Theoretical Optical Second-Harmonic Calculations for Surfaces

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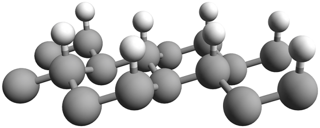
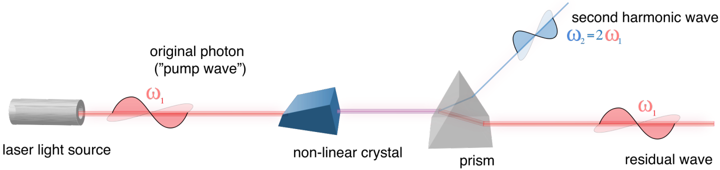


Second Harmonic Generation (SHG)

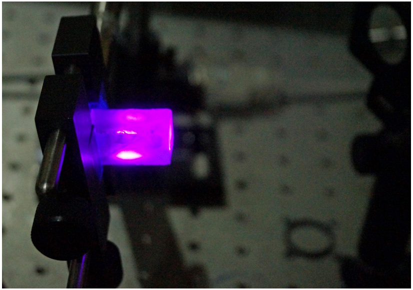
Characteristics[1]

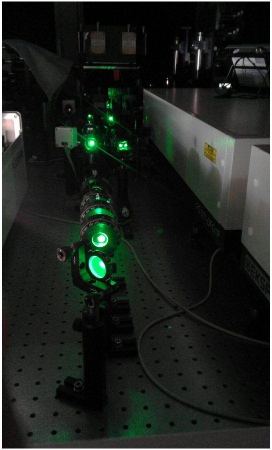
- Two photons of the same frequency combine
- Create one photon of double the frequency



[1] Image: Jon Chui

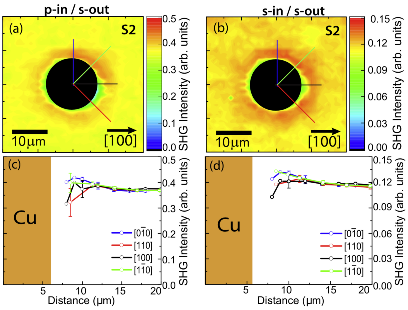
Frequency Conversion[2]



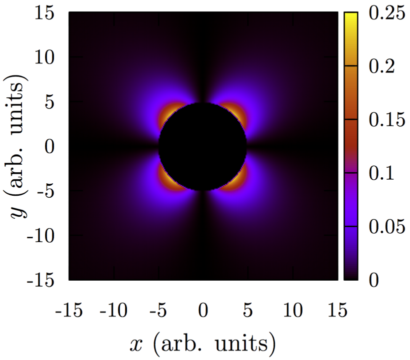


[2] Images: Dr. Ramón Carriles Jaimes, Cornelia Reitböck

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!

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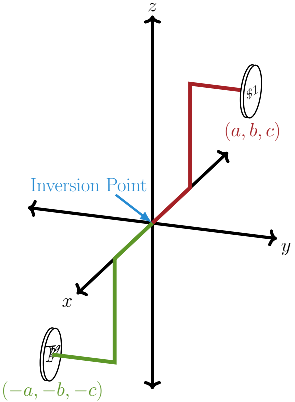
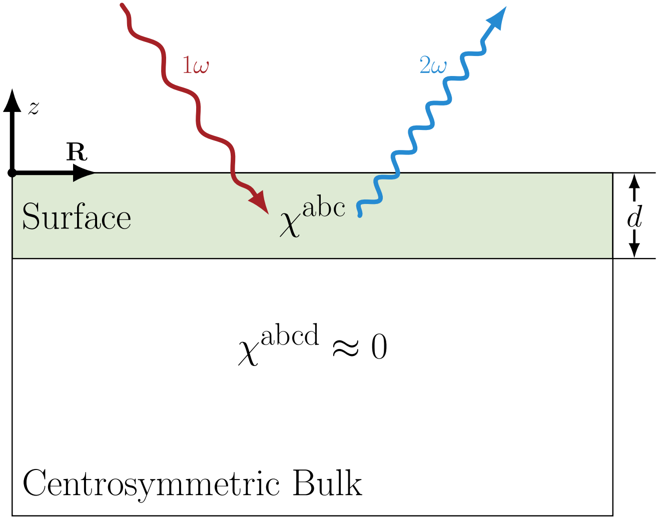
[5] *Armstrong et al.*, Phys. Rev. 127, 1918 (1962)

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

Centrosymmetric Materials

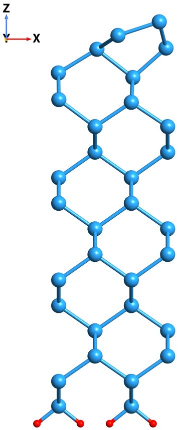
A centrosymmetric material is a material that displays inversion symmetry, such that $p(a,b,c) \rightarrow p(-a,-b,-c)$.



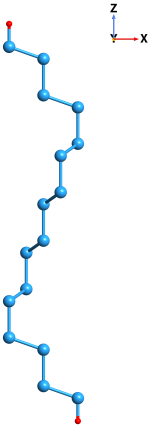


Semi-infinite system with a centrosymmetric bulk and a surface region is of thickness $\sim d$. Dipolar SHG is produced in reflection from the surface.

Two Si Test Cases



Si(001)(2×1)



Si(111)(1×1):H

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

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

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

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

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

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

We express the electron velocity operator as

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

where

$$\begin{aligned} \mathbf{v} &= \frac{\mathbf{p}}{m_e}, \\ \mathbf{v}^{\mathrm{nl}} &= \frac{1}{i\hbar}\left[\mathbf{r}, V^{\mathrm{nl}}\right], \\ \mathbf{v}^{\mathcal{S}} &= \frac{1}{i\hbar}\left[\mathbf{r}, S(\mathbf{r},\mathbf{p})\right], \\ \mathbf{v}^{\mathrm{LDA}} &= \mathbf{v} + \mathbf{v}^{\mathrm{nl}}. \end{aligned}$$

We also have that

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

Layered Cut Function (3)

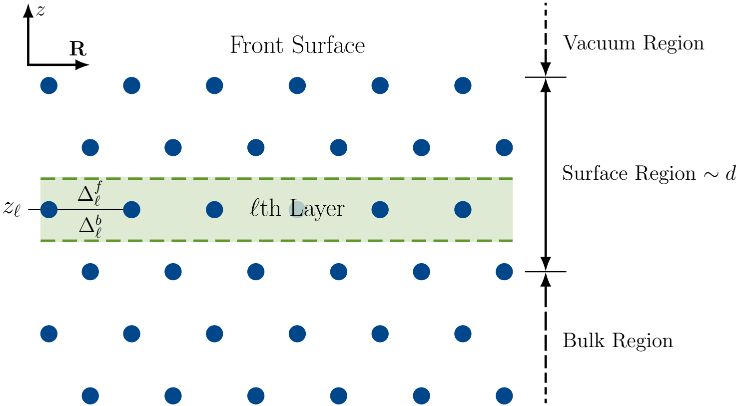
We introduce the cut function

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

that transforms any operator into its calligraphic counterpart as

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

Layered Cut Function (3)



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

Final Expressions

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

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

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

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

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

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

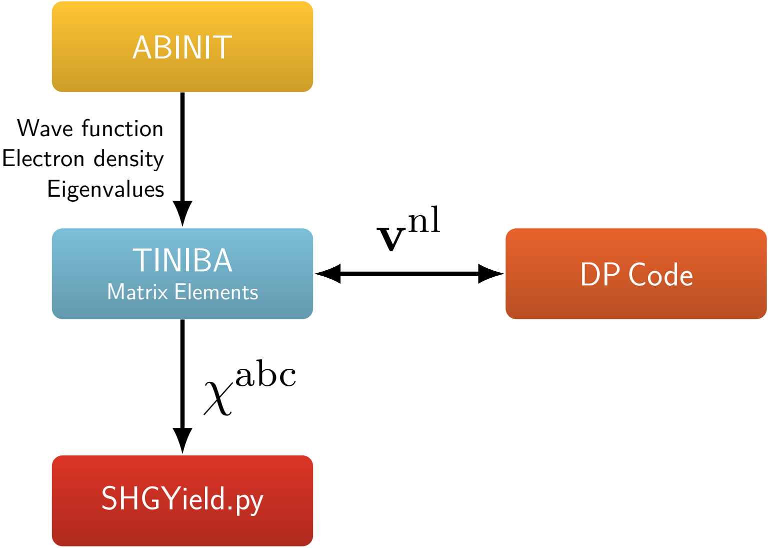
Medusa runs on free and open source software:

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

TINIBA

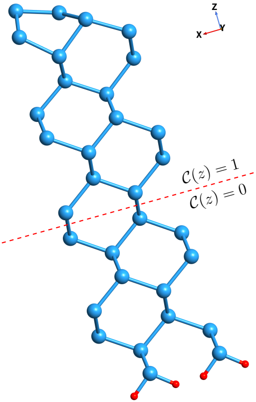
Combines Bash, Perl, Fortran, and ABINIT for calculating:

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


ABINIT
Wave function
Electron density
Eigenvalues
TINIBA
Matrix Elements
$\mathbf{v}^{\mathrm{nl}}$
DP Code
χ^{abc}
SHGYield.py

The Si(001)(2×1) Slab

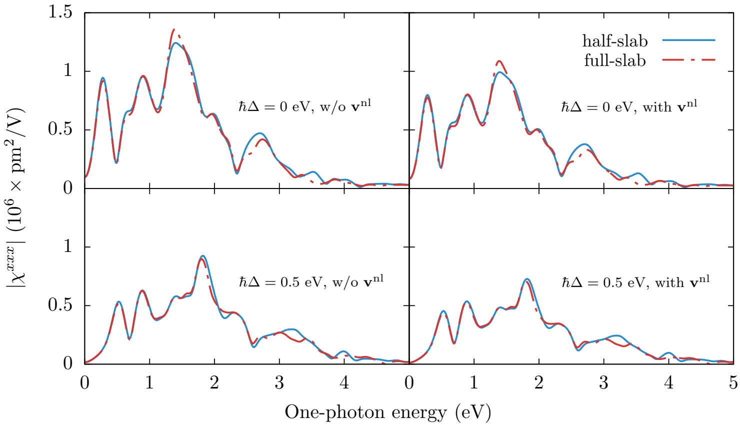
2×1 reconstruction $\Rightarrow \chi^{xxx}_{2\times 1} \neq 0$



H-terminated $\Rightarrow \chi^{xxx}_{\mathrm{H}} \approx 0$

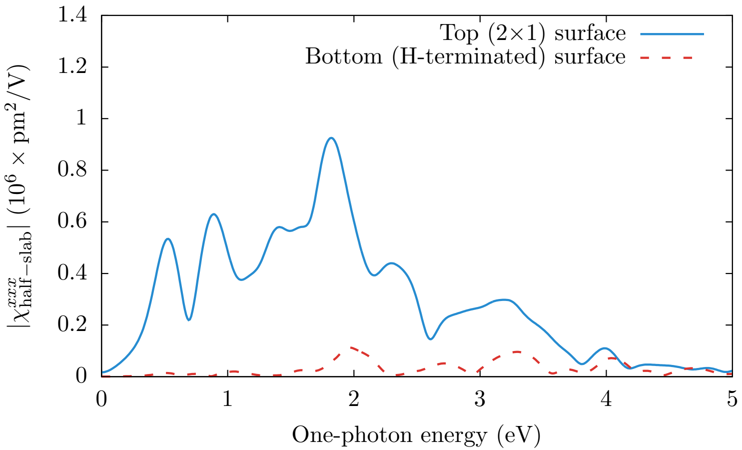
Convergence is achieved with 32 layers of Si.

Half-slab vs. Full-slab



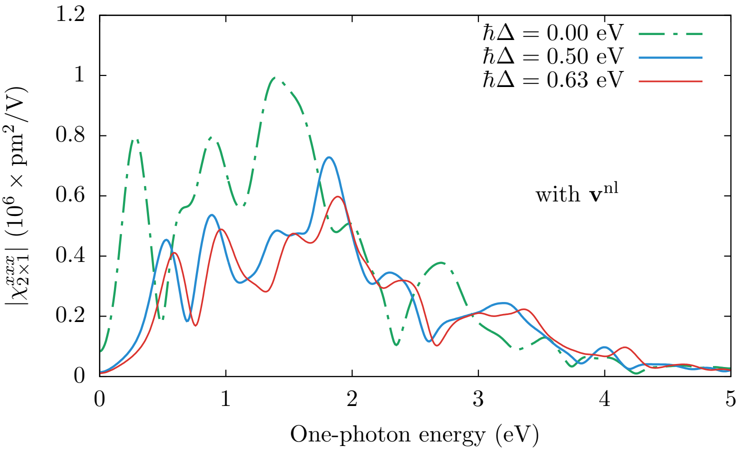
More layers would produce even better results.

Top vs. Bottom Surfaces



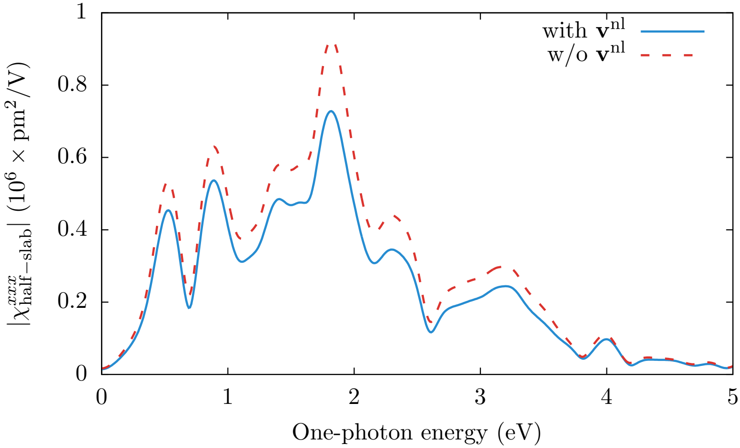
Improved with more layers and more precise division of slab.

Three Values of the Scissors Correction



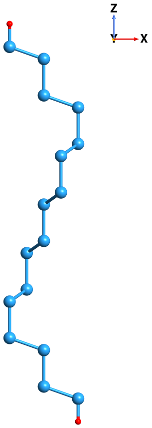
The 2×1 reconstructed surface has surface states, so the spectrum shifts non-rigidly.

With and Without $\mathbf{v}^{\mathrm{nl}}$



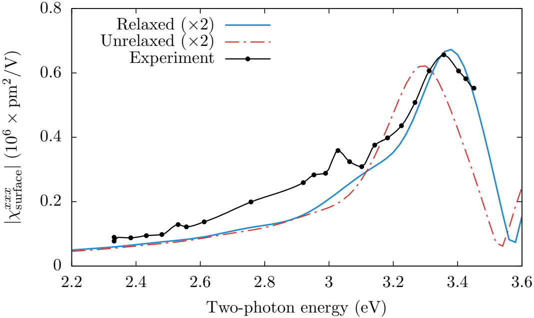
The effect of the nonlocal part of the pseudopotentials maintains the same line-shape but reduces the value by 15-20% on average.

The Si(111)(1×1):H surface



Si(111)(1×1):H

χ for the Si(111)(1×1):H surface[8]

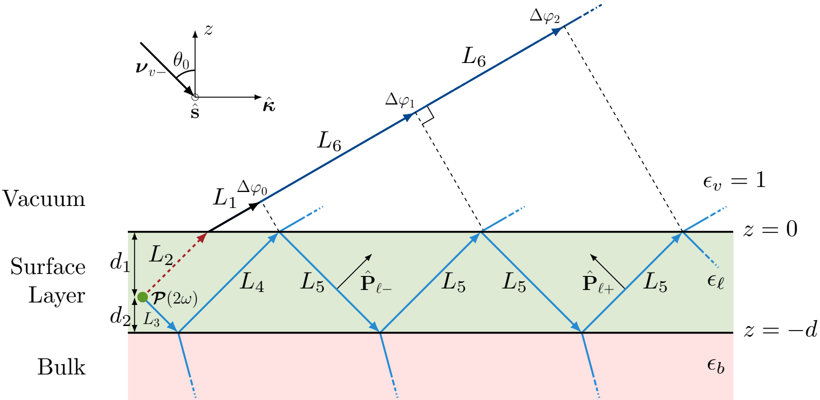


Relaxing the Structure

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

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

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)

Explicit Expressions for $\mathcal{R}$[9] [10]

The SSHG yield is

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

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

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

where,

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

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

[9] *Anderson, et al.*, Phys. Rev. B 93, 235304 (2016)
[10] *Anderson, et al.*, Phys. Rev. B, submitted

Explicit Expressions for $\mathcal{R}$

In particular, for the (111) surface we have

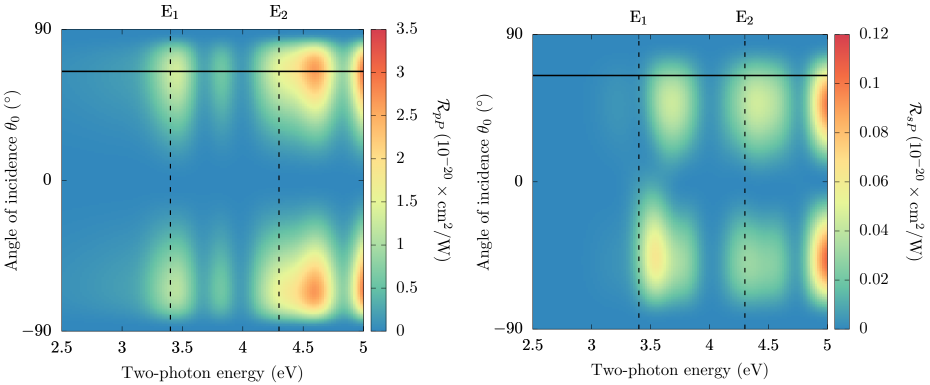
$$r_{pP}^{(111)} = R_p^{M+}\sin\theta_0\Big[\left(r_p^{M+}\right)^2\sin^2\theta_0\chi^{zzz} + \left(r_p^{M-}\right)^2 w_\ell^2\chi^{zxx}\Big] - R_p^{M-}w_\ell W_\ell\Big[2r_p^{M+}r_p^{M-}\sin\theta_0\chi^{xxz} + \left(r_p^{M-}\right)^2 w_\ell\chi^{xxx}\cos 3\phi\Big],$$

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

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

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

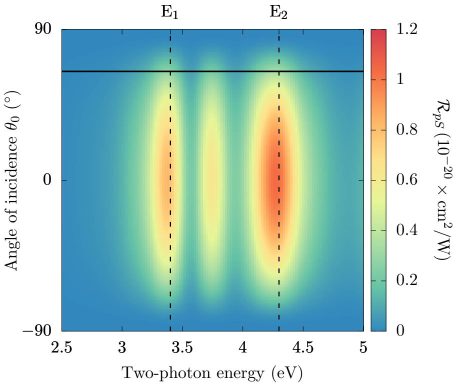
Si(111)(1×1):H – Outgoing P polarization



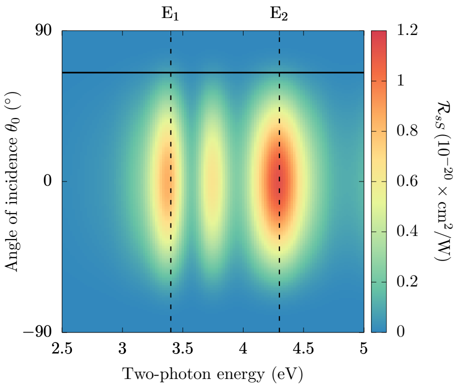
$\mathcal{R}_{pP}$ with $\phi = 45$

$\mathcal{R}_{sP}$ with $\phi = 45$

Si(111)(1×1):H – Outgoing S polarization

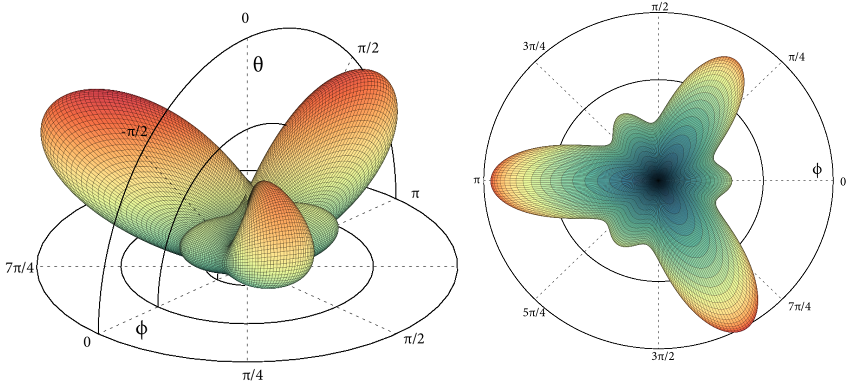


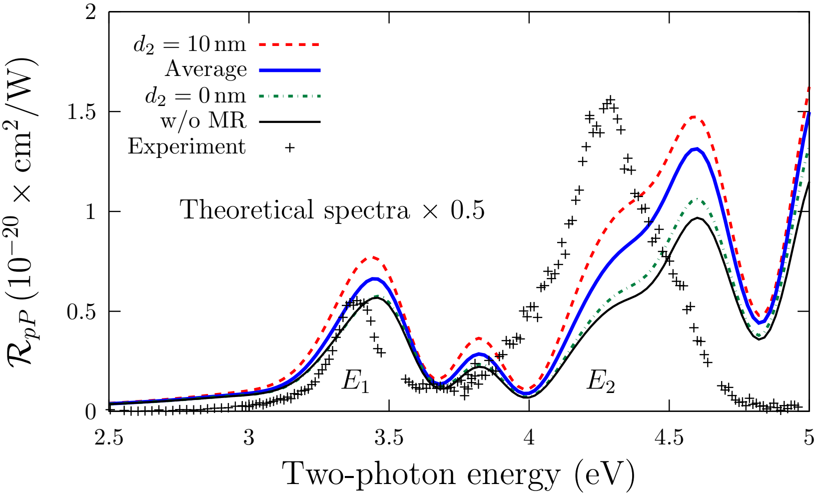
$\mathcal{R}_{pS}$ with $\phi = 45$



$\mathcal{R}_{sS}$ with $\phi = 45$

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

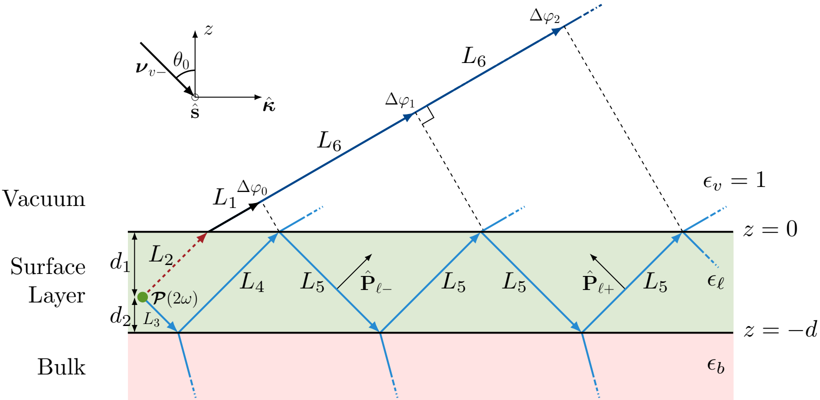




$\mathcal{R}_{pP}$ for $\theta = 65$ and $\phi = 45$ at room temperature[11]

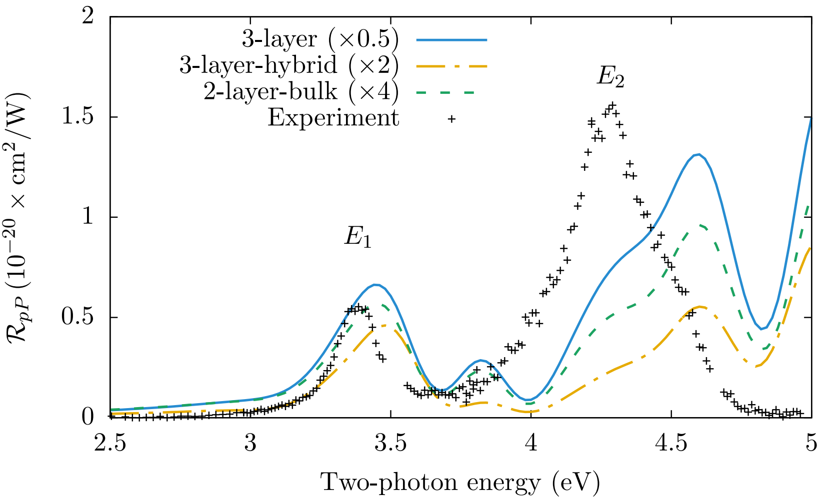
[11] Experimental data from *Mejia et al.*, Phys. Rev. B 66, 195329 (2002)

The Three Layer Model

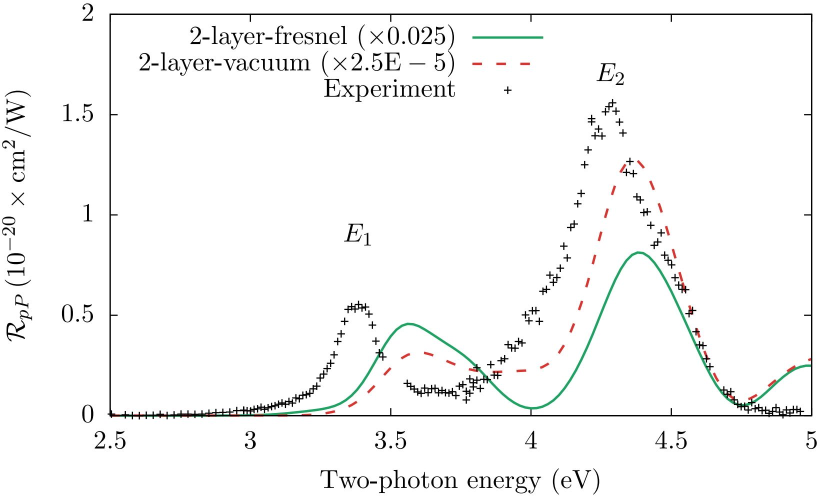


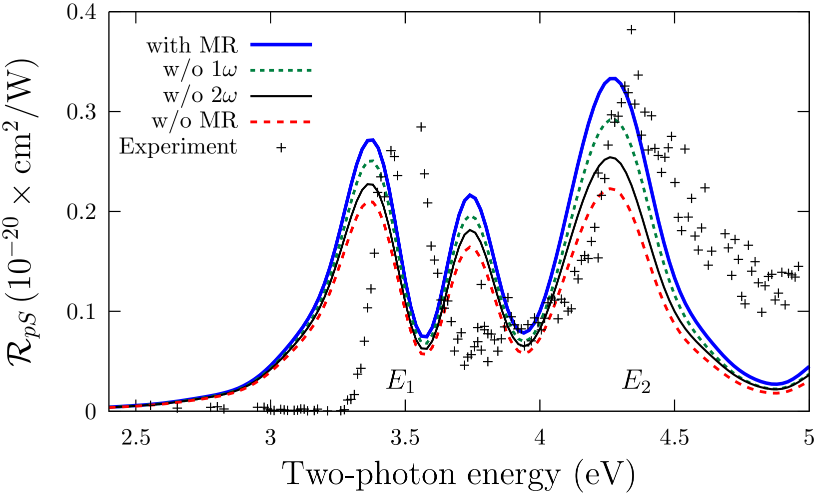
The nonlinear process occurs in a thin layer (ℓ) just below the surface, between the vacuum region (v) and the material bulk (b)

Other models



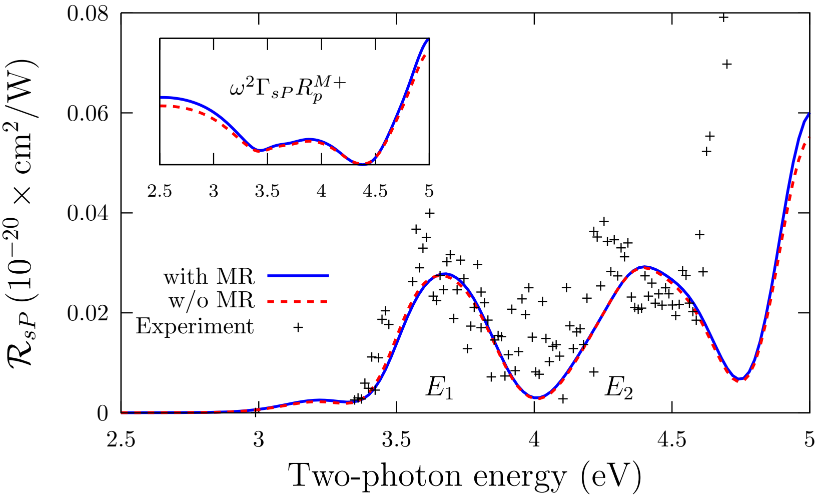
Other models





$\mathcal{R}_{pS}$ for $\theta = 65$ and $\phi = 45$ at room temperature[12]

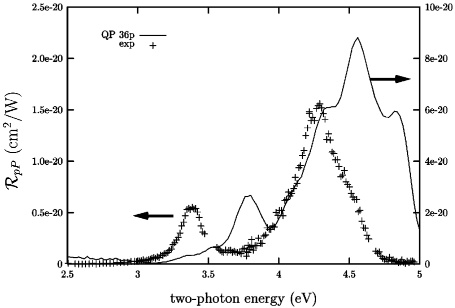
[12] Experimental data from *Mejia et al.*, Phys. Rev. B 66, 195329 (2002)



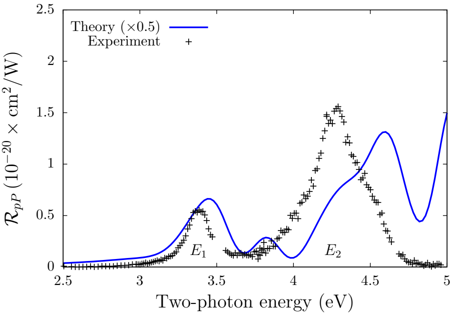
$\mathcal{R}_{sP}$ for $\theta = 65$ and $\phi = 45$ at room temperature[13]

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

$\mathcal{R}_{pP}$ – Old vs. New

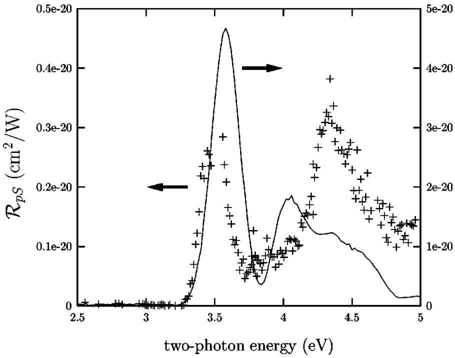


From *Mejia et al.*

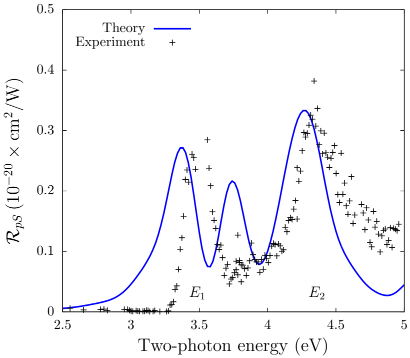


This work.

$\mathcal{R}_{pS}$ – Old vs. New



From *Mejia et al.*

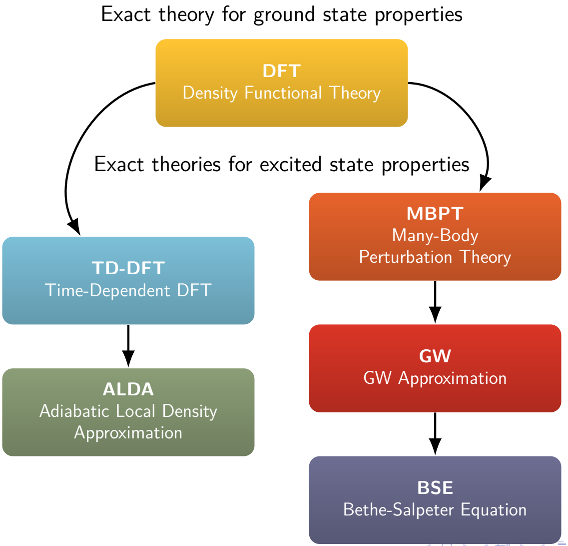


This work.

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?

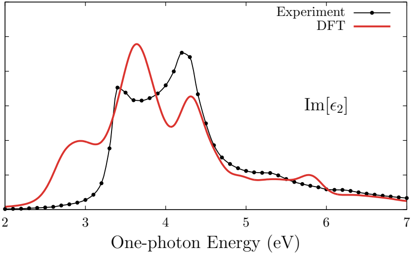

Exact theory for ground state properties
DFT
Density Functional Theory
Exact theories for excited state properties
TD-DFT
Time-Dependent DFT
ALDA
Adiabatic Local Density Approximation
MBPT
Many-Body Perturbation Theory
GW
GW Approximation
BSE
Bethe-Salpeter Equation

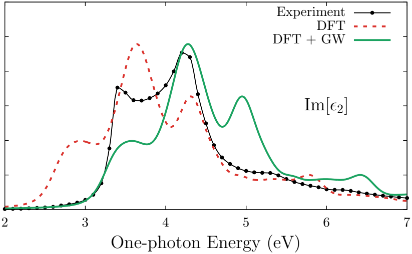
Where We Stand

DFT
Density Functional Theory

$\left(\begin{array}{c}\text{Scissors}\\\text{Correction}\end{array}\right)$
$+$

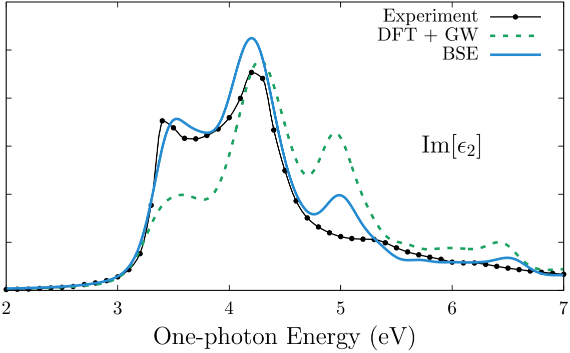
GW
GW Approximation





The State of the Art

BSE
Bethe-Salpeter Equation



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)

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)

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

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

http://www.abinit.org

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 weigths=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 weigths
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

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

SHGYield.py

```
def shgyield(gamma, riF): # function for the final yield
    RiF = SCALE * M2TOCM2 * PREFACTOR * (ONEE ** 2) * \
                    np.absolute((1/nl) * gamma * riF)**2
    broadened = broad(RiF, SIGMA)
    return broadened


#### Init ####
PARAM = parse_input(sys.argv[1]) # parses input file
MODE = str(PARAM['mode']) # establishes mode
MULTIREF = str(PARAM['multiref']) # if multiple reflections are considered
```

https://github.com/roguephysicist/SHGYield