A Python Approach to Non-linear Spectroscopy Phasematch Modeling

Dr. Kent Meyer

University of Wisconsin-Madison

The interaction of multiple oscillating electric fields in a material generates a local polarization that can launch new electric fields, many of which are at combinations of the inputs. The output fields can become detectable when the inputs are strong enough to distort molecules within the overlapping volume. Typically, the input fields are established with short, intense laser pulses concentrated at a focus in a sample. The output non-linear fields are increased as the input fields approach molecular resonances. Often, these resonances can be correlated with other resonances in a multi-dimensional manner. The non-linear optical methods encompassing these particular processes form the basis for a specialized field called coherent multidimensional spectroscopy (CMDS).

In thick samples, the output fields launched at the beginning of a sample can become out of phase with the fields launched at the end of the sample. This occurs because the launched electric field within in the sample is at a speed reduced by its refractive index, while the input fields generating the sample are moving at a speed given by their own refractive indices. As a result, the launched wave can be said to interfere with waves generated earlier. Often, the goal of CMDS is to maximize the signal by ensuring the fields constructively interfere through the entire sample, and even change the ways in which fields interact to cause constructive interference. This can be done in several ways but two important ones can be through the change in laser input angles with respect to the sample, and possibly modifying the wavelength of a beam that is not necessarily resonant. These ways modify the wavevector of at least one of the input beams such that the constructive interference can be maintained.

In an isotropic sample, the lowest order form of non-linear spectroscopy is called four-wave mixing (FWM) as it involves the interaction of three fields to launch a final fourth field. For FWM, an early work [1] presented a useful expression for describing the phasematching effects in such a medium. In that work, the FWM intensity I for a single layer isotropic sample was found to be proportional to its thickness *l* as

$$I \propto |M|^2 l^2,$$

Where

$$M = e^{-\frac{1}{2}a_4 l} \times \left(\frac{e^{i(\Delta k)l} e^{-\frac{1}{2}(\Delta a)l} - 1}{(i\Delta k - \frac{1}{2}\Delta a)l} \right),$$

and

$$\Delta a = (a(\omega_4) - (a(\omega_1) + a(\omega_2) + a(\omega_3))),$$
$$\Delta k = k_{4z} - (k_{1z} \pm k_{2z} \pm k_{3z}),$$

and implicit that $a_4 \equiv a(\omega_4)$. The *a* terms represent extinction coefficients and the expression is generally used with CGS units. It assumes the wavevectors of the input beams are pre-dominantly defined by their z-components, where z is the coordinate normal to the sample surface and the k_z terms being the projections of each wavevector along z. It is necessary to use $|M|^2 l^2$ for testing the validity of the calculations, since it is necessary to incorporate the *l* term to generate the simpler and more well-known expression $I \propto \sin c^2\left(\frac{(\Delta k) l}{2}\right)$ in the limit where $a_i \to 0 \; \forall \; i$.

The elegance to the above expression lies in the ability to generalize a model with multiple *m* layers. Assuming all layers *m* are isotropic and that the wavevectors for the beams are all dominated by a "z" coordinate, each successive layer's *M* factor can be determined by the expression:

$$M_m = \left(\prod_{\lambda=0}^{m} e^{-\frac{1}{2}a_{4,\lambda} l_\lambda}\right)\left(\prod_{\lambda=0}^{m-1} e^{i\Delta k_\lambda l_\lambda} e^{-\frac{1}{2}\Delta a_\lambda l_\lambda}\right) \times \left(\frac{e^{i\Delta k_m l_m} e^{-\frac{1}{2}\Delta a_m l_m} - 1}{(i\Delta k_m - \frac{1}{2}\Delta a_m) l_m}\right).$$

The above model can be useful for thin films and low-order attempts to model changes input electric fields may make in a thicker layer via simple discretization (e.g., refractive index changes based on $n_2 I$). The above expression assumes each field *i* interacts once (whether it be minus or plus), but if the input angles are fixed, it may be possible to simulate FWM using the same equation but with placing integer coefficients simulating the number of interactions (including zero) such that the sum of the absolute values equals 3, in the form of:

$$\begin{aligned}
&\Delta a = (a(\omega_s) - (|c_1| a(\omega_1) + |c_2| a(\omega_2) + |c_3| a(\omega_3))), \\
&\Delta k = k_{4z} - (c_1 k_{1z} + c_2 k_{2z} + c_3 k_{3z}), \\
&|c_1| + |c_2| + |c_3| = 3.
\end{aligned}$$

For simple geometries such as a "plus-sign" (aka "BOXCARS[2]") and planar geometries, and using linearly polarized input fields, the expression may be all that is required to described the interference of FWM per specific tensor element, as the Fresnel equations governing the transmission and reflection losses as fields pass within each layer are readily described then. If the input fields are limited to 3 using simple geometries such as the above, higher order phenomena may be treated by the *c* coefficients. It then becomes apparent under these approximations that a computational method that builds up the layers of a sample and applies the above expression as a function of the input lasers and angles can be readily developed.

Code

The Python library consists of three classes and a series of methods utilizing them. Two of the classes are IsoSample and Layer, with an IsoSample being a simple descriptor and ordered list of Layers. Layers can be developed by loading them from spreadsheet files of frequency, extinction coefficient, and refractive index, as well as its thickness. The lowest order index of the list represents the first layer interacted by the inputs, the second layer being the second interacted, and so on.

The third class Lasers represents the arrangement of Lasers entering the isotropic sample as defined by a standardized geometry. An object instantiated from the Lasers class ultimately consists of an ordered (likely three-member) array of the input field frequencies, their angles entering the sample, their polarizations, and a coefficient representing the number of bra or ket side interactions (plus or minus, or zero if not being simulated for that computation).

The methods allow for a computation of the factor *M* for each layer given the sample and Laser object, compute Fresnel coefficients, calculate the expected launch angle for the FWM field, and can also estimate an ideal angle for phasematching for a specific input frequency or an ideal frequency for a specific angle.

The Solvers for an ideal angle or frequency use SymPy's Sets to frame the result. Thus it allows for solves where the answer is "all real numbers" or "no solutions found", i.e. $\{\mathbb{R}\}$ and $\{\varnothing\}$ respectively but requires Sympy to be installed on the PC.

[1] Carlson, R.J.; Wright, J.C. *Applied Spectroscopy* **43,** *7*, 1195-1208 (1989).

[2] Shirley, J.A.; Hall, R.J.; Eckbreth, A.C. *Optics Letters* **5,** *9*, 380-382 (1980).