A Python Approach to Non-linear Spectroscopy Phasematch Modeling

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The interaction of multiple oscillating electric fields in a material can launch new electric fields at combinations of the inputs. The output fields can become detectable when the inputs are strong enough to distort molecules within the interaction 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 driven by other input fields in a multi-dimensional manner. The non-linear optical methods encompassing these processes form the basis for a specialized field called coherent multidimensional spectroscopy (CMDS), with the coherent electric fields originated by laser inputs.

In thick samples, the output fields launched towards the beginning of a sample can become out of phase with the fields launched towards the end. This occurs because the launched electric field within 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 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 are through the change in laser input angles with respect to the sample and 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

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

where

$$M = e^{-a_4 l} \times \left(\frac{\left(1 - e^{\Delta\alpha \cdot l}\right)^2 + 4e^{\Delta\alpha \cdot l} \sin^2\left(\frac{\Delta k \cdot l}{2}\right)}{\left(\Delta\alpha \cdot l\right)^2 + \left(\Delta k \cdot l\right)^2} \right),$$

and

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

and it is implicit that $a_4 \equiv a(\omega_4)$. Here, $\Delta k \cdot l$ represents the projection of the input wavevectors on the launched wavevector k_4 so that z is the direction of the launched wavevector rather than the normal to the surface. The *a* terms represent extinction coefficients with units in cm^{-1} if the expression uses CGS.

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). If the input angles are fixed, FWM can use the general equations above by placing integer coefficients simulating the number of interactions (including zero) such that the sum of the absolute values equals 3, in the form of:

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

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 that emit at the same angle may be treated by the *c* coefficients.

The norm-squared *M* factor can be expressed as a phasor $M = |Ae^{i\delta}|^2$ where *A* is simply the square root of equation 18b and

$$\delta = \arctan\left(\frac{\Delta k \cdot l + e^{\Delta\alpha \cdot l}\left[-\Delta k \cdot l\cos(\Delta k \cdot l) + \Delta\alpha \cdot l\sin(\Delta k \cdot l)\right]}{-\Delta\alpha \cdot l + e^{\Delta\alpha \cdot l}\left[\Delta\alpha \cdot l\cos(\Delta k \cdot l) + \Delta k \cdot l\sin(\Delta k \cdot l)\right]}\right),$$

this term having potential use in discretizing thick layers into several smaller layers with small changes such as for the coarse investigation of pulse effects on refractive indexes, i.e.,

$$M = \left|\sum_m A_m e^{i(\delta_m - \delta_{m-1})}\right|^2,$$

with δ_0 being set to 0 or the phase of some kind of layer prior to the discrete set.

Code

The Python library consists of three classes and a series of methods utilizing them.   Two of the classes are 'IsoSample' and 'Layer'.   IsoSample is an ordered list of Layers.   Layers can be developed by loading them from spreadsheet files of frequency, extinction coefficient, refractive index, thickness, and other material quantities. 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] Murdoch, K.M.; Thompson, D.E.; Meyer, K.A.; Wright, J.C. *Applied Spectroscopy* 54**,** 1495 (2000).

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