Theoretical Optical Second-Harmonic Calculations for Surfaces

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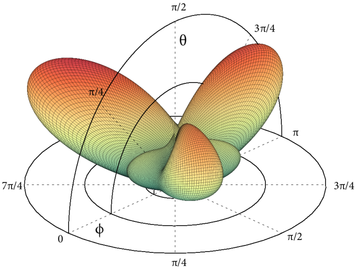
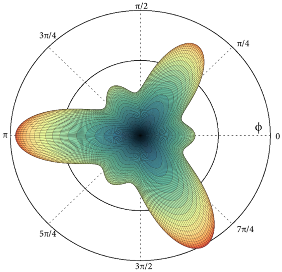
June 21, 2016

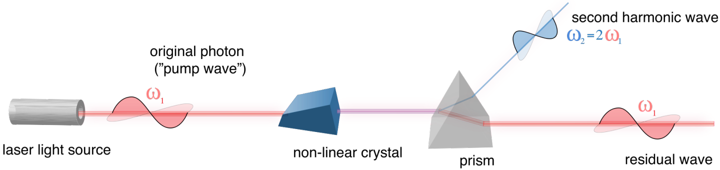




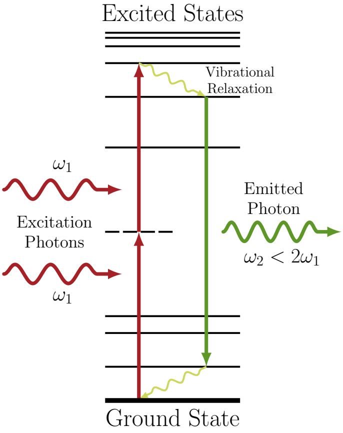
Second Harmonic Generation (SHG)

Characteristics[1]

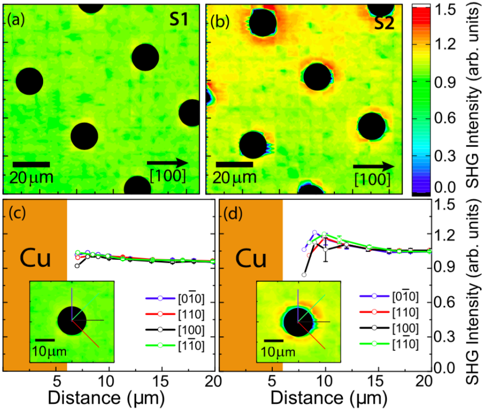
- Two photons of the same frequency combine
- Create one photon of double the frequency



[1] Image: Jon Chui


Excited States
Vibrational Relaxation
ω_1
Excitation Photons
ω_1
Emitted Photon
$\omega_2 < 2\omega_1$
Ground State
Virtual State
ω_1
Excitation Photons
ω_1
Emitted Photon
$\omega_2 = 2\omega_1$
Ground State

Applications



Test[2]

[2] *Cho et al.*, Appl. Phys. Lett. 108, 151602 (2016)

Second-order Nonlinear Effects

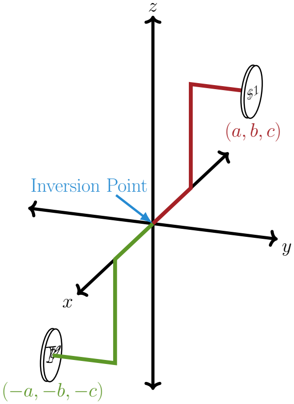
Second-order nonlinear processes[3] [4]

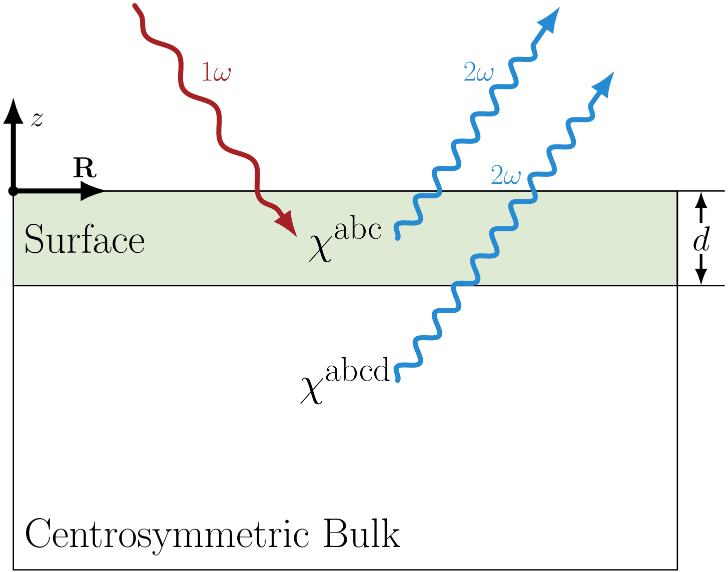
- Are dipole forbidden in the bulk of centrosymmetric materials
- Are related to $\chi^{(2)}$, the nonlinear susceptibility
- Have bigger dipolar (surface) than quadrupolar contributions

[3] *Armstrong et al.*, Phys. Rev. 127, 1918 (1962)
[4] *Bloembergen et al.*, Phys. Rev. 128, 606 (1962)

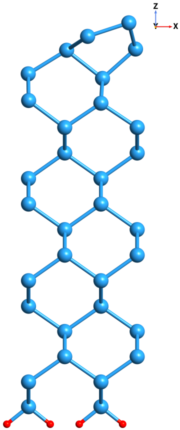
Centrosymmetric Materials

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

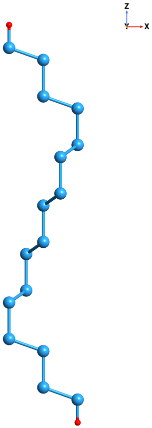



1ω
2ω
2ω
z
$\mathbf{R}$
Surface
χ^{abc}
d
χ^{abcd}
Centrosymmetric Bulk

Test Cases



Si(001)(2×1)



Si(111)(1×1):H

Our new formulation adds three contributions:[5]

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

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

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

We express the electron velocity operator as

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

which includes the nonlocal part of the pseudopotential and the scissors correction, where

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

Layered Cut Function (3)

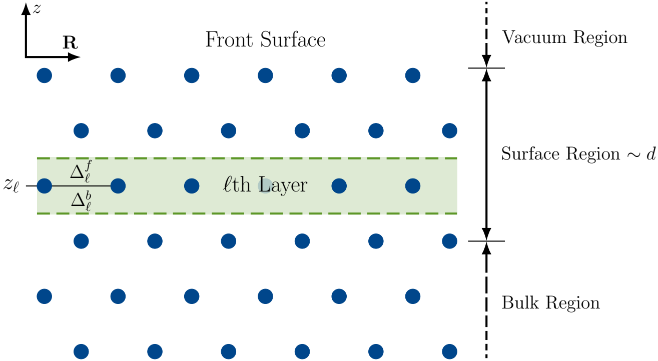
We introduce the cut function

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

that transforms any operator into its calligraphic counterpart as

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

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

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

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

Intraband Contribution

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

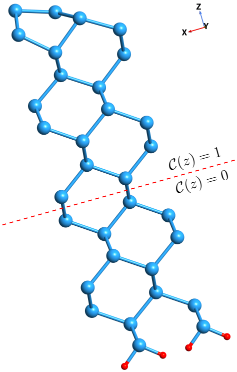
$$\mathrm{Im}[\chi^{\mathrm{abc}}_{i,2\omega}] = \frac{\pi|e|^3}{2\hbar^2}\int\frac{d^3k}{8\pi^3}\sum_{vc}\frac{4}{(\omega^\Sigma_{cv})^2}\left[\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a}}_{vc}\left\{\left(r^{\mathrm{b}}_{cv}\right)_{;k^{\mathrm{c}}}\right\}\right] - \frac{2\mathrm{Re}\left[\mathcal{V}^{\Sigma,\mathrm{a}}_{vc}\left\{r^{\mathrm{b}}_{cv}\Delta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

Coding

abinit, DP, tiniba

The Si(001)(2×1) Slab

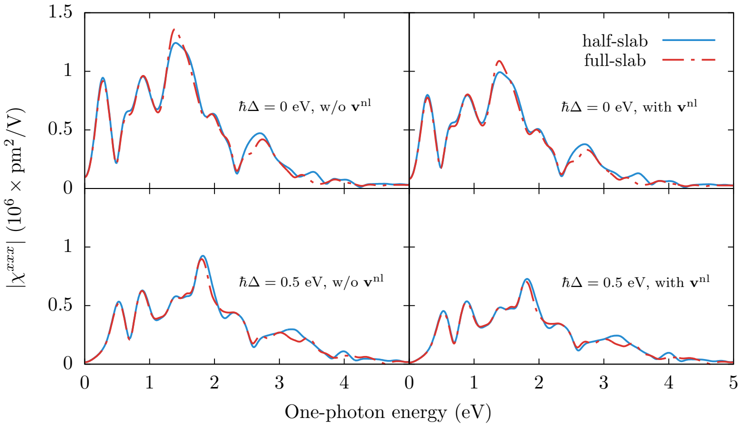
2×1 reconstruction $\Rightarrow \chi^{xxx}_{2\times1} \neq 0$



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

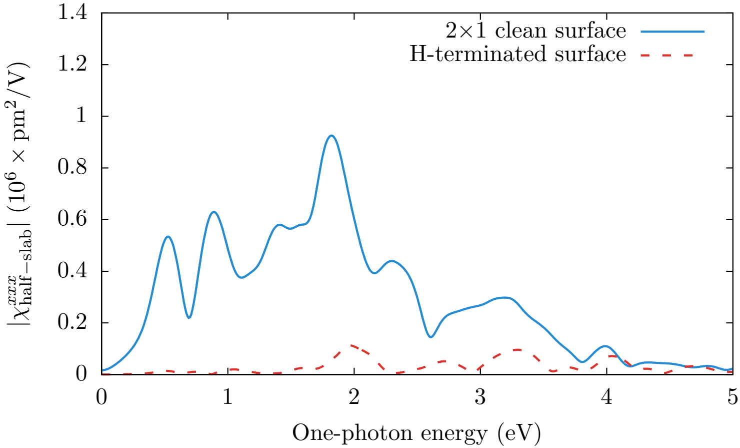
Convergence is achieved with 32 layers of Si.

Half-slab vs. Full-slab



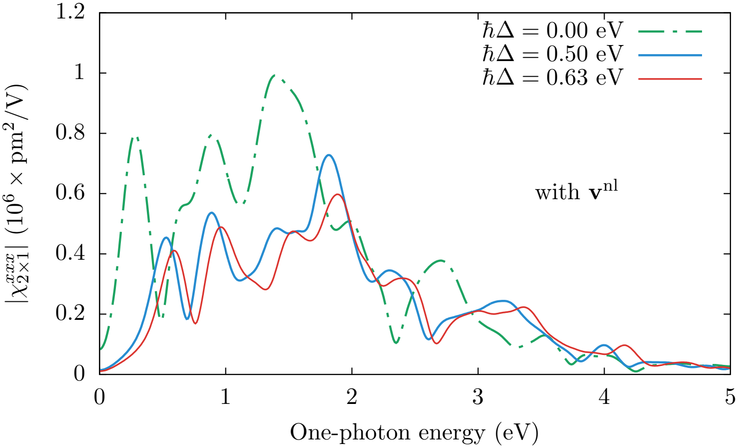
More layers would produce even better results.

oh snap mofo



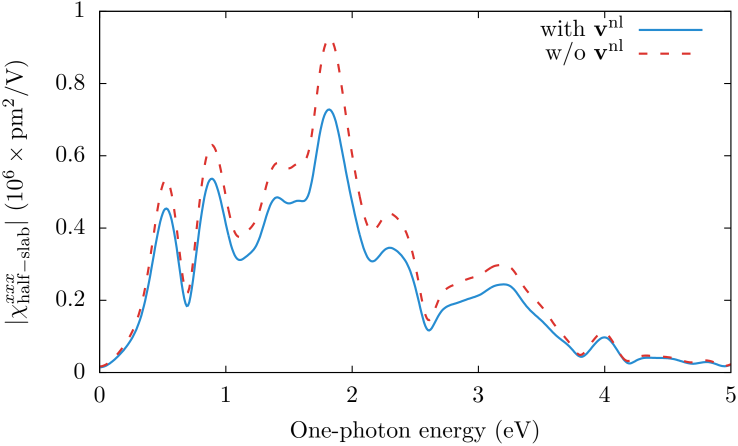
wait until calc finishes yo

Three Values of the Scissors Correction



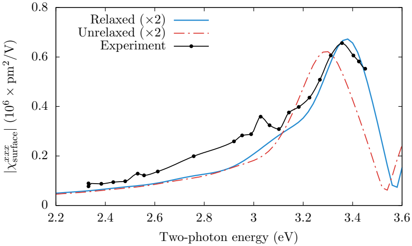
The 2×1 reconstructed surface has surface states, so the spectrum shifts non-rigidly.

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 of by 15-20%.

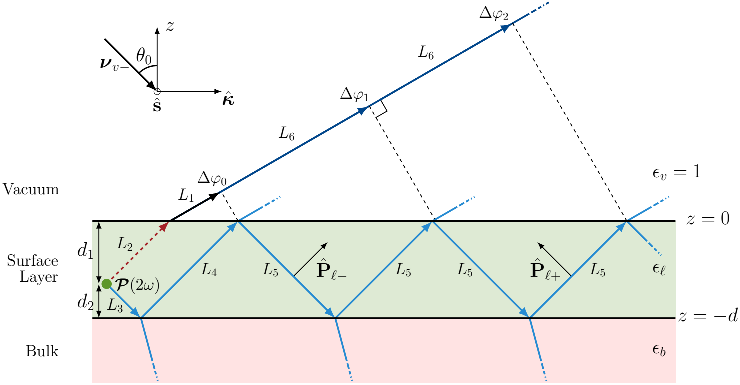
χ for the Si(111)(1×1):H surface[6]



Relaxing the Structure

1. Worth the time and effort
2. We'll talk about temp later

[6] Experimental data from Appl. Phys. A 63, 533 (1996)


z
θ_0
$\boldsymbol{\nu}_{v-}$
$\hat{\mathbf{s}}$
$\hat{\boldsymbol{\kappa}}$
$\Delta\varphi_2$
L_6
$\Delta\varphi_1$
L_6
$\Delta\varphi_0$
L_1
Vacuum
$\epsilon_v = 1$
$z = 0$
d_1
L_2
Surface Layer
L_4
L_5
$\hat{\mathbf{P}}_{\ell-}$
L_5
L_5
$\hat{\mathbf{P}}_{\ell+}$
L_5
ϵ_ℓ
$\boldsymbol{\mathcal{P}}(2\omega)$
d_2
L_3
$z = -d$
Bulk
ϵ_b

Explicit Expressions for $\mathcal{R}$

The SSHG yield is

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

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,

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

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

Explicit Expressions for $\mathcal{R}$

In particular, for the (111) surface we have

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

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

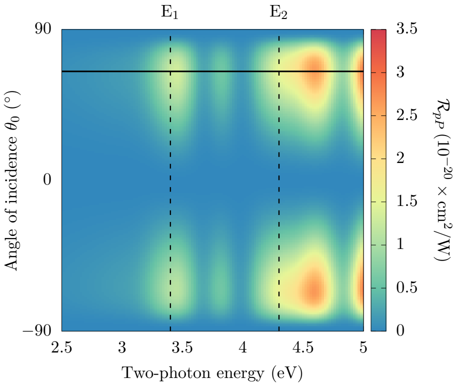
$$
r_{pS}^{(111)} = -\left(r_p^{M-}\right)^2 w_\ell^2\chi^{xxx}\sin 3\phi,
$$

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

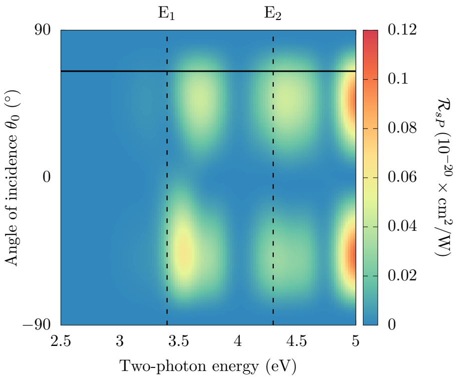
About the Code

python, shgyield.py, github, robustness

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

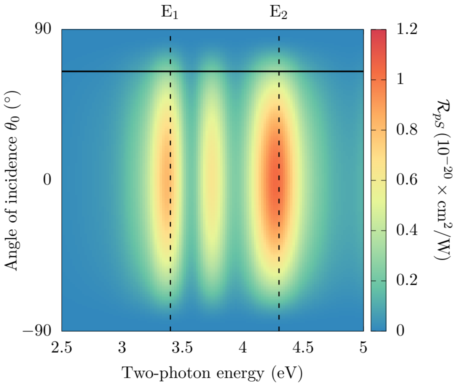


$\mathcal{R}_{pP}$

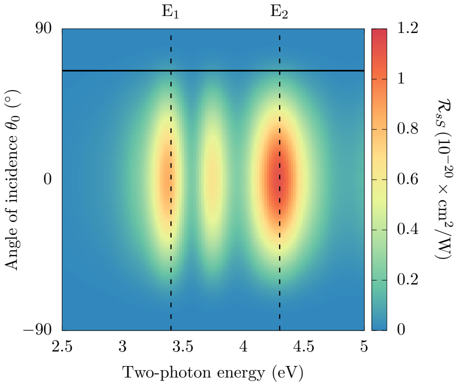


$\mathcal{R}_{sP}$

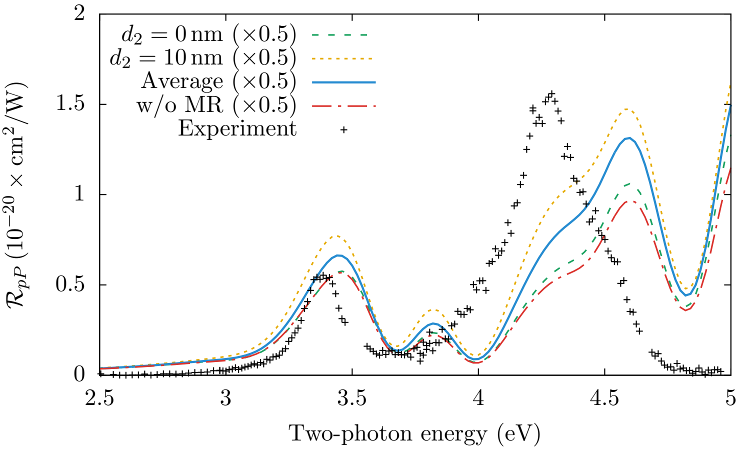
Si(111)(1×1):H – Outgoing S polarization

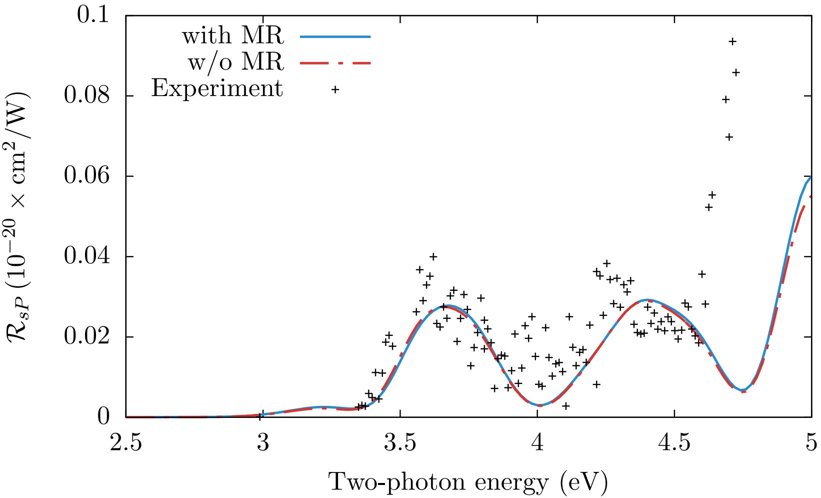


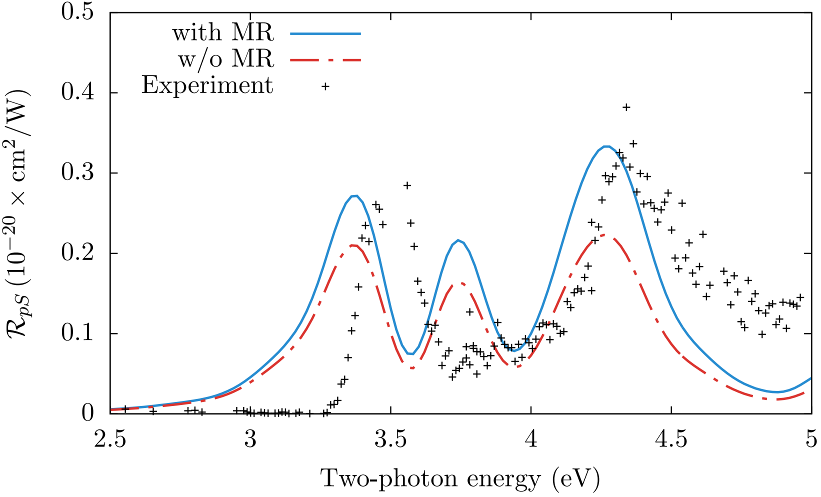
$\mathcal{R}_{pS}$



$\mathcal{R}_{sS}$


$d_2 = 0\,\mathrm{nm}$ (×0.5)
$d_2 = 10\,\mathrm{nm}$ (×0.5)
Average (×0.5)
w/o MR (×0.5)
Experiment
$\mathcal{R}_{pP}$ ($10^{-20} \times \mathrm{cm}^2/\mathrm{W}$)
Two-photon energy (eV)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5


with MR
w/o MR
Experiment
0.1
0.08
0.06
0.04
0.02
0
2.5
3
3.5
4
4.5
5
$\mathcal{R}_{sP}$ ($10^{-20}\times$ cm^2/W)
Two-photon energy (eV)


with MR
w/o MR
Experiment
0.5
0.4
0.3
0.2
0.1
0
2.5
3
3.5
4
4.5
5
$\mathcal{R}_{pS}\,(10^{-20} \times \mathrm{cm}^2/\mathrm{W})$
Two-photon energy (eV)

Title

- Item 1
- Item 2
- Item 3

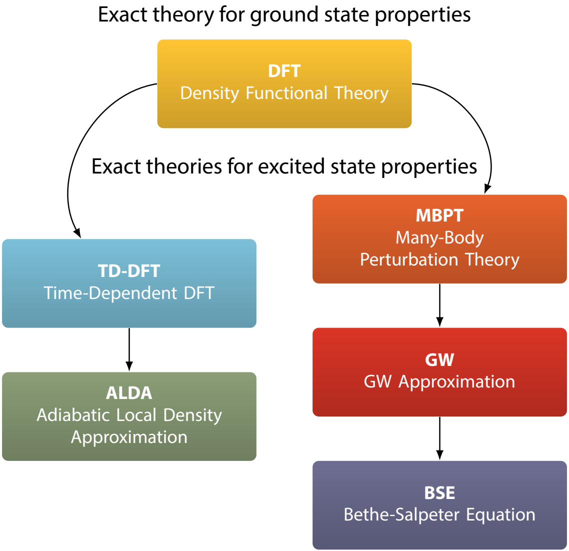
Some starting text,

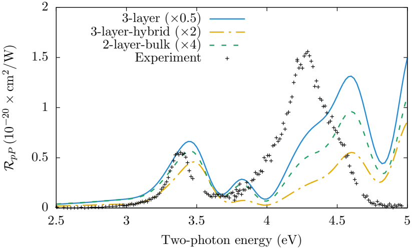
$$E = mc^2,$$

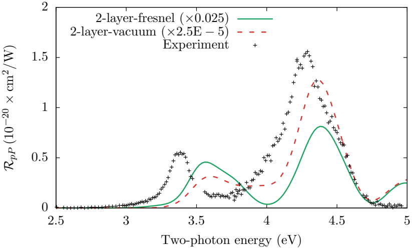
and more text.

A block

- Item 1
- Item 2


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


3-layer (×0.5)
3-layer-hybrid (×2)
2-layer-bulk (×4)
Experiment
$\mathcal{R}_{pP}$ (10^{-20} × cm^2/W)
Two-photon energy (eV)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5


2-layer-fresnel (×0.025)
2-layer-vacuum (×2.5E − 5)
Experiment
$\mathcal{R}_{pP}$ (10^{-20} × cm^2/W)
Two-photon energy (eV)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5