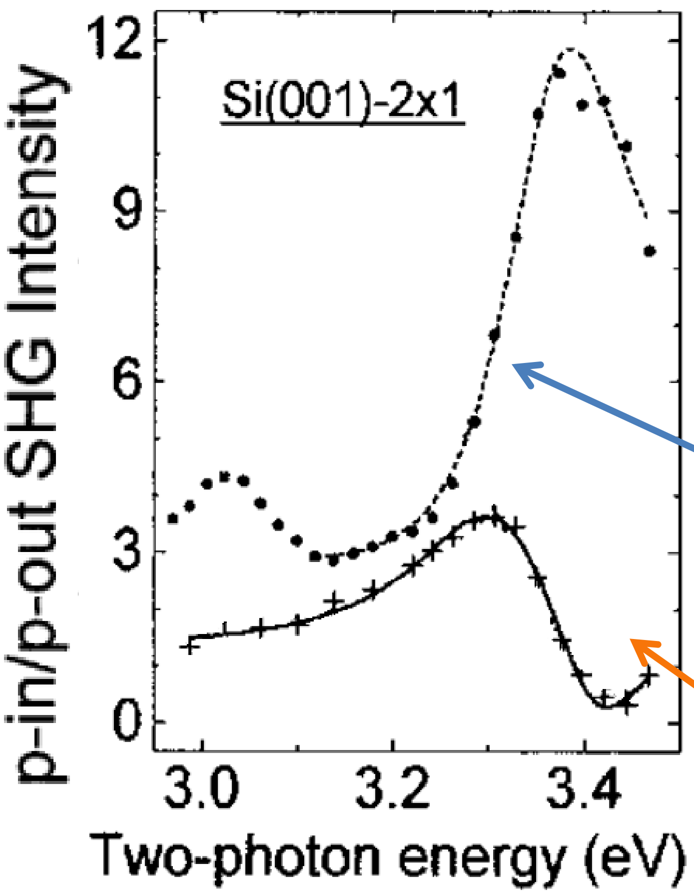
$$\left[Id - \chi_{\rho\rho}^{(0)S} v\right]\chi_{\rho\rho\rho}^{(2)S} = \chi_{\rho\rho\rho}^{(0)S}\left[Id + v\chi_{\rho\rho}^{(1)}\right]\left[Id + v\chi_{\rho\rho}^{(1)}\right]$$

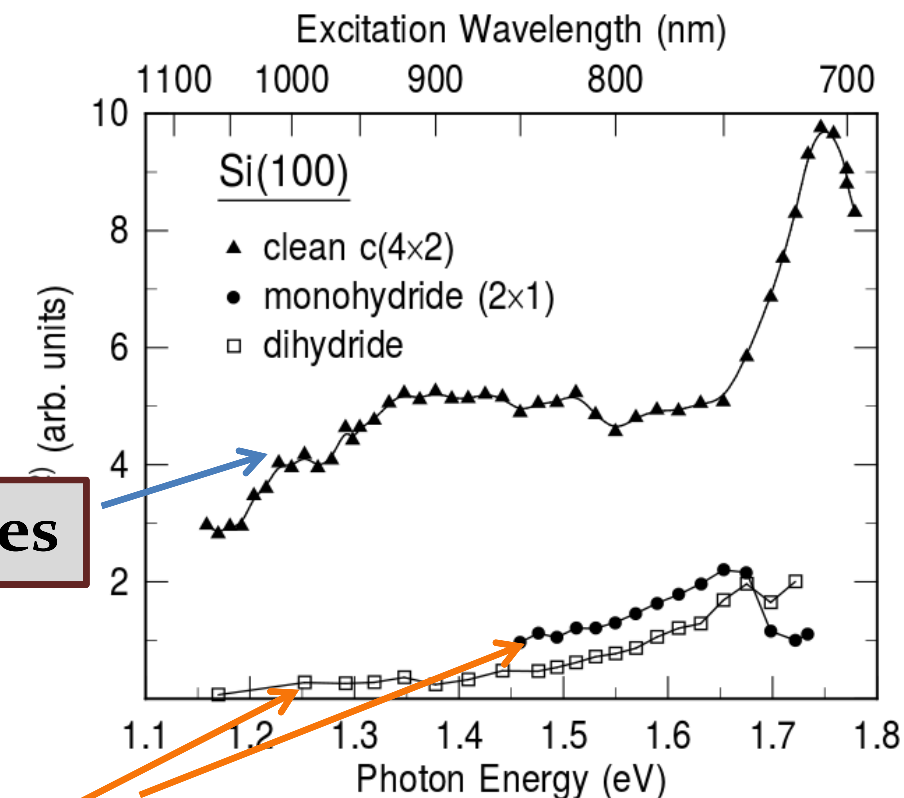
with $\left[Id - \chi_{\rho\rho}^{(0)} v\right]\chi_{\rho\rho}^{(1)} = \chi_{\rho\rho}^{(0)}$

Including local field effects (LFE)

[1] **N. T-D** and V. Véniard, *in preparation*

# Some experimental results for Si(001)



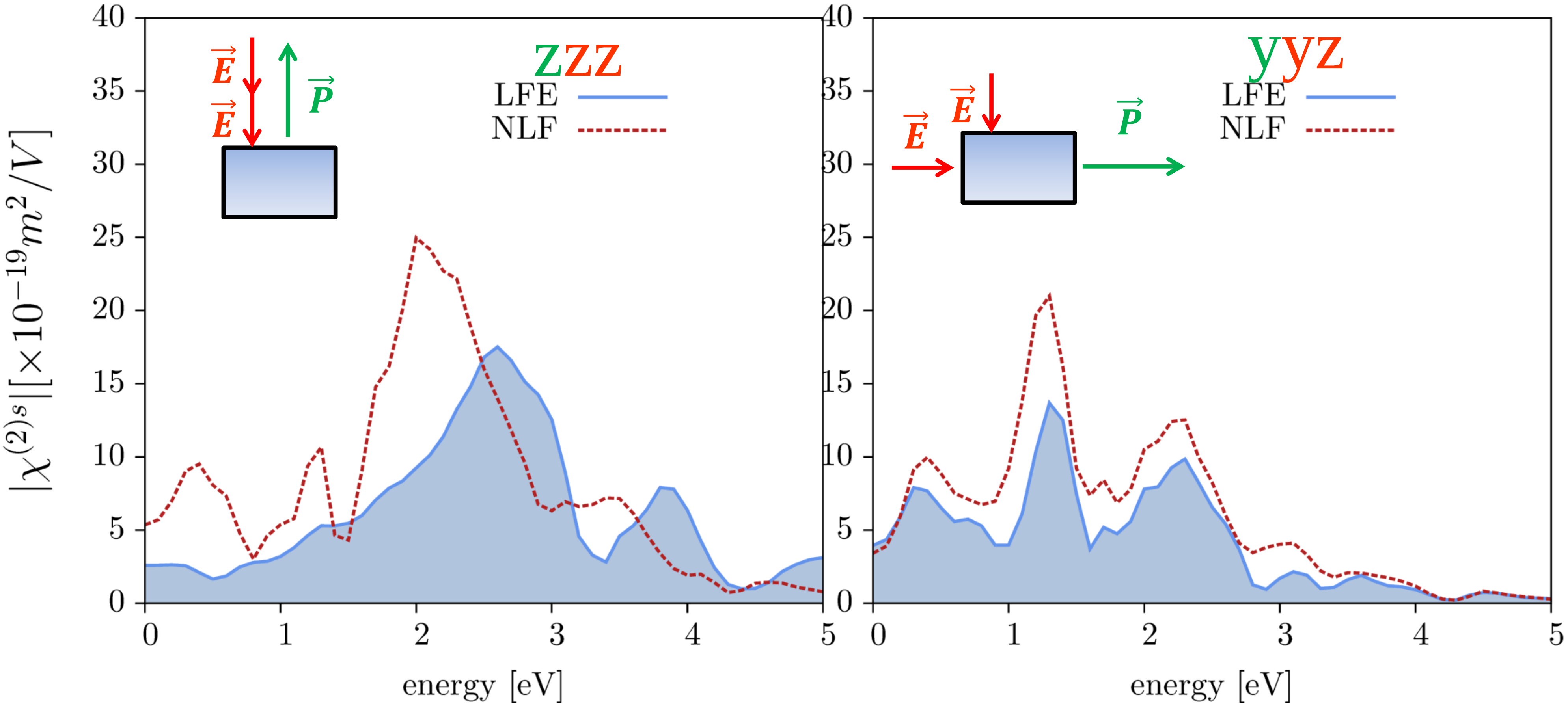

**Clean surfaces**

**Hydrogenated surfaces**

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

Taken from
U. Höfer, Appl. Phys. A 63, 533 (1996)

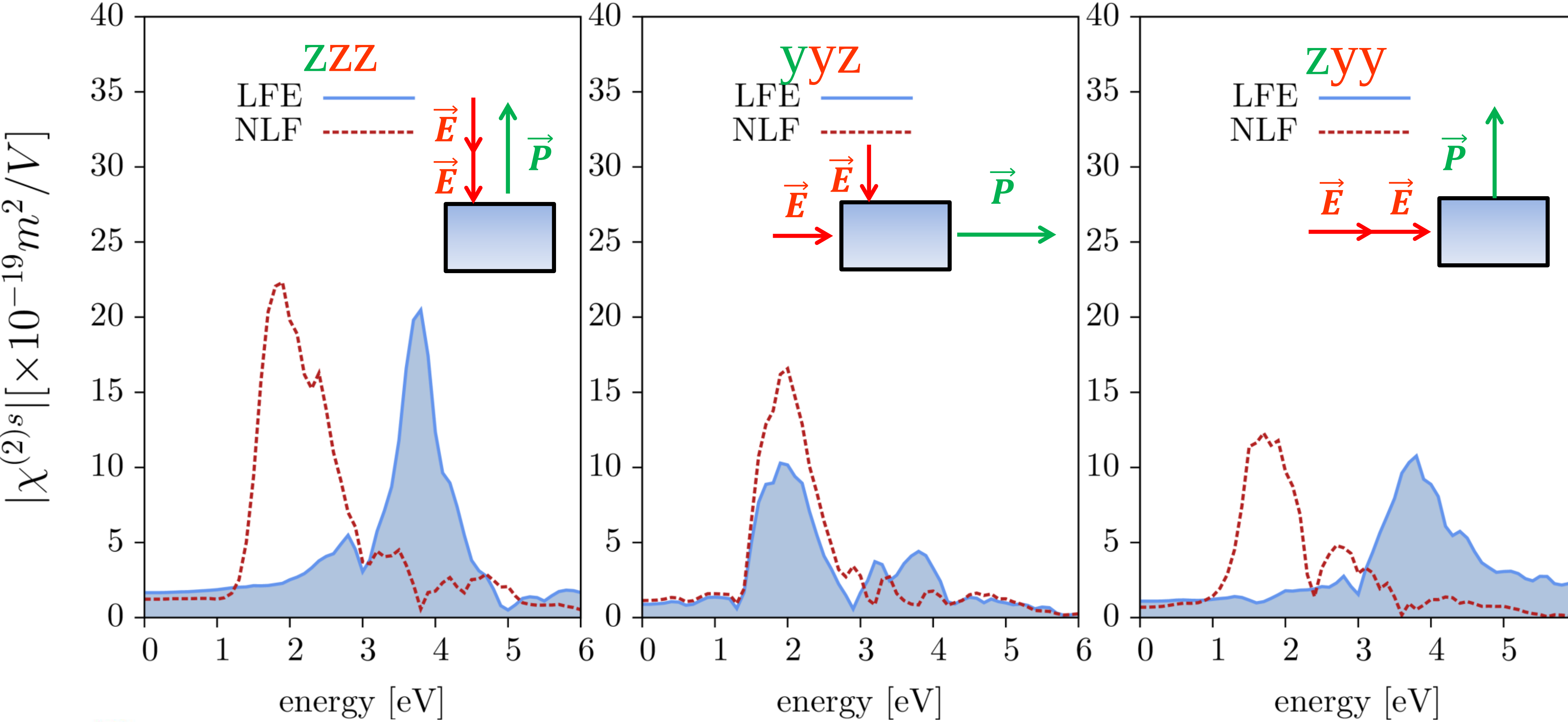
# Local field effects (LFE) on $\chi^{(2)s}$ Clean Surface




**Si(001)2x1**

24 Si layers – 256 k-points

# Local field effects (LFE) on $\chi^{(2)s}$ Hydrogenated surface

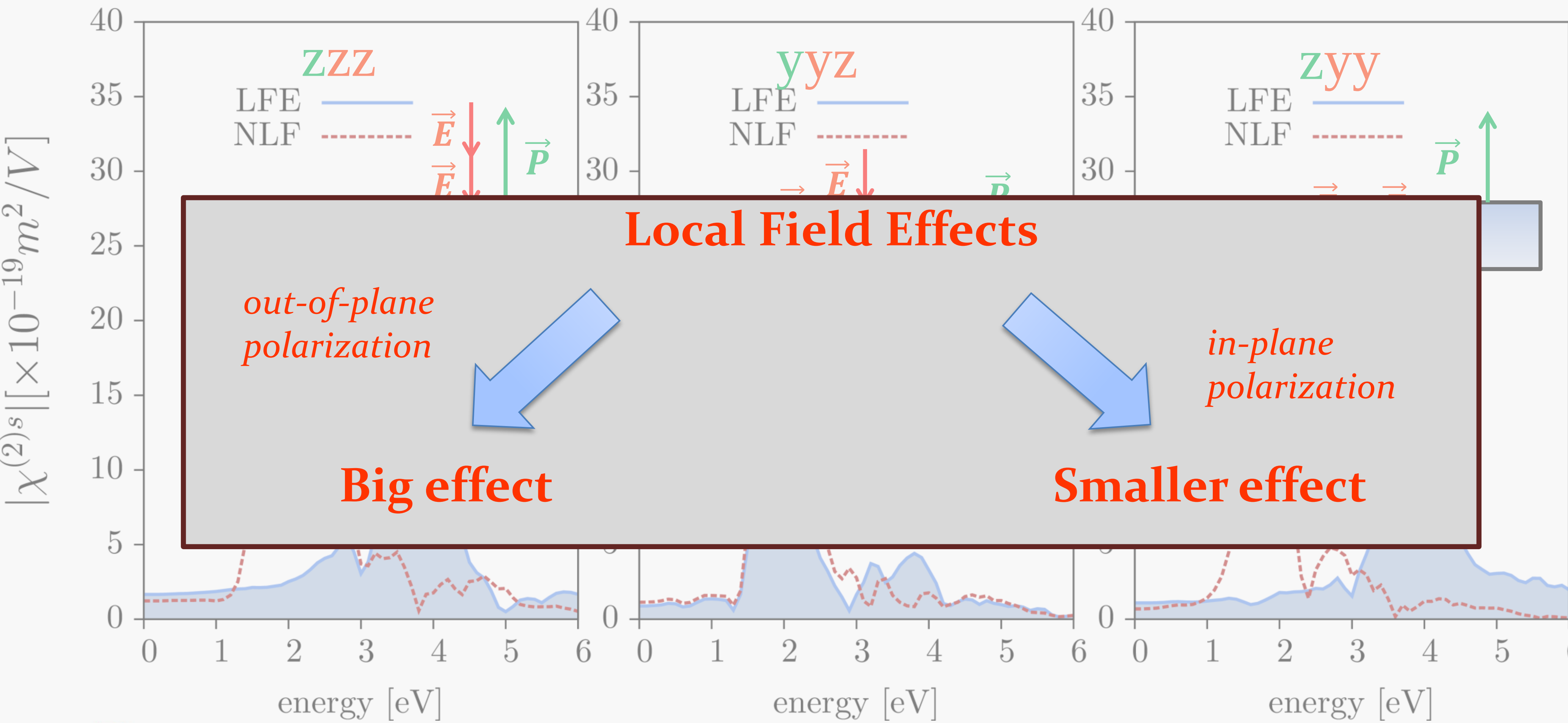



2light

**Si(001)1x1:2H**

24 Si layers – 288 k-points

# Local field effects (LFE) on $\chi^{(2)s}$ Hydrogenated surface




**Local Field Effects**

*out-of-plane polarization* → **Big effect**

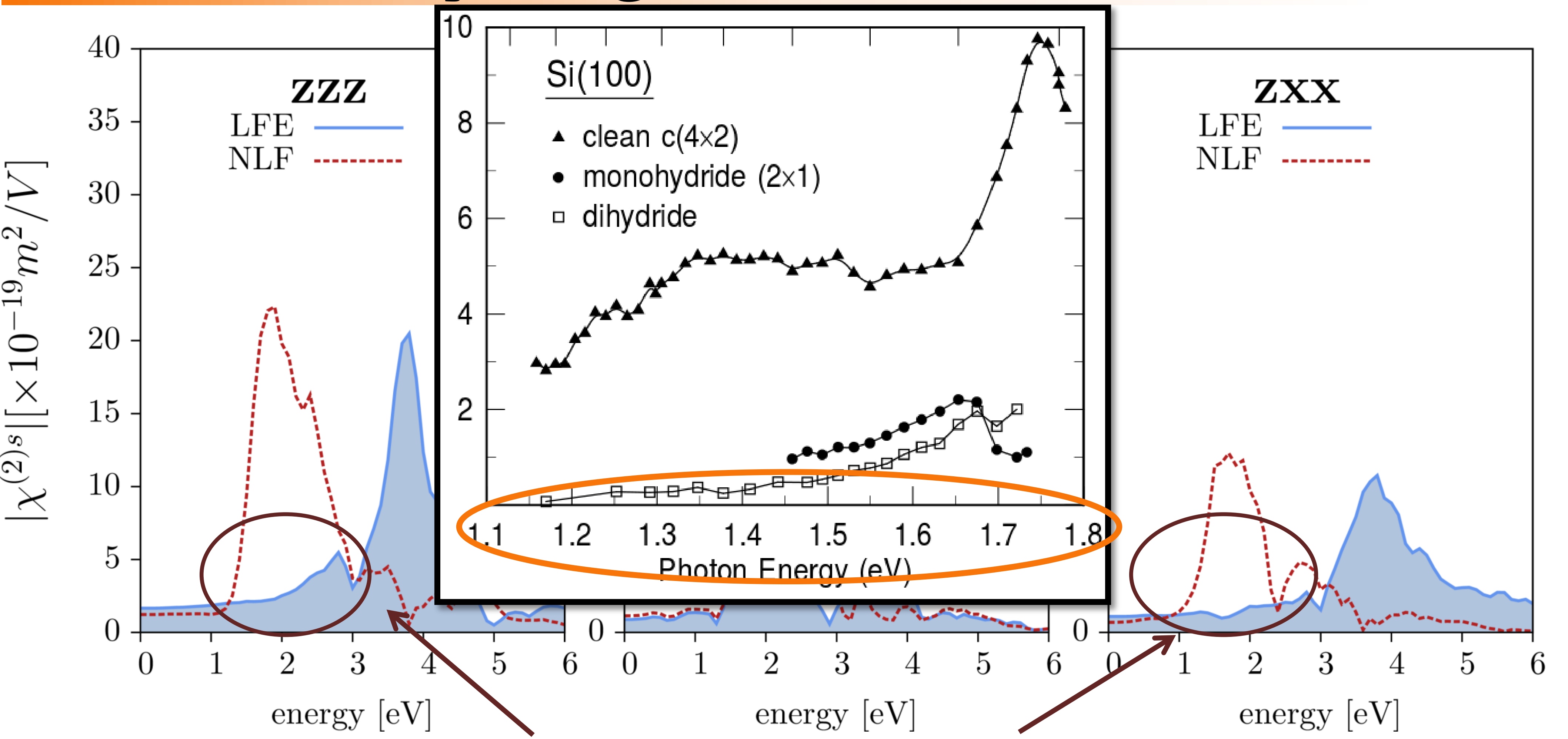
*in-plane polarization* → **Smaller effect**

2light

**Si(001)1x1:2H**

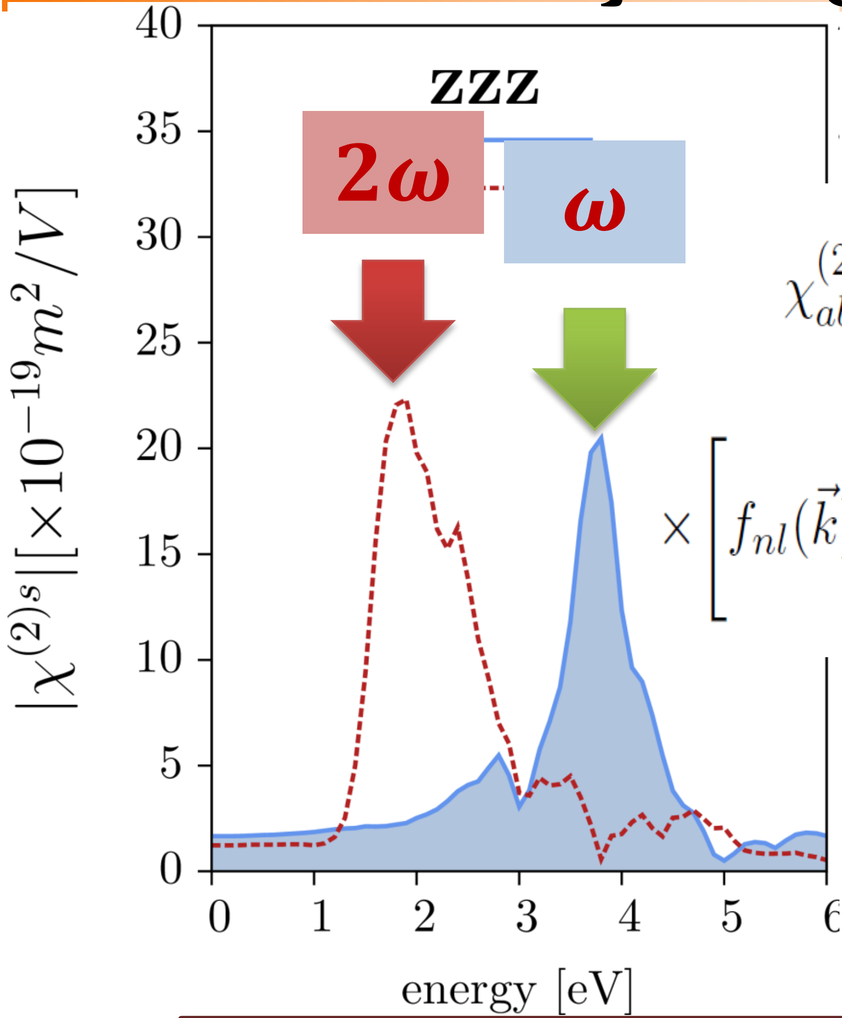
24 Si layers – 288 k-points

# Local field effects (LFE) on $\chi^{(2)s}$ Hydrogenated surface




**Strong quenching in region probed experimentally**

# Local field effects (LFE) on $\chi^{(2)s}$ Hydrogenated surface




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

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

**Redistribution of spectral weight between *ω* and 2*ω* transitions**

# Conclusion

## Conclusion

- Formalism for including the local field effects on surface second harmonic generation (SSHG)
- Local field effects are important for describing SSHG
- Possible explanation of the difference between the clean and the hydrogenated surface signal

## Perspective

- Further analysis of hydrogen and ad-atom effects
- Inclusion of other many-body effects

# Thank you for your attention

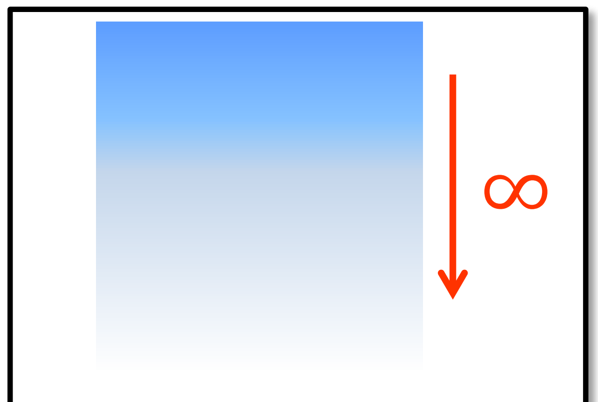
# Model of surface – Super-cells

What we want

**Surface**

Real Space

Loosing in-plane periodicity




Plane-waves
Super-cell
(atoms + vacuum)

System with 2 surfaces (slab)

Best representation of a surface