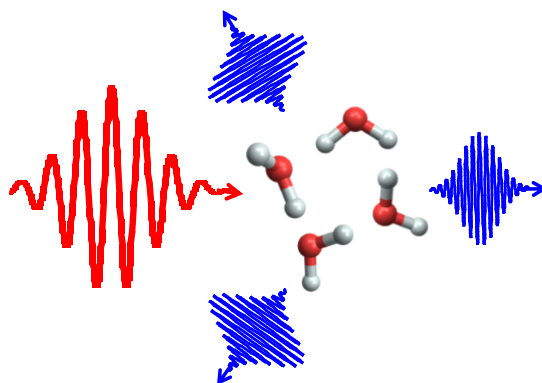


PySHS V2.0 : a Computational Second Harmonic Scattering Code



User Manual 2.0 Written by:

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This user manual is distributed along with the pySHS software to aid in setting up the input files required for carrying out a Second Harmonic Scattering simulation. Every effort is made to release the most updated and complete version of the manual. To report any inconsistencies, errors or missing information, or to suggest improvements, send email to pierre-marie.gassin@enscm.fr.

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The people who have contributed to the development of the code include:

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- Dr Gaelle Gassin

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Chapter 1

Introduction

1) What is new in PySHS V2.0?

PySHS V1 was a collection of different programs written in python which can compute the Second Harmonic Intensity Scattered by different classes of objects. For large systems with numerous correlated dipoles ($N > 1000$), the calculation in PySHS V1.0 can be very long because of the intrinsic limitation of the Python software. The new version, PySHS V2.0, has been entirely rewritten in C and it increases greatly the speed of the calculation.

The other modifications of the V2.0 code concern its ability to take imaginary refractive index for the medium as requested by some users. The definition of the Euler angle and the transformation matrix has been changed in order to increase the clarity and to avoid confusion. To summarize this software, PySHS V2.0 is able to compute the Second Harmonic Intensity Scattered by different classes of objects:

- incoherent molecules in solution (see program HRS)
- supramolecular structures formed by correlated molecules (see program SHS).
- colloidal sphere in solution. (see program sphere_SHS)

2) Distribution

PySHS has been written in C. So, a compilation step is required (see the following paragraph). After unpacking the pySHS distribution, the parent PySHS directory will contain the following subdirectories:

- Documentation

It contains the user_guide. You may find most answers to your questions here.

- Examples

Contains some examples of calculation and in particular the input and output files.

- Src

Contains the pySHS source code and some scripts used to generate the input files.

- Work

It is the directory where the user can store the input and output files.

3)Compilation and Run

A C compiler has to be installed (on macOS or linux, gcc is normally already install, to check it, write in a command line: `gcc --version`). To compile PySHS under MacOS or linux, enter in a terminal:

```
>gcc -o Work/SHS Src/SHS.c -lm
```

This command will create the SHS executable file in the Work directory.

Do the same things for the sphere_SHS program and for th HRS_program:

```
>gcc -o Work/sphere_SHS Src/sphere_SHS.c -lm
```

```
>gcc -o Work/HRS Src/HRS.c -lm
```

Running a pySHS calculation

Depending of the pySHS program used, it requires one (sphere_SHS or HRS programs) or two input files (SHS program) in order to run.

to launch, the SHS program, in the PySHS_V2 directory enter:

```
>./Work/SHS <Keyword> <inputbeta> <input orientation> <outputfile>
```

where <Keyword> is equal to “polarplot_90” or “polarplot_180” or “angle_scattering” depending on the computation you want to perform. <inputbeta>, <input_orientation> and <outputfile> are respectively the name of the input file containing the hyperpolarizability of the molecule, the name of the input file containing the orientation and position of the molecules and the output file.

to launch, the sphere_SHS program, enter:

```
>./Work/sphere_SHS <Keyword> <inputbeta> <outputfile>
```

where <Keyword> is equal to “polarplot_90” or “polarplot_180” or “angle_scattering” depending on the computation you want to perform.

inputbeta, and outputfile are respectively the name of the input file containing the hyperpolarizability of the molecule, and the output file. Another output files formatted to be plotted with gnuplot (<http://www.gnuplot.info>) are also generated: out_plot and out_arrows_gnuplot.

Chapter 2

General Equations Implemented in PySHS

1) The Notation

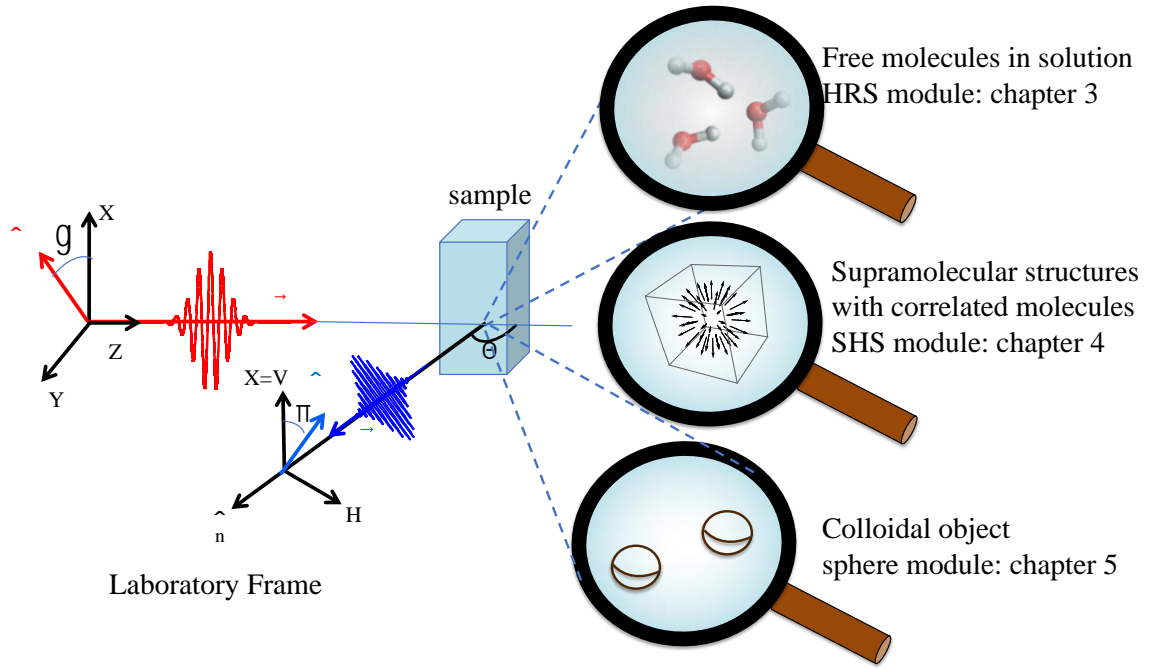


Figure 1: definition and notation

The fundamental light at the ω frequency is defined by its wave vector $\vec{k} = k\hat{e}_z$ and its polarization direction \hat{e}_{p-in} . The input polarization angle γ is equal to the angle between $(\hat{e}_x, \hat{e}_{p-in})$

The second harmonic scattered light at the 2ω frequency is defined by its wave vector $\vec{K} = K\hat{e}_n$ and the angle (\hat{e}_z, \hat{e}_n) defines the scattered angle Θ . The polarization of the second harmonic scattered light is defined by \hat{e}_{p-out} and the output polarization angle Π is equal to the angle between $(\hat{e}_x, \hat{e}_{p-out})$. In the laboratory frame, we have the following relation:

$$\hat{e}_n = \begin{pmatrix} 0 \\ \sin(\Theta) \\ \cos(\Theta) \end{pmatrix} \quad \hat{e}_{p-in} = \begin{pmatrix} \cos(\gamma) \\ \sin(\gamma) \\ 0 \end{pmatrix} \quad \hat{e}_{p-out} = \begin{pmatrix} \cos(\Pi) \\ \sin(\Pi)\cos(\Theta) \\ \sin(\Pi)\sin(\Theta) \end{pmatrix} \quad (1-a,b,c)$$

The scattered wave vector $\vec{\Delta k}$ is defined as follow: $\vec{\Delta k} = 2\vec{k} - \vec{K} = \begin{pmatrix} 0 \\ -K\sin(\Theta) \\ 2k - K\cos(\Theta) \end{pmatrix} \quad (2)$

2) Expression of the SHS Intensity

2.1) Incoherent Second Harmonic Scattering

The Second Harmonic Scattering of uncorrelated molecule in solution is usually referred as Hyper Rayleigh Scattering (HRS) and can be expressed as:

$$I_{HRS}(\hat{e}_{p-in}, \hat{e}_{p-out}, \hat{e}_n) = I_{HRS}(\gamma, \Pi, \Theta) = \langle \vec{\beta}_{eff}(\gamma, \Pi, \Theta) \cdot \vec{\beta}_{eff}^*(\gamma, \Pi, \Theta) \rangle \quad (3)$$

Here $\vec{\beta}_{eff} = (\hat{e}_n \times \vec{\beta} : \hat{e}_p \hat{e}_p \times \hat{e}_n)$ and $\vec{\beta}$ is the second order hyperpolarisability of the molecule expressed in the laboratory frame. The link between the expression of $\vec{\beta}$ in the laboratory and microscopic frames is:

$$\beta_{IJK, Labo}(\varphi, \theta, \psi) = \sum_i \sum_j \sum_k T_{Ii}(\varphi, \theta, \psi) T_{Jj}(\varphi, \theta, \psi) T_{Kk}(\varphi, \theta, \psi) \beta_{ijk, microscopic} \quad (4)$$

The angle φ, θ, ψ are defined in the figure 2 and the transformation matrix $T(\varphi, \theta, \psi)$ between the microscopic and the laboratory frame is given within the ‘ZYZ’ convention:

$$T(\varphi, \theta, \psi) = \begin{pmatrix} \cos[\theta] \cos[\varphi] \cos[\psi] - \sin[\varphi] \sin[\psi] & -\cos[\psi] \sin[\varphi] - \cos[\theta] \cos[\varphi] \sin[\psi] & \cos[\varphi] \sin[\theta] \\ \cos[\theta] \cos[\psi] \sin[\varphi] + \cos[\varphi] \sin[\psi] & \cos[\varphi] \cos[\psi] - \cos[\theta] \sin[\varphi] \sin[\psi] & \sin[\theta] \sin[\varphi] \\ -\cos[\psi] \sin[\theta] & \sin[\theta] \sin[\psi] & \cos[\theta] \end{pmatrix} \quad (5)$$

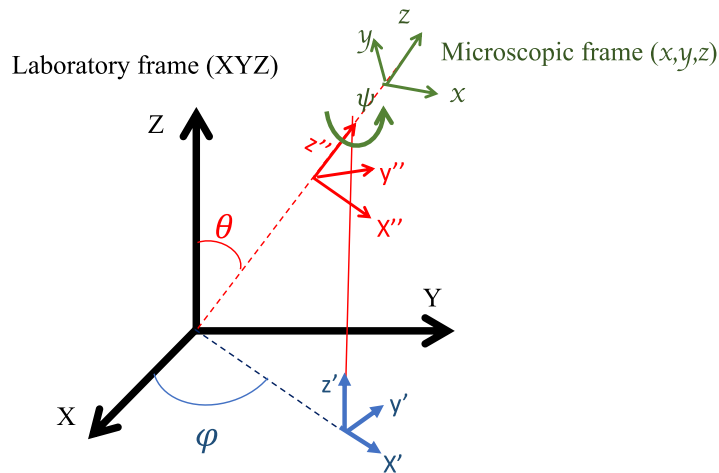


Figure 2: Definition of the angles φ, θ, ψ which describe the orientation of the scattered object in the laboratory frame.

Finally, the bracket means the average over all the orientation of the scattered object.

$$\langle . \rangle = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} \int_{\psi=0}^{2\pi} \sin\theta d\theta d\varphi d\psi \quad (6)$$

The development of the above equations gives the following expression of $\vec{\beta}_{eff}$ expressed in term of the tensor β components.

$$\vec{\beta}_{eff}(\gamma, \theta) = \begin{pmatrix} \beta_{XXX} \cdot \cos^2(\gamma) + 2 \beta_{XXY} \cdot \cos(\gamma) \sin(\gamma) + \beta_{XYY} \cdot \sin^2(\gamma) \\ [\beta_{YYY} \cdot \cos^2(\gamma) + 2 \beta_{YXY} \cdot \cos(\gamma) \sin(\gamma) + \beta_{YYY} \cdot \sin^2(\gamma)] \cdot \cos^2(\theta) - [\beta_{ZYY} \cdot \cos^2(\gamma) + 2 \beta_{ZXY} \cdot \cos(\gamma) \sin(\gamma) + \beta_{ZYY} \cdot \sin^2(\gamma)] \cdot \cos(\theta) \sin(\theta) \\ - [\beta_{YYY} \cdot \cos^2(\gamma) + 2 \beta_{YXY} \cdot \cos(\gamma) \sin(\gamma) + \beta_{YYY} \cdot \sin^2(\gamma)] \cdot \cos(\theta) \sin(\theta) + [\beta_{ZYY} \cdot \cos^2(\gamma) + 2 \beta_{ZXY} \cdot \cos(\gamma) \sin(\gamma) + \beta_{ZYY} \cdot \sin^2(\gamma)] \sin^2(\theta) \end{pmatrix} \quad (7)$$

2.2) Coherent Second Harmonic Scattering of N fully correlated molecules

The Second Harmonic Scattering of N fully correlated molecule in solution can be expressed as:

$$I_{SHS}(\hat{e}_{p-in}, \hat{e}_{p-out}, \hat{e}_n) = I_{SHS}(\gamma, \Pi, \Theta) = \langle \vec{\beta}_{eff}(\gamma, \Pi, \Theta) \cdot \vec{\beta}_{eff}^*(\gamma, \Pi, \Theta) \rangle \quad (8)$$

$$\text{Here } \vec{\beta}_{eff} = (\hat{e}_n \times \vec{\beta}_t : \hat{e}_p \hat{e}_p \times \hat{e}_n) \quad \text{with } \vec{\beta}_t = \sum_j^N \vec{\beta}_j e^{i\vec{\Delta k} \cdot \vec{r}_j} \quad (9-10)$$

where $\vec{\beta}_j$ is the second order hyperpolarisability of the molecule j located at the position \vec{r}_j and $\vec{\Delta k}$ has been defined above. To perform the I_{SHS} calculation, the user needs to specify the position $\vec{r}_j = (X'_j, Y'_j, Z'_j)$ and orientation $(\varphi'_j, \theta'_j, \psi'_j)$ of each molecule in the mesoscopic frame.

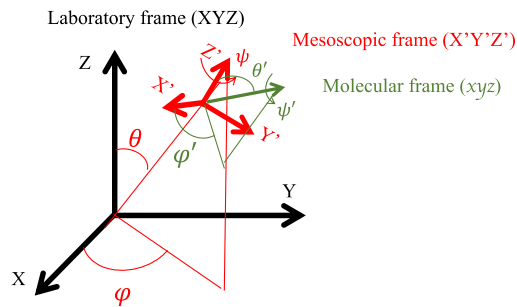


Figure 3: Definition of the angles φ , θ , ψ and φ' , θ' , ψ' which describe the orientation of the scattered object in the laboratory and mesoscopic frame.

2.3) Second Harmonic Scattering by a sphere

In the case of colloidal object in solution like a sphere, we can express the I_{SHS} intensity by introducing an effective nonlinear susceptibility $\overleftrightarrow{\Gamma}^{(2)}$, which represents the nonlinear response of the entire particle surface¹:

$$I_{SHS}(\hat{e}_{p-in}, \hat{e}_{p-out}, \hat{e}_n) = I_{SHS}(\gamma, \Pi, \Theta) = \langle \vec{\beta}_{eff}(\gamma, \Pi, \Theta) \cdot \vec{\beta}_{eff}^*(\gamma, \Pi, \Theta) \rangle \quad (11)$$

$$\text{Here } \vec{\beta}_{eff} = (\hat{e}_n \times \overleftrightarrow{\Gamma}^{(2)} : \hat{e}_p \hat{e}_p \times \hat{e}_n) \quad (12)$$

$$\text{and } \overleftrightarrow{\Gamma}^{(2)} = \oint_{\text{surface of the particle}} \overleftrightarrow{\chi}^{(2)} \cdot e^{i\overleftrightarrow{\Delta k} \cdot \vec{r}} d\vec{r} \quad (13)$$

where $\overleftrightarrow{\chi}^{(2)}$ is the surface second order nonlinear susceptibility of the particle.

¹ Roke and al Phys. Rev. B **70**, 115106 (2004)

Chapter 3

Incoherent Second Harmonic Scattering : HRS program

1) The different input/output

The program HRS compute the polarization resolved incoherent SHS Intensity at an angle of $\Theta = 90^\circ$ or $\Theta = 0^\circ$. The only input parameters of this program is:

- the microscopic hyperpolarizability tensor. Those components are passed through the input_beta file.

Format of the input_beta file:

line 1: comments

line 2: "xxx" space value

line3: "xxy" space value

And so on...

The output calculation are the coefficient a_{Π}^{Θ} , b_{Π}^{Θ} , c_{Π}^{Θ} where $\Pi = V$ or H and $\Theta = 90^\circ$ or 0 .

They are defined by:

$$I_{SHS}^{\Theta}(\gamma, \Pi) = a_{\Pi}^{\Theta} \cdot \cos^4(\gamma) + b_{\Pi}^{\Theta} \cdot \cos^2(\gamma) \sin^2(\gamma) + c_{\Pi}^{\Theta} \cdot \sin^4(\gamma) \quad (14)$$

The comparison with equation (7) gives:

$$a_V^{90} = a_V^{180} = \langle \beta_{XXX} \beta_{XXX}^* \rangle \quad (15)$$

$$c_V^{90} = c_V^{180} = \langle \beta_{XYY} \beta_{XYY}^* \rangle \quad (16)$$

$$b_V^{90} = b_V^{180} = \langle 4\beta_{XXY} \beta_{XXY}^* + \beta_{XXX} \beta_{XYY}^* + \beta_{XXX}^* \beta_{XYY} \rangle \quad (17)$$

$$a_H^{90} = \langle \beta_{ZXX} \beta_{ZXX}^* \rangle \quad (18)$$

$$a_H^{180} = \langle \beta_{YXX} \beta_{YXX}^* \rangle \quad (19)$$

$$c_H^{90} = \langle \beta_{ZYY} \beta_{ZYY}^* \rangle \quad (20)$$

$$c_H^{180} = \langle \beta_{YYX} \beta_{YYX}^* \rangle \quad (21)$$

$$b_H^{90} = \langle 4\beta_{ZXY} \beta_{ZXY}^* + \beta_{ZXX} \beta_{ZYY}^* + \beta_{ZXX}^* \beta_{ZYY} \rangle \quad (22)$$

$$b_H^{180} = \langle 4\beta_{YXY} \beta_{YXY}^* + \beta_{YXX} \beta_{YYX}^* + \beta_{YXX}^* \beta_{YYX} \rangle \quad (23)$$

Additional coefficient I_2 and I_4 are also given. They are defined by:

$$I_2^{\Theta, \Pi} = \frac{4(a_{\Pi}^{\Theta} - c_{\Pi}^{\Theta})}{(3a_{\Pi}^{\Theta} + b_{\Pi}^{\Theta} + 3c_{\Pi}^{\Theta})} \quad (24)$$

$$I_4^{\Theta, \Pi} = \frac{(a_{\Pi}^{\Theta} - b_{\Pi}^{\Theta} + c_{\Pi}^{\Theta})}{(3a_{\Pi}^{\Theta} + b_{\Pi}^{\Theta} + 3c_{\Pi}^{\Theta})} \quad (25)$$

The program will also show a graphic with the polarization plot.

The program can also compute the angle resolved incoherent SHS Intensity for different polarization states:

- $I_H(0^\circ) = I_{HRS}(\gamma = 0^\circ, \Pi = 90^\circ, \Theta)$
- $I_H(90^\circ) = I_{HRS}(\gamma = 90^\circ, \Pi = 90^\circ, \Theta)$
- $I_V(0^\circ) = I_{HRS}(\gamma = 0^\circ, \Pi = 0^\circ, \Theta)$
- $I_V(90^\circ) = I_{HRS}(\gamma = 90^\circ, \Pi = 0^\circ, \Theta)$

The user has to specify the number of point between 0 and 180° that he want to compute.

2) Command line

In a terminal and in the PySHS_V2 directory, enter the following command:

```
>./Work/HRS <Keyword> <inputbeta> <outputfile>
```

where <Keyword> is equal to “polarplot_90” or “polarplot_180” or “angle_scattering” depending on the computation you want to perform.

inputbeta, and outputfile are respectively the name of the input file containing the hyperpolarizability of the molecule, and the output file.

To plot the polarization plot with gnuplot, (<http://www.gnuplot.info>), open gnuplot and enter in the command:

```
>plot for [col=2:3] "out_plot" using 1:col with lines title columnheader
```

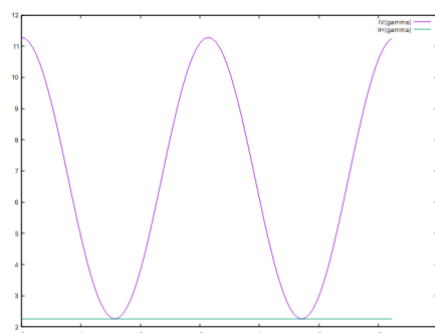


Figure 4: Polarization plot using gnuplot

Chapter 4

Coherent Second Harmonic Scattering of Supramolecular structures : SHS Module

1) The different input/output

The program SHS compute the polarization resolved SHS Intensity at an angle of respectively $\Theta = 90^\circ$ or $\Theta = 0^\circ$ or can also compute the angle resolved SHS Intensity for different polarization state as explained in chap 3. The user has to specify the number of point to be compute.

Different input parameters have to be given:

- microscopic hyperpolarizability tensor components are expressed in a file input_beta like in chap 3.
- the position and orientation of each dipole of the aggregate are expressed in the mesoscopic frame in an input_file2. The format of this input file is a 6 columns per line containing in the order $(\varphi'_j, \theta'_j, \psi'_j, x'_j, y'_j, z'_j)$ which represent the orientation and position of the molecule j. The number of line is the number of molecule in the aggregate. The angles $\varphi'_j, \theta'_j, \psi'_j$ **have to be given in radian**.

Some specific script also given in ./Scr folder can generate these input files for different geometry (sphere, cylinder ...)

- the refractive index, the laser wavelength (expressed in nanometer), the number of dipole in the aggregate. All these argument are asked by the program.

The output calculation are the coefficient a_{Π}^{Θ} , b_{Π}^{Θ} , c_{Π}^{Θ} , $I_2^{\Theta, \Pi}$ and $I_4^{\Theta, \Pi}$ as explained in the HRS module. Additionnal coefficient $b1_{\Pi}^{\Theta}$ and $b2_{\Pi}^{\Theta}$ are also given. Indeed, in the developpment of equation (3) appears 2 terms that are zero in HRS calculus but may be eventually no vanished in some special case in SHS calculus, so their values are also given in the output. Those term are defined by:

$$I_{SHS}^{\Theta}(\gamma, \Pi) = a_{\Pi}^{\Theta} \cos^4(\gamma) + b_{\Pi}^{\Theta} \cos^2(\gamma) \sin^2(\gamma) + c_{\Pi}^{\Theta} \sin^4(\gamma) + b1_{\Pi}^{\Theta} \cos^3(\gamma) \sin(\gamma) + b2_{\Pi}^{\Theta} \cos(\gamma) \sin^3(\gamma) \quad (26)$$

2)Command line

In a terminal, enter the following command:

```
>./Work/SRS <Keyword> <inputbeta> <input_position_orientation> <outputfile>
```

where <Keyword> is equal to polarplot_90 or polarplot_180 or angle_scattering depending on the computation you want to perform.

inputbeta, input_orientation and outputfile are respectively the name of the input file containing the hyperpolarizability of the molecule, the name of the input file containing the orientation and position of the molecules and the output file.

To plot the polarization plot with gnuplot, open gnuplot and enter in the command:

```
>plot for [col=2:3] "out_plot" using 1:col with lines title columnheader
```

To see the position of each dipole in space, open gnuplot and enter in the command:

```
>splot "out_arrows_gnuplot" with vectors filled
```

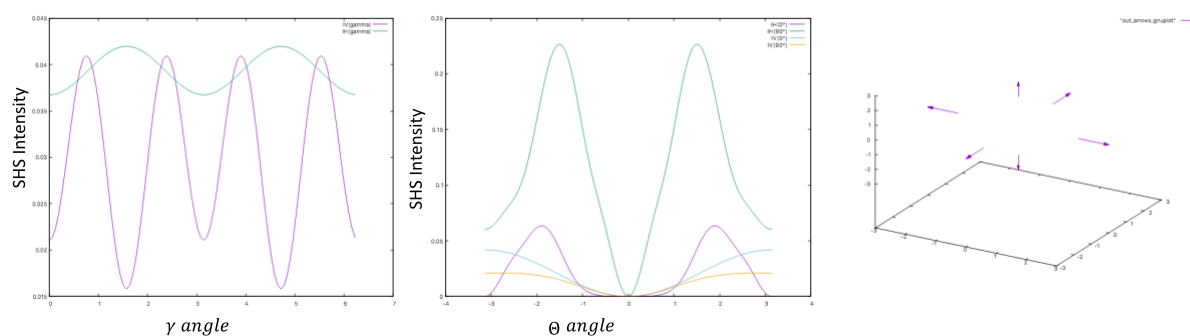


Figure 5: polarization plot at 90° (left), angle resolved SHS Intensity (middle) and position orientation of each dipole in the supramolecular aggregate (right).

Chapter 5

Coherent Second Harmonic Scattering of Colloidal object : Sphere Module

1) The different input/output

Program sphere_SHS compute the polarization resolved SHS Intensity of a sphere with a surface nonlinear susceptibility at an angle of respectively $\Theta = 90^\circ$ and $\Theta = 0^\circ$ or can also compute the angle resolved SHS Intensity for different polarization state as explained in chap 3.

Different input parameters have to be given:

- Surface second order susceptibility tensor components are expressed in a file input_ki(2) like in chap 3.
- the refractive index, the laser wavelength (expressed in nm), the radius of the sphere. All these argument are asked by the program.
- The output calculation are the coefficient a_{Π}^{Θ} , b_{Π}^{Θ} , c_{Π}^{Θ} , $I_2^{\Theta,\Pi}$ and $I_4^{\Theta,\Pi}$ for the polarplot calculation and the IH(0°); IH(90°); IV(0°), IV(90°) for the angular distribution calculation.

Chapter 6

Additional Scripts and Perspectives

1) Scripts to generate orientation-position inputfile in SHS module

- “script_sphere.py” : It generates the position of N dipoles onto a sphere of specified radius and with a radial orientation. This script is based on this code². The input parameters asked by the program are the radius of the sphere and number of dipoles.
- “script_sphere_random.py”: It generates the position of N dipoles onto a sphere of specified radius and with a specified normal distribution orientation around the radial direction. The input parameters asked by the program are the radius of the sphere, number of dipoles and the standard deviation (sigma) of the normal distribution around the radial direction.
- “script_spheroid.py”: It generates the position of N dipoles onto a spheroid of specified radius a and c and with a normal orientation.
- “script_spheroid_random.py”: It generates the position of N dipoles onto a spheroid of specified a and c radius and with a specified normal distribution orientation around the normal direction.
- “script_cylinder.py”: It generates the position of dipoles uniformly spaced onto a cylinder of specified length and radius with a normal orientation.
- “script_cube.py”: It generates the position of dipoles uniformly spaced onto a cube of specified length with a normal orientation.

In all script, the command line is:

² <https://bduvenhage.me/geometry/2019/07/31/generating-equidistant-vectors.html>
<https://www.openprocessing.org/sketch/41142>

```
>python3 Src/script_XXX.py Work/output_script
```

Where “XXX” is “sphere” or “sphere_random” or “spheroid” or “cylinder” or “cube”.

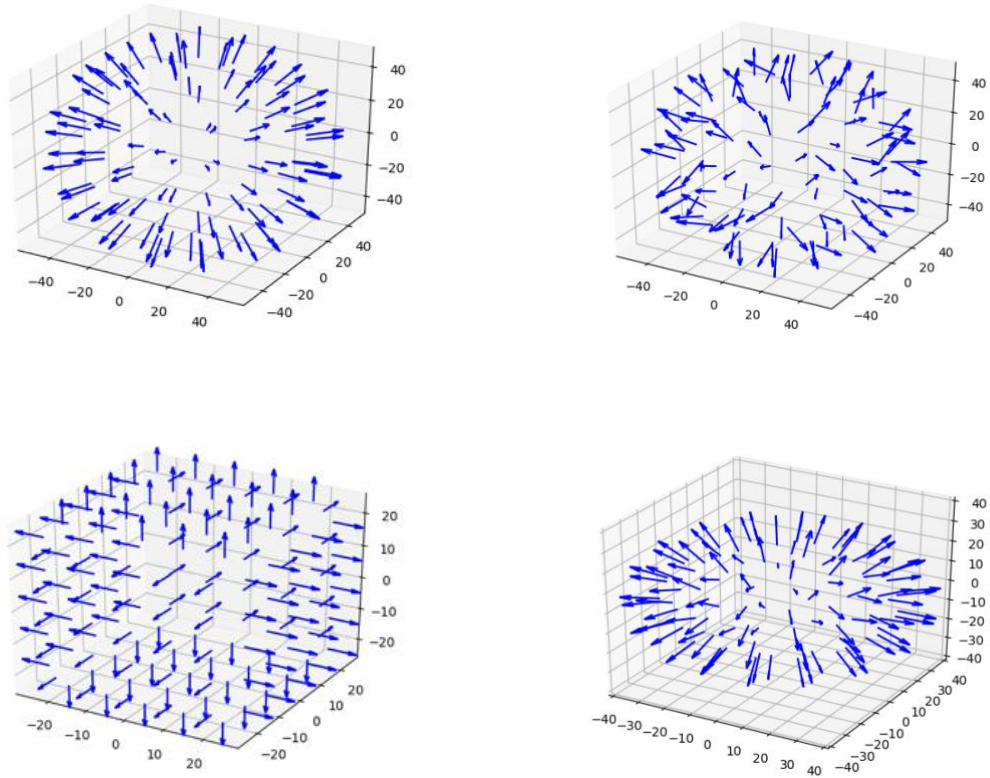


Figure 7 : Some dipoles organization obtained with the various script, in the order: script_sphere.py (radius =50, N=100), script_sphere_random.py (radius =50, N=100, sigma=0.5), script_cube.py (length=50, N=100), script_spheroid.py (a=40,c=20, N=100).

2) Perspectives

PySHS will likely evolved. This evolution will include other kind of geometry in sphere module, like cylinder, cubic geometry etc...

Moreover ki(3) effect, which are not taken into account in PySHS V2.0 will probably be added in a future version.