

Theoretical Optical Second-Harmonic Calculations for Surfaces

Sean M. Anderson

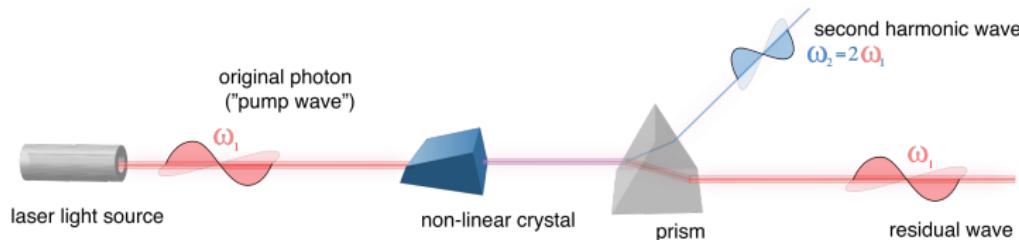
Centro de Investigaciones en Óptica, A.C

July 14, 2016

Second Harmonic Generation (SHG)

Characteristics¹

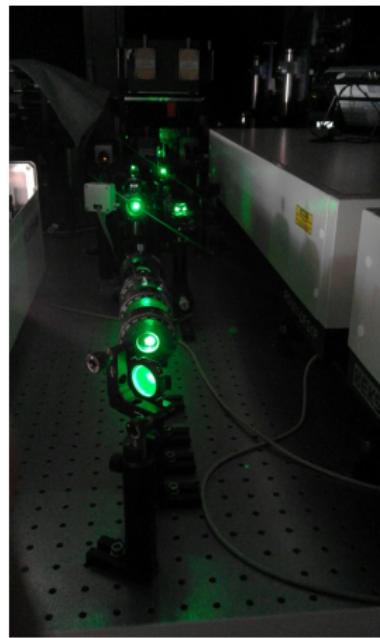
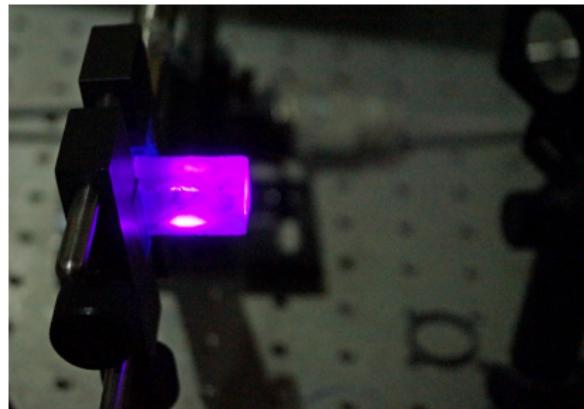
- Two photons of the same frequency combine
- Create one photon of double the frequency



¹Image: Jon Chui

- └ Introduction
- └ Applications

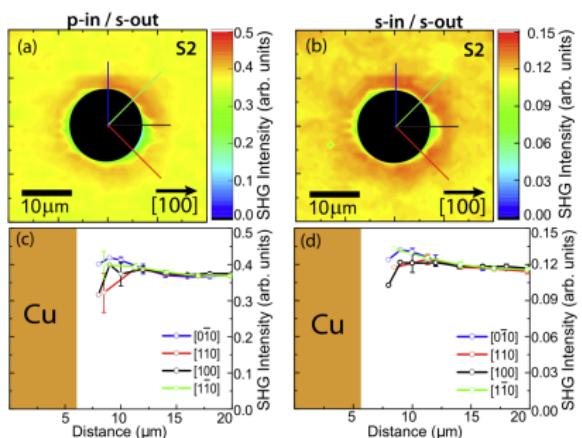
Frequency Conversion²



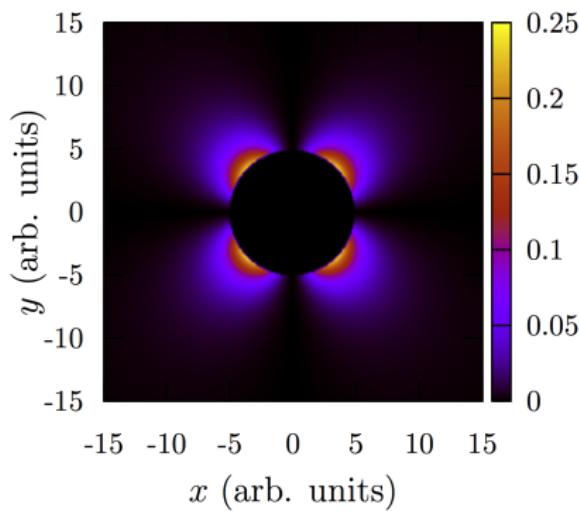
²Images: Dr. Ramón Carriles Jaimes, Cornelia Reitböck

- └ Introduction
- └ Applications

Strain in TSVs^{3 4}



Experiment



Theory

³ Cho et al., Appl. Phys. Lett. 108, 151602 (2016)

⁴ Mendoza et al., Phys. Status Solidi B 253, 2 (2016)

Second-order Nonlinear Effects

Second-order nonlinear processes^{5 6}

- Are dipole forbidden in the bulk of centrosymmetric materials
- Are related to $\chi^{(2)}$, the nonlinear susceptibility
- Have bigger dipolar (surface) than quadrupolar contributions

Summary

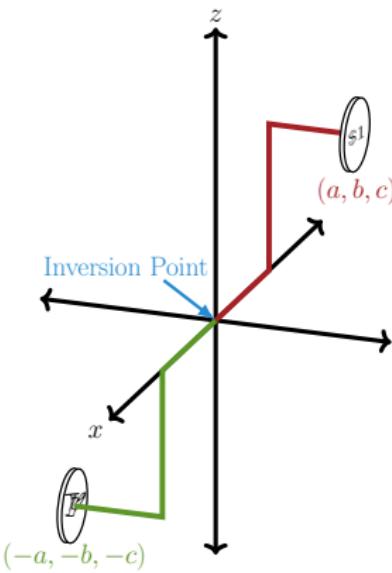
SHG is well suited for studying surfaces and interfaces!

⁵ Armstrong et al., Phys. Rev. 127, 1918 (1962)

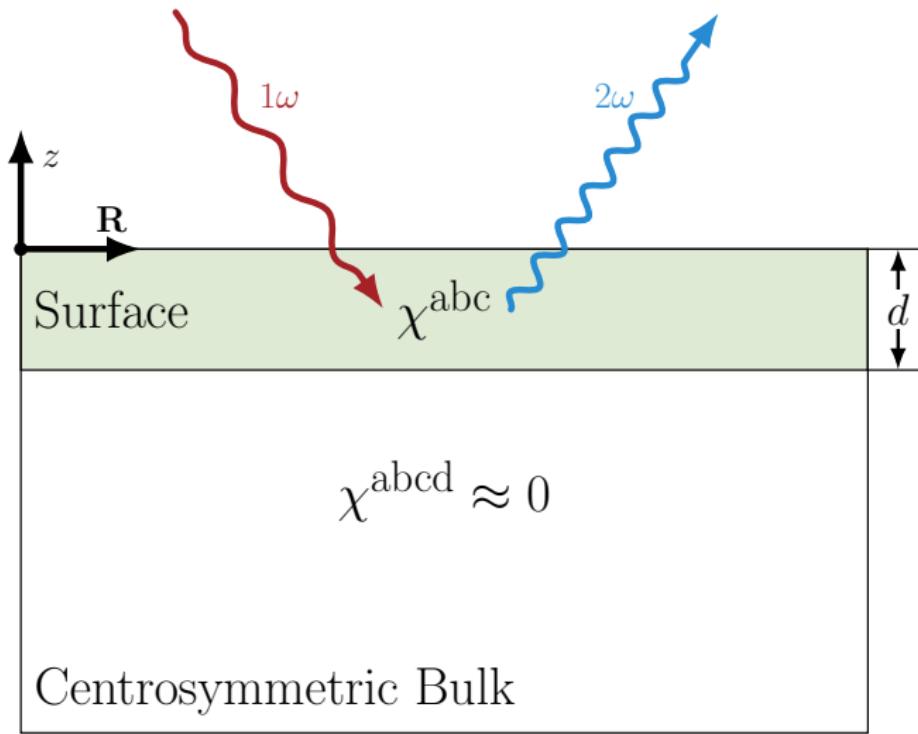
⁶ Bloembergen et al., Phys. Rev. 128, 606 (1962)

Centrosymmetric Materials

A centrosymmetric material is a material that displays inversion symmetry, such that $p(a, b, c) \rightarrow p(-a, -b, -c)$.



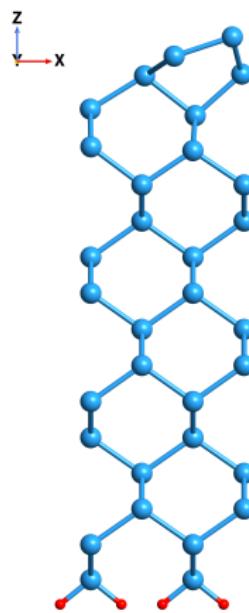
└ Introduction



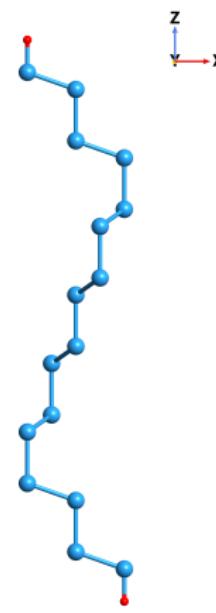
Semi-infinite system with a centrosymmetric bulk and a surface region is of thickness $\sim d$. Dipolar SHG is produced in reflection from the surface.

└ Introduction

Two Si Test Cases



Si(001)(2×1)



Si(111)(1×1):H

└ The Nonlinear Surface Susceptibility

 └ Nonlocal Operators

New Contributions to the Theory

Our new formulation adds three contributions (within the IPA):⁷

- 1 The scissors correction
- 2 The contribution from the nonlocal part of the pseudopotential
- 3 The layered cut function

⁷Anderson et al., Phys. Rev. B. 91, 075302 (2015)

- └ The Nonlinear Surface Susceptibility

- └ Nonlocal Operators

Electron Position Operator

We have the electron position operator as

$$\mathbf{r} = \mathbf{r}_i + \mathbf{r}_e,$$

for interband (e) and intraband (i) transitions. The matrix elements of \mathbf{r}_i and \mathbf{r}_e are given by

$$\langle n\mathbf{k}|\mathbf{r}_i|m\mathbf{k}'\rangle = \delta_{nm} [\delta(\mathbf{k} - \mathbf{k}')\xi_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k} - \mathbf{k}')],$$

$$\langle n\mathbf{k}|\mathbf{r}_e|m\mathbf{k}'\rangle = (1 - \delta_{nm})\delta(\mathbf{k} - \mathbf{k}')\xi_{nm}(\mathbf{k}).$$

└ The Nonlinear Surface Susceptibility

 └ Nonlocal Operators

Scissors Operator and \mathbf{v}^{nl} (1 & 2)

We express the electron velocity operator as

$$\mathbf{v}^{\Sigma} = \mathbf{v} + \mathbf{v}^{\text{nl}} + \mathbf{v}^{\mathcal{S}} = \mathbf{v}^{\text{LDA}} + \mathbf{v}^{\mathcal{S}},$$

where

$$\mathbf{v} = \frac{\mathbf{p}}{m_e},$$

$$\mathbf{v}^{\text{nl}} = \frac{1}{i\hbar} [\mathbf{r}, V^{\text{nl}}],$$

$$\mathbf{v}^{\mathcal{S}} = \frac{1}{i\hbar} [\mathbf{r}, S(\mathbf{r}, \mathbf{p})],$$

$$\mathbf{v}^{\text{LDA}} = \mathbf{v} + \mathbf{v}^{\text{nl}}.$$

We also have that

$$\mathbf{r}_{nm}(\mathbf{k}) = \frac{\mathbf{v}_{nm}^{\Sigma}(\mathbf{k})}{i\omega_{nm}^{\Sigma}(\mathbf{k})} = \frac{\mathbf{v}_{nm}^{\text{LDA}}(\mathbf{k})}{i\omega_{nm}^{\text{LDA}}(\mathbf{k})}.$$

└ The Nonlinear Surface Susceptibility

└ Layered Cut Function

Layered Cut Function (3)

We introduce the cut function

$$\mathcal{C}(z) = \Theta(z - z_\ell + \Delta_\ell^b) \Theta(z_\ell - z + \Delta_\ell^f),$$

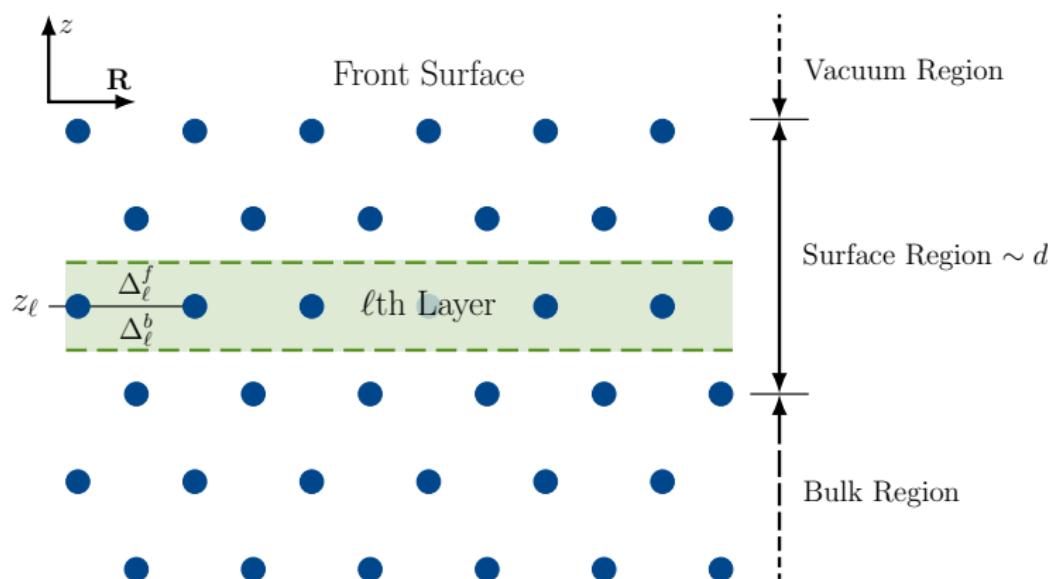
that transforms any operator into its calligraphic counterpart as

$$\mathbf{V} \rightarrow \mathcal{V} = \frac{\mathcal{C}(z)\mathbf{V} + \mathbf{V}\mathcal{C}(z)}{2},$$

└ The Nonlinear Surface Susceptibility

└ Layered Cut Function

Layered Cut Function (3)



Sketch of the super-cell. The atomic slab corresponds to the circles representing the atoms of the system.

└ The Nonlinear Surface Susceptibility

└ Summary

Final Expressions

Interband Contribution $\langle n\mathbf{k}|\mathbf{r}_e|m\mathbf{k}'\rangle = (1 - \delta_{nm})\delta(\mathbf{k} - \mathbf{k}')\xi_{nm}(\mathbf{k})$

$$\text{Im}[\chi_{e,\omega}^{\text{abc}}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} \sum_{q \neq (v,c)} \frac{1}{\omega_{cv}^\Sigma} \left[\frac{\text{Im}[\mathcal{V}_{qc}^{\Sigma,a}\{r_{cv}^b r_{vq}^c\}]}{(2\omega_{cv}^\Sigma - \omega_{cq}^\Sigma)} - \frac{\text{Im}[\mathcal{V}_{qv}^{\Sigma,a}\{r_{qc}^c r_{cv}^b\}]}{(2\omega_{cv}^\Sigma - \omega_{qv}^\Sigma)} \right] \delta(\omega_{cv}^\Sigma - \omega)$$

$$\text{Im}[\chi_{e,2\omega}^{\text{abc}}] = -\frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} \frac{4}{\omega_{cv}^\Sigma} \left[\sum_{v' \neq v} \frac{\text{Im}[\mathcal{V}_{vc}^{\Sigma,a}\{r_{cv}^b r_{v'v}^c\}]}{2\omega_{cv'}^\Sigma - \omega_{cv}^\Sigma} - \sum_{c' \neq c} \frac{\text{Im}[\mathcal{V}_{vc}^{\Sigma,a}\{r_{cc'}^c r_{c'v}^b\}]}{2\omega_{c'v}^\Sigma - \omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - 2\omega)$$

Intraband Contribution $\langle n\mathbf{k}|\mathbf{r}_i|m\mathbf{k}'\rangle = \delta_{nm} \left[\delta(\mathbf{k} - \mathbf{k}')\xi_{nn}(\mathbf{k}) + i\nabla_{\mathbf{k}}\delta(\mathbf{k} - \mathbf{k}') \right]$

$$\text{Im}[\chi_{i,\omega}^{\text{abc}}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{cv} \frac{1}{(\omega_{cv}^\Sigma)^2} \left[\text{Re} \left[\left\{ r_{cv}^b (\mathcal{V}_{vc}^{\Sigma,a})_{;k^c} \right\} \right] + \frac{\text{Re} [\mathcal{V}_{vc}^{\Sigma,a}\{r_{cv}^b \Delta_{cv}^c\}]}{\omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - \omega)$$

$$\text{Im}[\chi_{i,2\omega}^{\text{abc}}] = \frac{\pi|e|^3}{2\hbar^2} \int \frac{d^3k}{8\pi^3} \sum_{vc} \frac{4}{(\omega_{cv}^\Sigma)^2} \left[\text{Re} \left[\mathcal{V}_{vc}^{\Sigma,a} \left\{ (\mathbf{r}_{cv}^b)_{;k^c} \right\} \right] - \frac{2\text{Re} [\mathcal{V}_{vc}^{\Sigma,a}\{r_{cv}^b \Delta_{cv}^c\}]}{\omega_{cv}^\Sigma} \right] \delta(\omega_{cv}^\Sigma - 2\omega)$$

└ The Nonlinear Surface Susceptibility

└ Software

Medusa runs on free and open source software:

- CentOS 6.7 GNU/Linux
- Intel MPI & OpenMP
- Intel MKL
- Intel FORTRAN & C
- Bash, Perl, Python

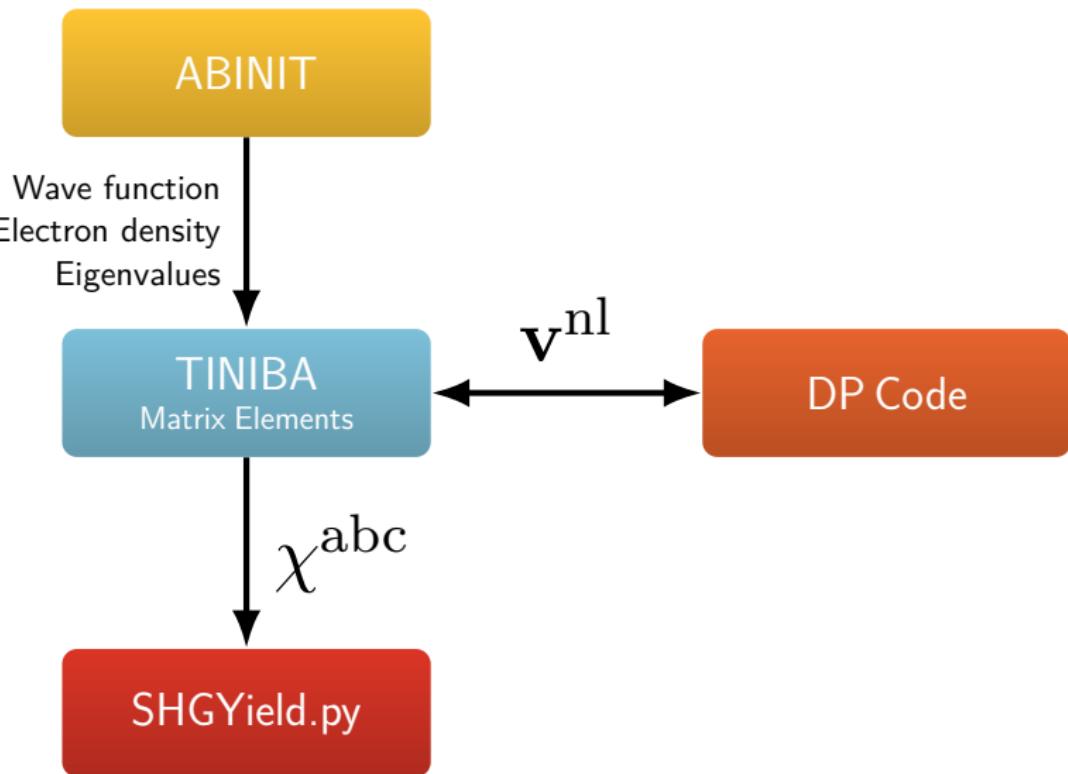
TINIBA

Combines Bash, Perl, Fortran, and ABINIT for calculating:

- Optical response of semiconductors
- Optical response of nanomaterials
- Spin injection in materials
- Nonlinear optical response for surfaces and interfaces

└ The Nonlinear Surface Susceptibility

└ Software

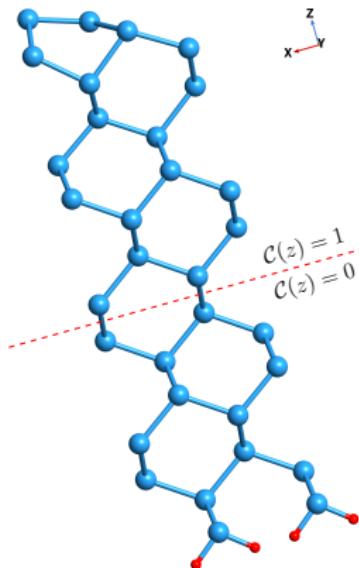


└ The Nonlinear Surface Susceptibility

└ Results for χ : Si(001)(2×1)

The Si(001)(2×1) Slab

2×1 reconstruction $\Rightarrow \chi_{2\times 1}^{xxx} \neq 0$



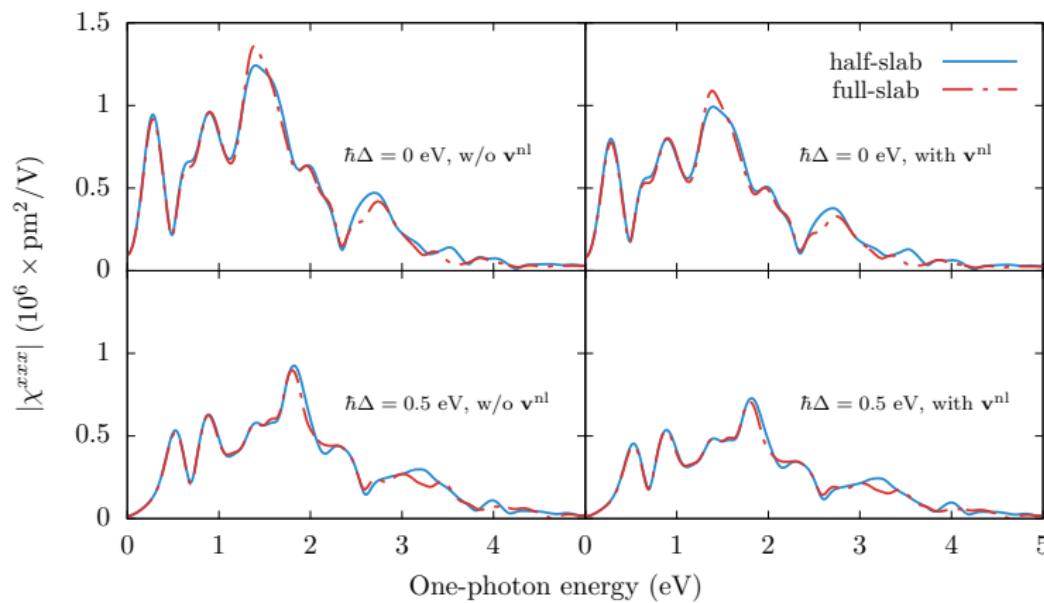
H-terminated $\Rightarrow \chi_H^{xxx} \approx 0$

Convergence is achieved with 32 layers of Si.

└ The Nonlinear Surface Susceptibility

└ Results for χ : Si(001)(2×1)

Half-slab vs. Full-slab

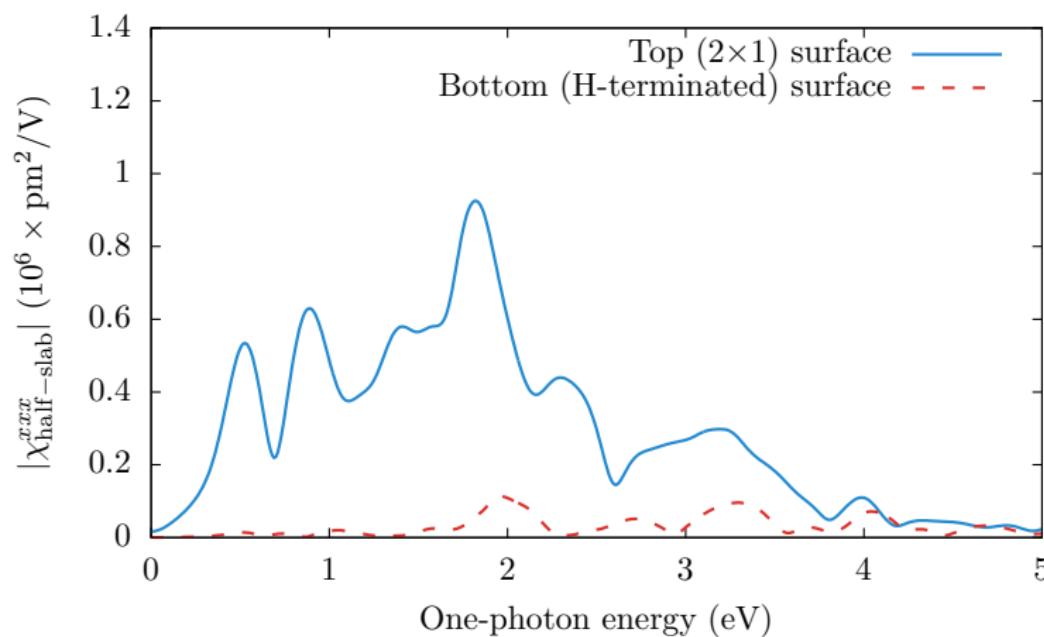


More layers would produce even better results.

└ The Nonlinear Surface Susceptibility

└ Results for χ : Si(001)(2×1)

Top vs. Bottom Surfaces

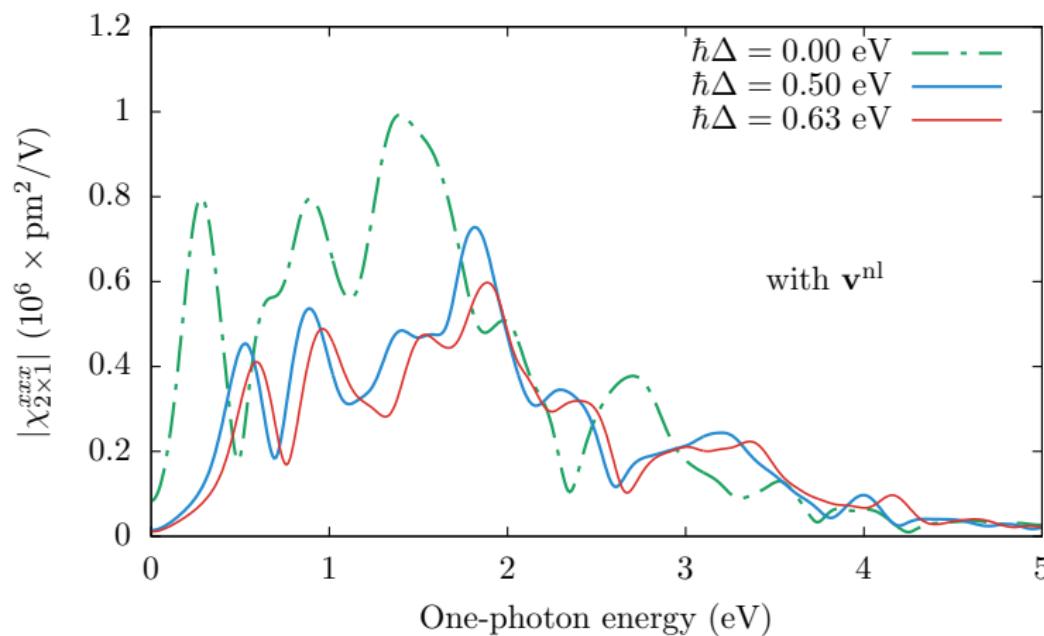


Improved with more layers and more precise division of slab.

└ The Nonlinear Surface Susceptibility

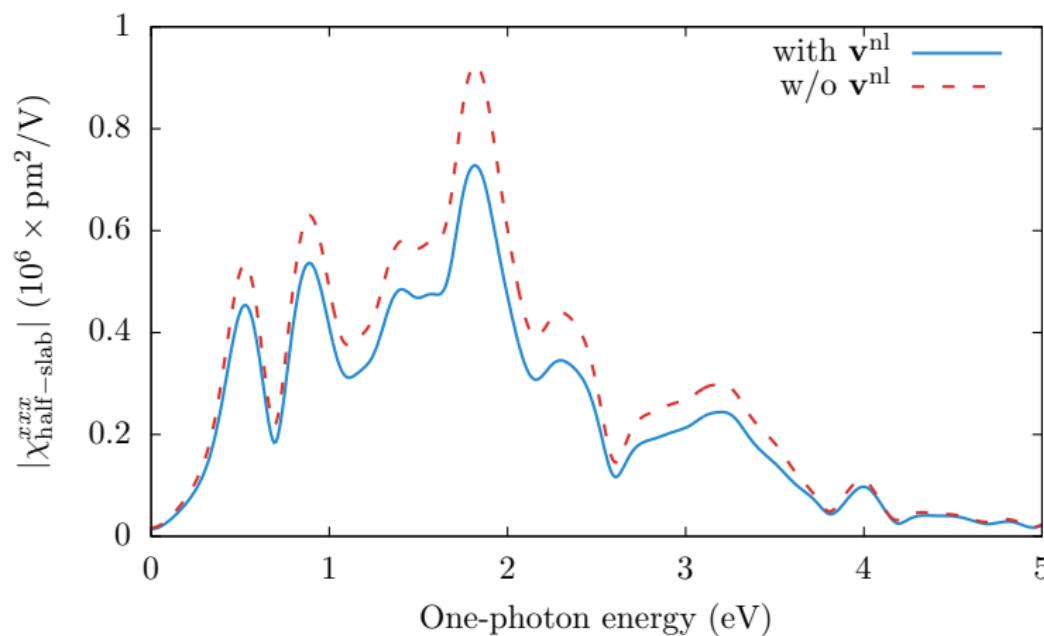
└ Results for χ : Si(001)(2×1)

Three Values of the Scissors Correction



The 2×1 reconstructed surface has surface states, so the spectrum shifts non-rigidly.

└ The Nonlinear Surface Susceptibility

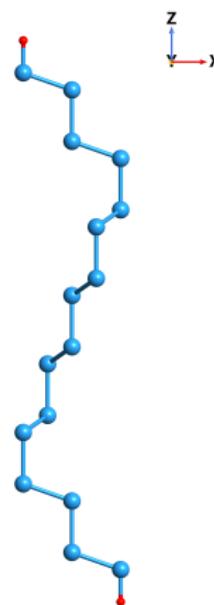
└ Results for χ : Si(001)(2×1)With and Without \mathbf{v}^{nl} 

The effect of the nonlocal part of the pseudopotentials maintains the same line-shape but reduces the value by 15-20% on average.

└ The Nonlinear Surface Susceptibility

└ Results for χ : Si(111)(1×1):H

The Si(111)(1×1):H surface

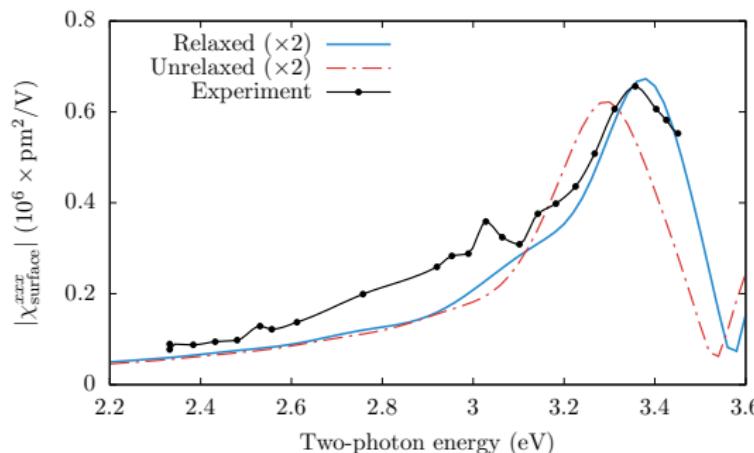


Si(111)(1×1):H

└ The Nonlinear Surface Susceptibility

└ Results for χ : Si(111)(1×1):H

χ for the Si(111)(1×1):H surface⁸



Relaxing the Structure

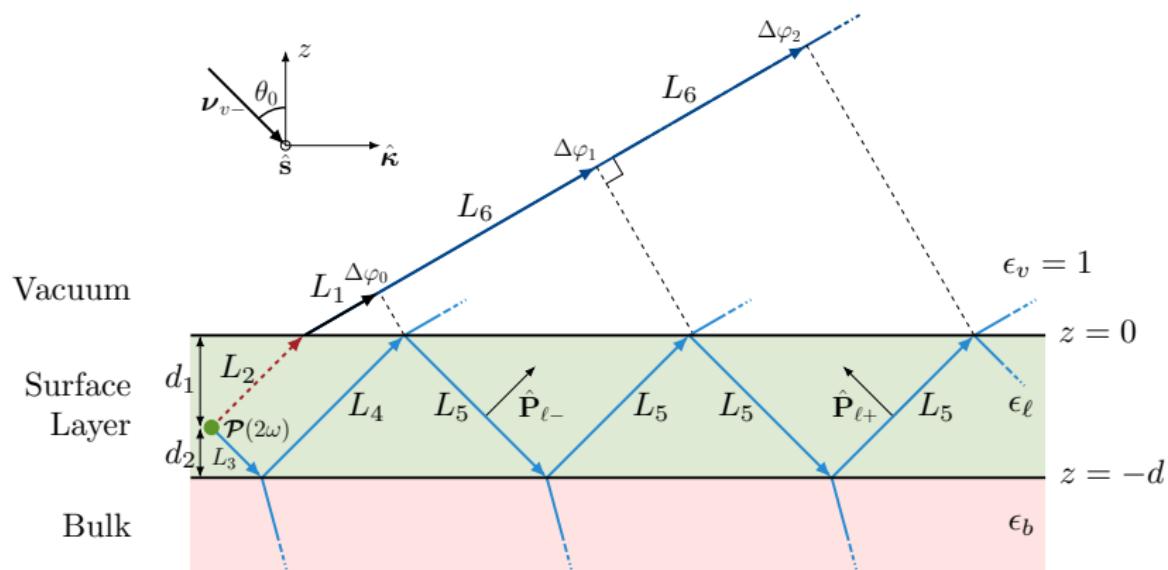
- 1 Worth the time and effort
- 2 Experimental data taken at low temperature

⁸Experimental data from Höfer et al., Appl. Phys. A 63, 533 (1996)

└ The SSHG Yield

└ Deriving \mathcal{R}

The Three Layer Model



The nonlinear process occurs in a thin layer (ℓ) just below the surface, between the vacuum region (v) and the material bulk (b)

- └ The SHHG Yield

- └ Deriving \mathcal{R}

Explicit Expressions for \mathcal{R} ^{9 10}

The SHHG yield is

$$\mathcal{R}_{iF}(2\omega) = \frac{\omega^2}{2\epsilon_0 c^3 \cos^2 \theta_0} \left| \frac{1}{n_\ell} \Upsilon_{iF} \right|^2 \left[\frac{m^2}{W} \right]$$

for each combination of polarizations of incoming and outgoing fields ($iF = pP, pS, sP$, and sS). We have that

$$\Upsilon_{iF} = \Gamma_{iF} r_{iF},$$

where,

$$\Gamma_{pP} = \frac{T_p^{v\ell}}{N_\ell} \left(\frac{t_p^{v\ell}}{n_\ell} \right)^2, \quad \Gamma_{sP} = \frac{T_p^{v\ell}}{N_\ell} \left(t_s^{v\ell} r_s^{M+} \right)^2,$$

$$\Gamma_{pS} = T_s^{v\ell} R_s^{M+} \left(\frac{t_p^{v\ell}}{n_\ell} \right)^2, \quad \Gamma_{sS} = T_s^{v\ell} R_s^{M+} \left(t_s^{v\ell} r_s^{M+} \right)^2,$$

⁹Anderson, et al., Phys. Rev. B 93, 235304 (2016)

¹⁰Anderson, et al., Phys. Rev. B, submitted

└ The SSHG Yield

└ Deriving \mathcal{R}

Explicit Expressions for \mathcal{R}

In particular, for the (111) surface we have

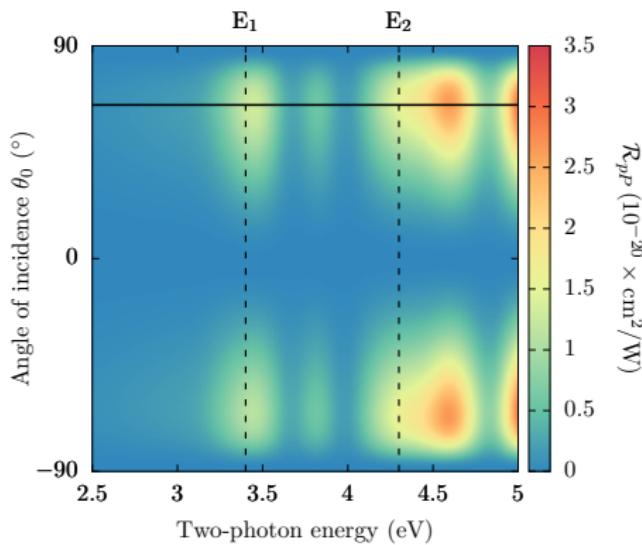
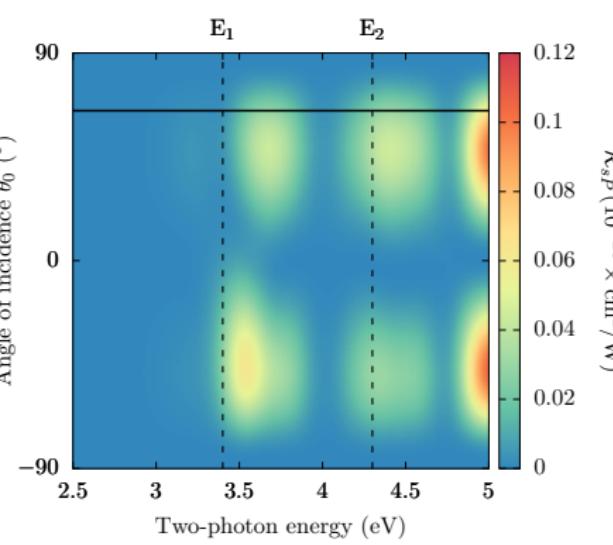
$$\begin{aligned} r_{pP}^{(111)} &= R_p^{M+} \sin \theta_0 \left[\left(r_p^{M+} \right)^2 \sin^2 \theta_0 \chi^{zzz} + \left(r_p^{M-} \right)^2 w_\ell^2 \chi^{zxx} \right] \\ &\quad - R_p^{M-} w_\ell W_\ell \left[2r_p^{M+} r_p^{M-} \sin \theta_0 \chi^{xxz} + \left(r_p^{M-} \right)^2 w_\ell \chi^{xxx} \cos 3\phi \right], \end{aligned}$$

$$r_{sP}^{(111)} = R_p^{M+} \sin \theta_0 \chi^{zxx} + R_p^{M-} W_\ell \chi^{xxx} \cos 3\phi,$$

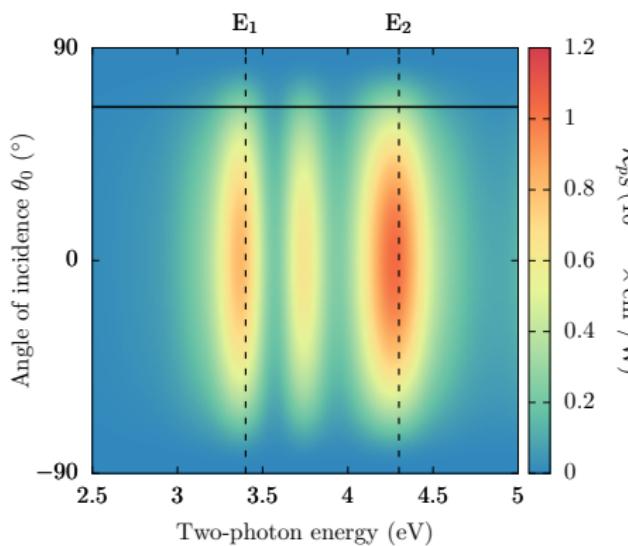
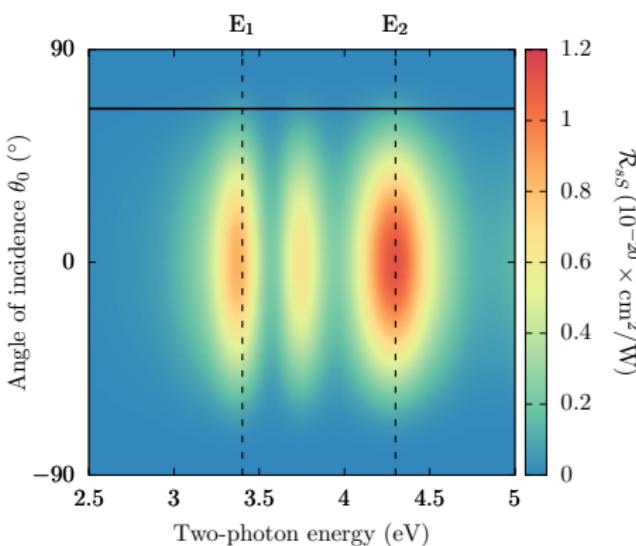
$$r_{pS}^{(111)} = - \left(r_p^{M-} \right)^2 w_\ell^2 \chi^{xxx} \sin 3\phi,$$

$$r_{sS}^{(111)} = \chi^{xxx} \sin 3\phi.$$

└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):HSi(111)(1×1):H – Outgoing P polarization \mathcal{R}_{pP} with $\phi = 45$  \mathcal{R}_{sP} with $\phi = 45$

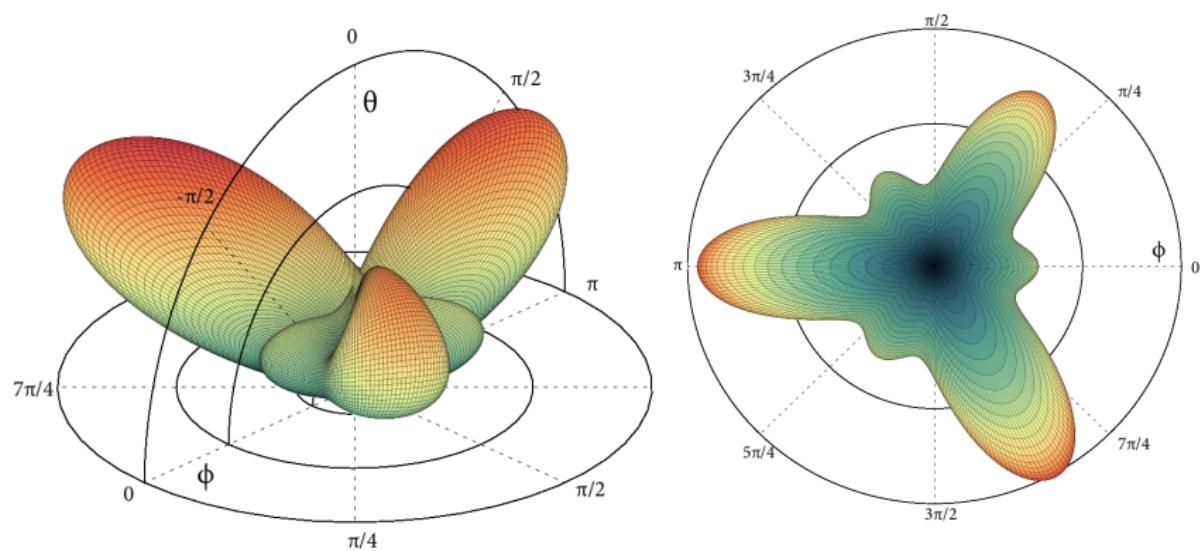
└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):HSi(111)(1×1):H – Outgoing S polarization \mathcal{R}_{pS} with $\phi = 45$  \mathcal{R}_{sS} with $\phi = 45$

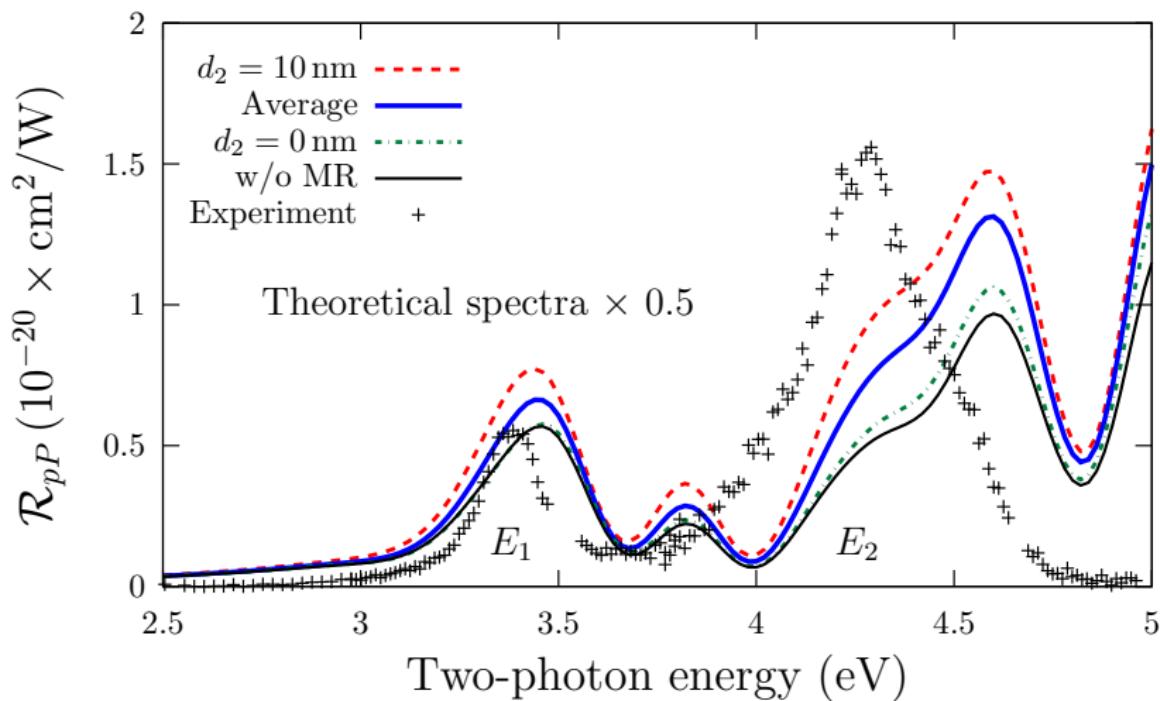
└ The SHHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

Si(111)(1×1):H – \mathcal{R}_{pP} at $E_1 = 3.4$ eV



└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

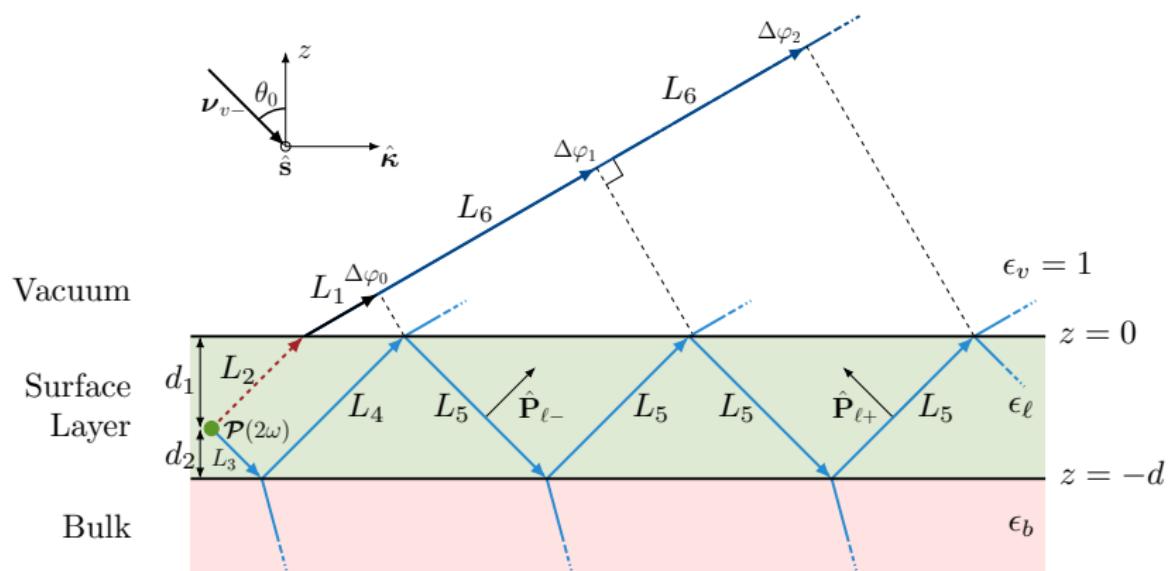
R_{pP} for $\theta = 65$ and $\phi = 45$ at room temperature¹¹

¹¹Experimental data from Mejia et al., Phys. Rev. B 66, 195329 (2002)

└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

The Three Layer Model

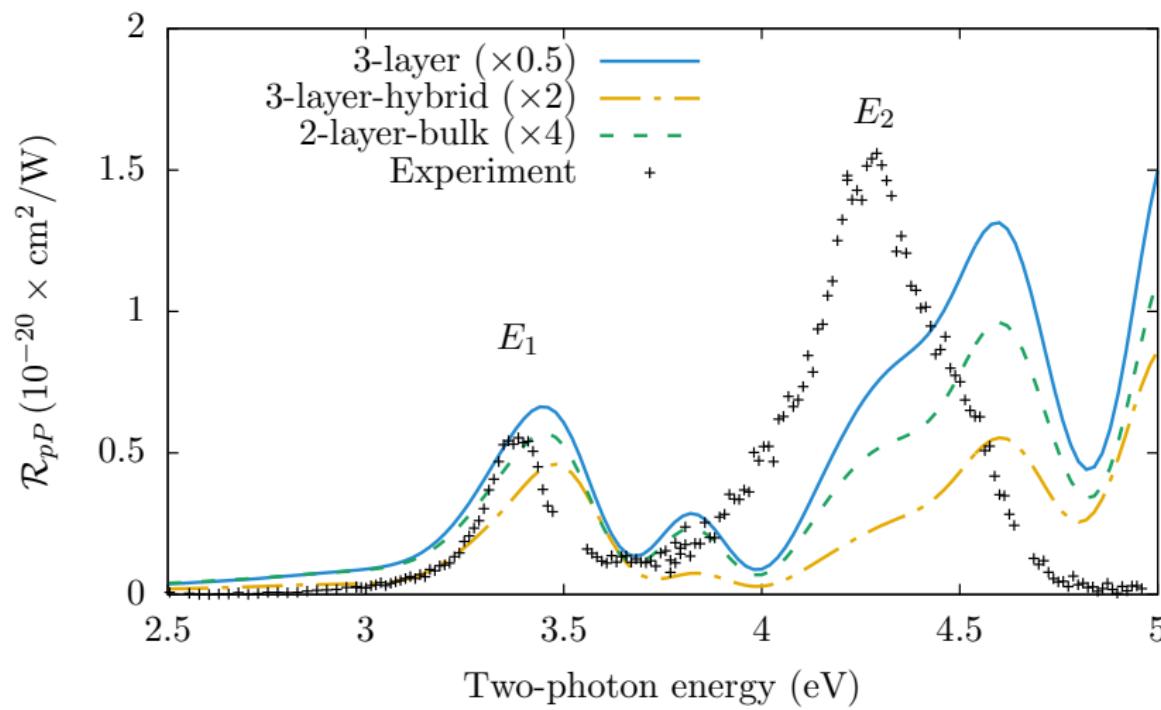


The nonlinear process occurs in a thin layer (ℓ) just below the surface, between the vacuum region (v) and the material bulk (b)

└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

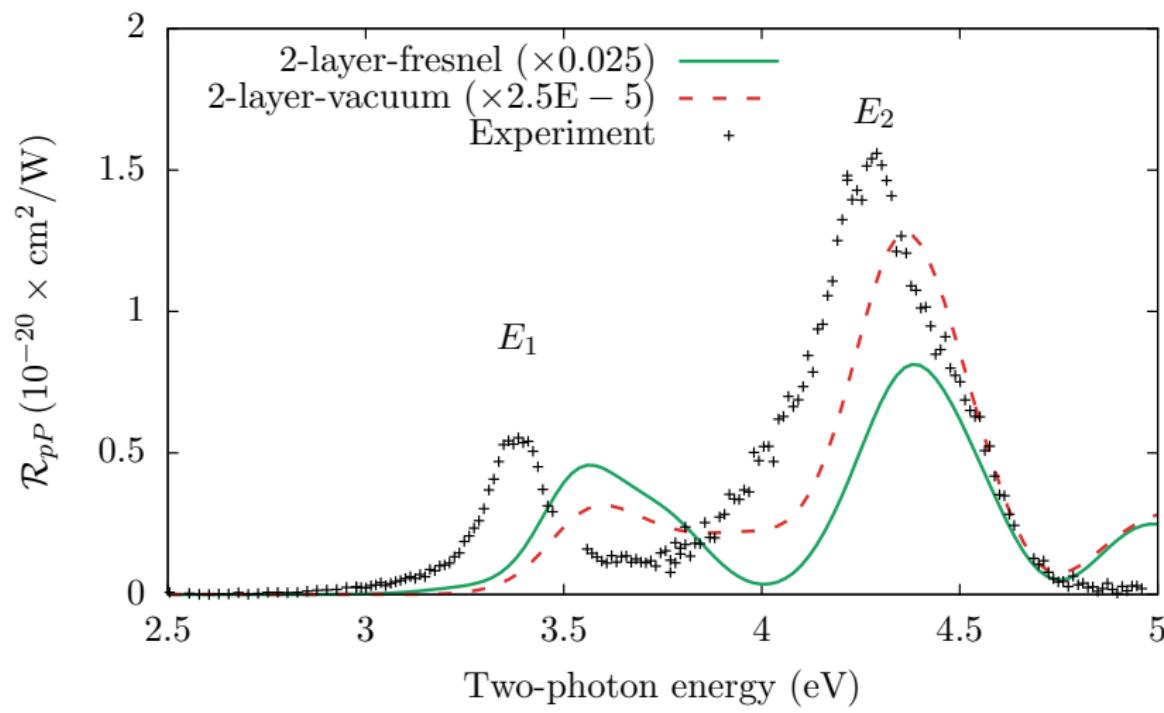
Other models



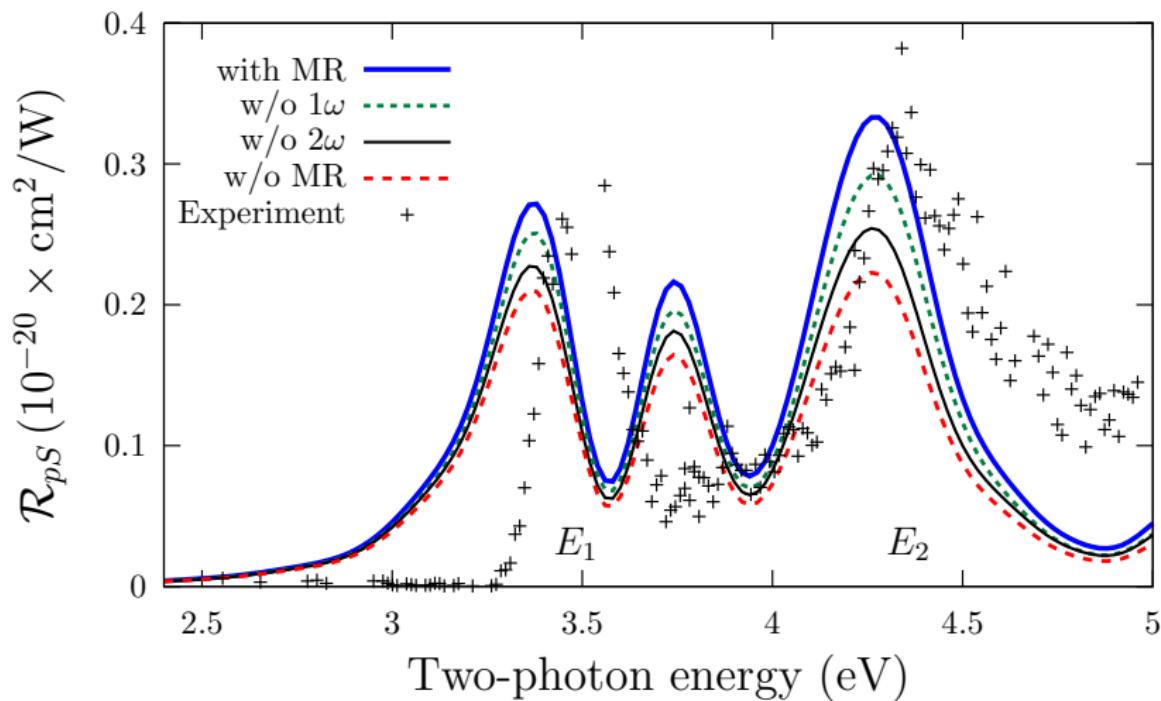
└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

Other models



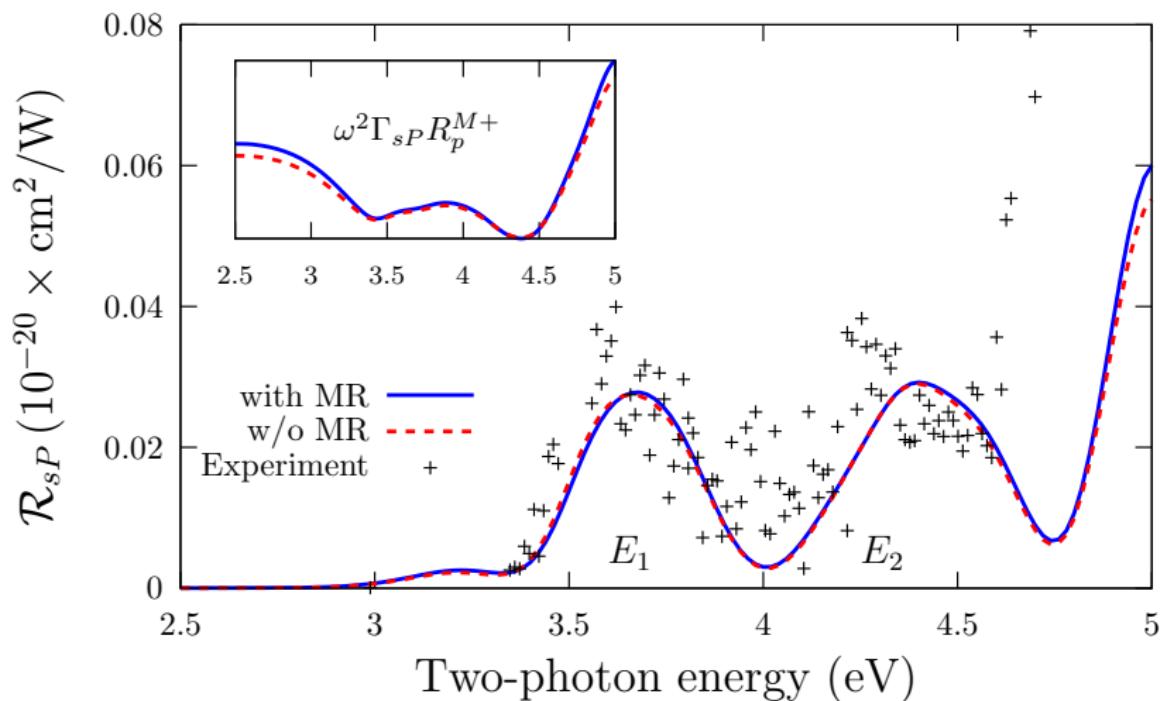
└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

\mathcal{R}_{pS} for $\theta = 65$ and $\phi = 45$ at room temperature¹²

¹²Experimental data from Mejia et al., Phys. Rev. B 66, 195329 (2002)

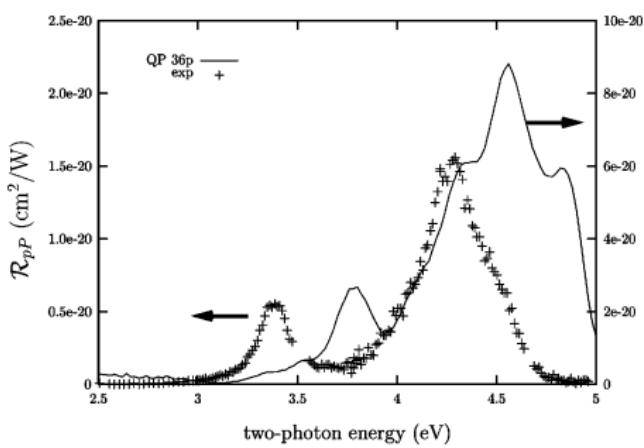
└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H

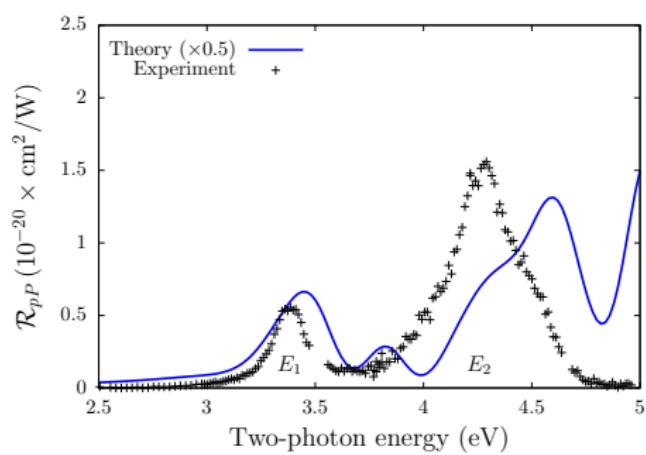
\mathcal{R}_{sP} for $\theta = 65$ and $\phi = 45$ at room temperature¹³

¹³Experimental data from Mejia et al., Phys. Rev. B 66, 195329 (2002)

└ The SSHG Yield

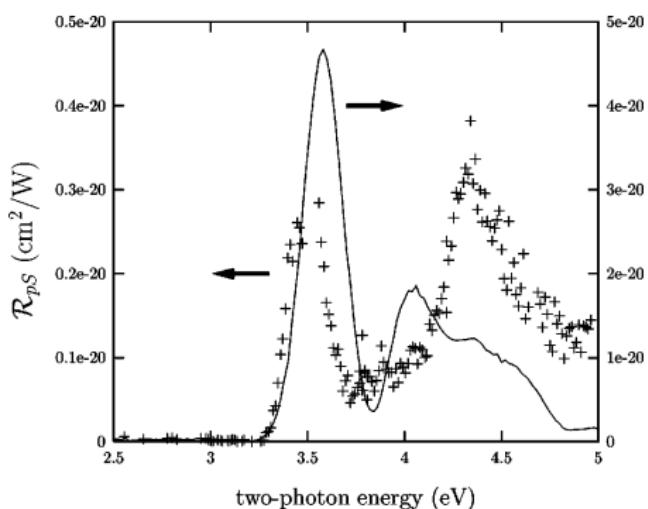
└ Results for \mathcal{R} : Si(111)(1×1):H \mathcal{R}_{pP} – Old vs. New

From Mejia *et al.*

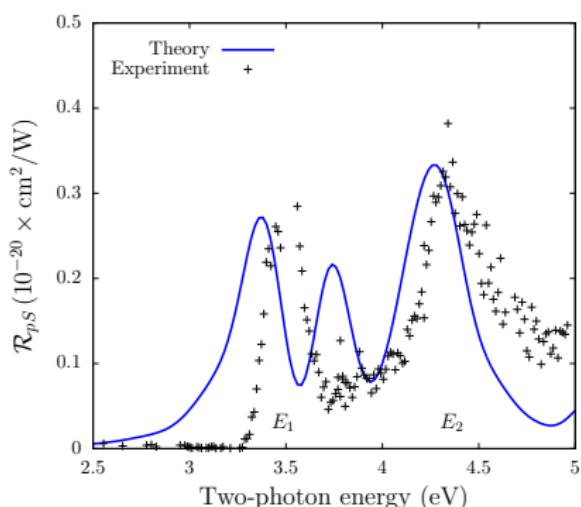


This work.

└ The SSHG Yield

└ Results for \mathcal{R} : Si(111)(1×1):H \mathcal{R}_{pS} – Old vs. New

From Mejia et al.



This work.

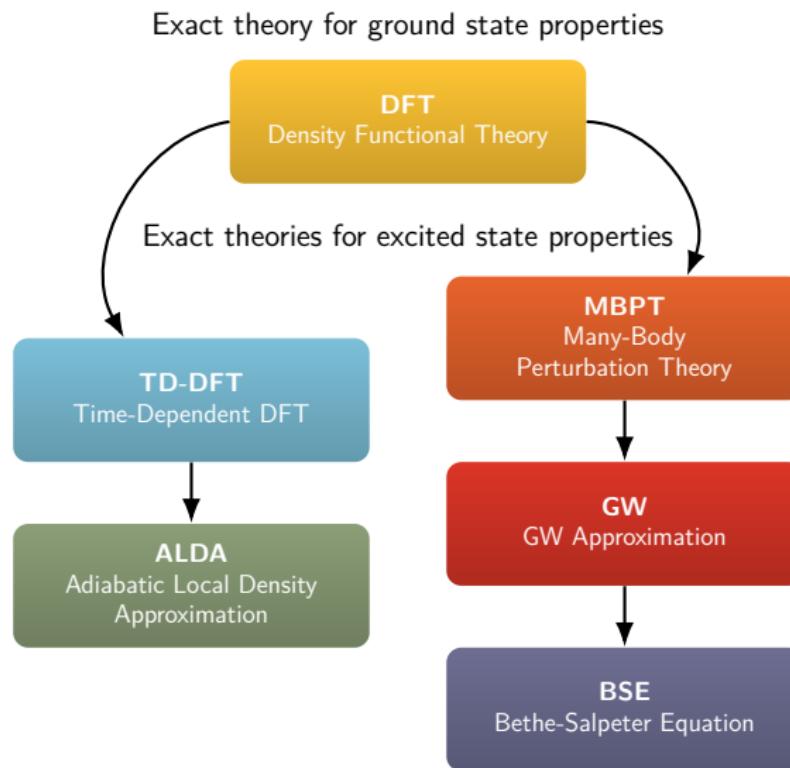
└ The SSHG Yield

 └ Results for \mathcal{R} : Si(111)(1×1):H

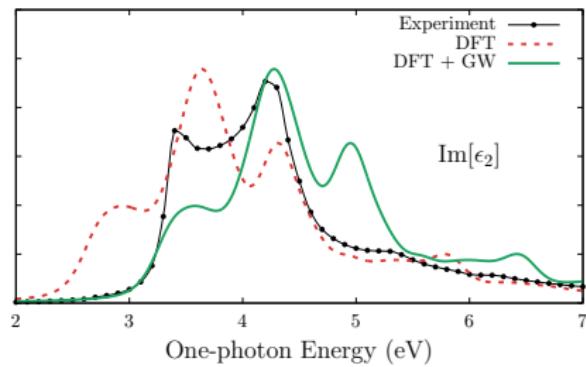
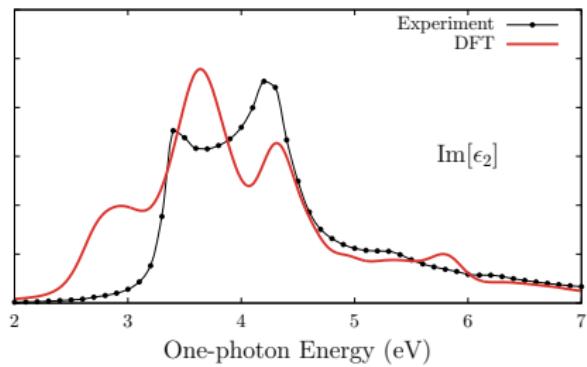
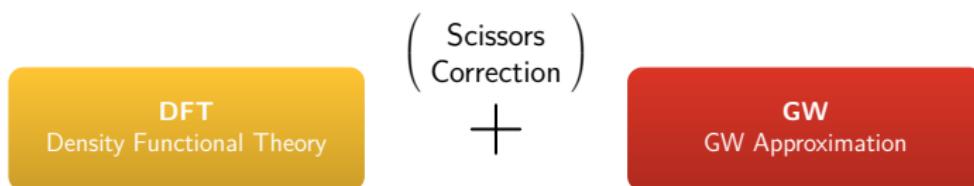
Summary

- Intensity is very close to experiment with unambiguous units.
No more arbitrary units!
- Peak position is also quite close, temperature effects are clear.
- Multiple reflections enhances peak proportions and intensity according to experiment.
- We can now have *quantitative* and predictive results for any surface!

What's Next?



Where We Stand

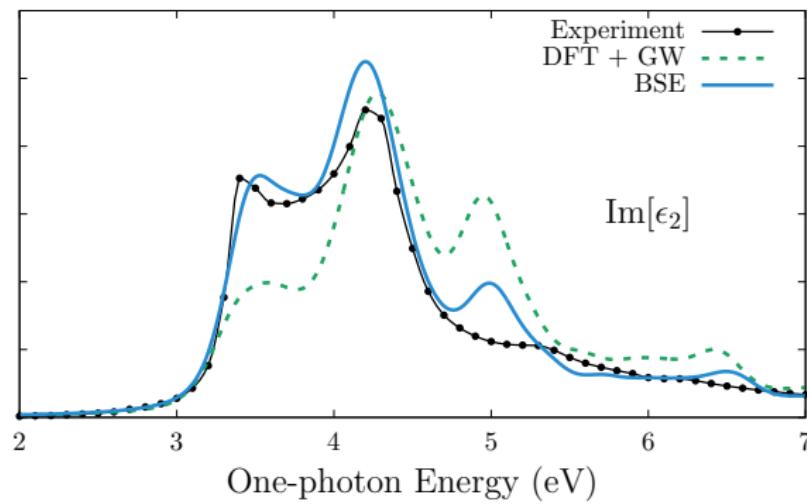


└ Conclusions

└ Methods

The State of the Art

BSE Bethe-Salpeter Equation



└ Conclusions

└ Credits

Productivity

Produced Articles

- *Anderson, et al.*, Phys. Rev. B 93, 235304 (2016)
- *Zapata-Peña, Anderson, et al.*, Phys. Status Solidi B 253, 408 (2016)
- *Anderson, et al.*, Phys. Rev. B 91, 075302 (2015)
- *Anderson, et al.*, arXiv:1604.07722 [physics.optics] (2016)
- *Anderson, et al.*, Phys. Rev. B, Submitted (2016)

Academic Stays

- Laboratoire des Solides Irradiés, École Polytechnique, France (2015)
- Laboratoire des Solides Irradiés, École Polytechnique, France (2014)

└ Conclusions

└ Credits

Conferences

- Psi-K 2015 (Ganador del Concurso de Posters Científicos)
- OSI-11 2015 (Poster)
- ENU-HPC 2012 (Submitted Talk)

Specialized Courses

- *Ab-initio* calculations with the DP/EXC Codes (2016) (Imparted)
- Control de versiones usando Git y GitHub (2013) (Imparted)
- Cómputo en paralelo mediante FORTRAN/C++ con MPI y OpenMP (2013)
- Cálculo de propiedades ópticas de la materia con el uso de teoría de muchos cuerpos (2013)

└ Conclusions

└ Credits

Acknowledgements

- Benevolent leader: Dr. Bernardo Mendoza
- Dr. Ramón Carriles Jaimes
- Dr. Norberto Arzate Plata
- Dr. Francisco Villa Villa
- Dr. Wolf Luis Mochán Backal
- Reinaldo Arturo Zapata Peña
- Valérie Véniard & Nicolas Tancogne-Dejean
- The CONACYT
- The CIO for 6 great years
- My parents, Mike & Ana
- All my friends
- Dra. Liliana Villafaña López

Thanks for coming!

ABINIT

```
1  ### Dataset 3 : variables for KSS file
2  ###           used to get the contribution of the non-local
3  ###           part of the pseudopotential to the
4  ###           velocity matrix elements
5  ### For KSS set nbandkss3 with the same numerical values as nband
6  nbandkss2      200
7  ### For KSS the following variables are a must
8  getden2        1
9  iscf2          -2
10 kptopt2        0
11 prtwf2         0
12 kssform2       3
13 nsym2          1
14 ###
```

<http://www.abinit.org>

└ Conclusions

└ Appendix

TINIBA

The following sets of k-points are available:

DiH_DiH_1x1_32layers.klist_130

```
=====
34 Layers: all, 132 bands (66-v 66-c), spin=1, ecut=08 and xe/it/qu weights=choose one: -r setkp...
number of plane waves = 6027
=====
```

Usage:

```
N_Layer=number of layers or half-slab
run_tiniba.sh -r run -k Nk -N N_Layer -x [serial-1 para-2] -C cores -P pwvs
options:
```

- w Wave function(k)
- m rho(z) for a set of k-points in case.klist_rho
- e Energies E_{m}(k)
- p Momentum Matrix Elements p_{mn}(k), includes m=n
- v V^LDA with DP for pwvs (Never use with Spin-Orbit psp)
- d Layered ndot Matrix Elements rho_{cc'}(l;k)
- c Layered Momentum Matrix Elements calp_{mn}(k) and calc_{mn}(k)
- V Layered V^LDA with DP for pwvs (Never use with Spin-Orbit psp)
- l Layered Diagonal Momentum Matrix Elements calp_{mm}(k)
- s Spin Matrix Elements S_{cc'}(k)
- n Layered Spin Matrix Elements calS_{cc'}(k)
- b bypass WF checkup (Never use on first run)

```
run_tiniba.sh -r setkp -k Nk -g xeon/itanium -G xeon/quad weights
run_tiniba.sh -r erase To erase the calculation from the nodes
run_tiniba.sh -r erasescf To erase the SCF calculation
=====
```

<https://github.com/roguephysicist/tiniba-manual>

Contribution of the Nonlocal Part of the Pseudopotential

$$\begin{aligned}
 \mathcal{V}_{nm}^{nl,\ell}(\mathbf{k}) = & \frac{1}{2\hbar} \sum_s \sum_{l=0}^{l_s} \sum_{m=-l}^l E_l \left[\right. \\
 & + \left(\sum_{\mathbf{G}''} \nabla_{\mathbf{G}''} f_{lm}^s(\mathbf{G}'') \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) \delta_{\mathbf{G}''||\mathbf{G}''||} f_\ell(G_z - G_z'') \right) \left(\sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') f_{lm}^{s*}(\mathbf{K}') \right) \\
 & + \left(\sum_{\mathbf{G}''} f_{lm}^s(\mathbf{G}'') \sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) \delta_{\mathbf{G}''||\mathbf{G}''||} f_\ell(G_z - G_z'') \right) \left(\sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \nabla_{\mathbf{K}'} f_{lm}^{s*}(\mathbf{K}') \right) \\
 & + \left(\sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) \nabla_{\mathbf{G}} f_{lm}^s(\mathbf{G}) \right) \left(\sum_{\mathbf{G}''} f_{lm}^{s*}(\mathbf{G}'') \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \delta_{\mathbf{G}''||\mathbf{G}''||} f_\ell(G_z'' - G_z') \right) \\
 & \left. + \left(\sum_{\mathbf{G}} A_{n\mathbf{k}}^*(\mathbf{G}) f_{lm}^s(\mathbf{G}) \right) \left(\sum_{\mathbf{G}''} \nabla_{\mathbf{G}''} f_{lm}^{s*}(\mathbf{G}'') \sum_{\mathbf{G}'} A_{m\mathbf{k}}(\mathbf{G}') \delta_{\mathbf{G}''||\mathbf{G}''||} f_\ell(G_z'' - G_z') \right) \right].
 \end{aligned}$$

SHGYield.py

```
1 def shgyield(gamma, rif): # function for the final yield
2     Rif = SCALE * M2TOCM2 * PREFACTOR * (ONEE ** 2) * \
3             np.absolute((1/nl) * gamma * rif)**2
4     broadened = broad(Rif, SIGMA)
5     return broadened
6
7
8 ##### Init #####
9 PARAM = parse_input(sys.argv[1]) # parses input file
10 MODE = str(PARAM['mode']) # establishes mode
11 MULTIREF = str(PARAM['multiref']) # if multiple reflections are considered
```

<https://github.com/roguephysicist/SHGYield>