

IV.

Nonlinear Optics Mathcad Exercise for Undergraduate Students

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Abstract: An educational experience in numerical modeling for physics majors at Virginia Military Institute has been created as part of the undergraduate research learning paradigm. As part of the independent project course required of all physics majors at VMI, those joining the thin films research group are taught the various stages of numerical modeling applied to complex problems (such as optical limiting) as a precursor to experimental work. Students are introduced to a realistic method of research involving open-ended experiments by this exercise. By teaching students how to design, create, and test a complex numerical model, they gain insight into how an experiment is set up and executed as well as what results can be anticipated. We present an exercise in which undergraduate students use Mathcad in their modeling and calculations.

1. Introduction

The paper describes the work derived from a specific independent project class required for Physics majors. The main motivation for this project is that optics is such an important scientific field with numerous applications in consumer technologies, telecommunications, medicine, health, defense, to mention just few. Physics majors at VMI are required to take optics and this is a good opportunity for them to further expand their knowledge and appreciation of the field. In addition, our department has a strong optics background through faculty expertise and research areas: laser spectroscopy, statistical optics, nonlinear optical properties of organic materials and thin films, and observational astronomy. As part of their curriculum, physics majors learn Mathcad and are also required to take an Independent project course which is two semesters long during their junior year. For this particular independent project students combine concepts from optics with Mathcad and further expand to nonlinear optics (NLO), specifically optical limiting (OL). This was done as a precursor to experimental work on OL properties of fullerene materials.

2. Theoretical Concepts

Step 1 – Basic optics (transmission, Beer's law)

At the beginning of the project the student is reminded of basic concepts of optics¹, including index of refraction, intensity of light, and propagation of light waves in a dielectric. The concepts that are reviewed also include the expression of the energy flux density through a dielectric, given by:

$$I = I_0 e^{-\alpha z}$$

where $\alpha = 2k_l$ is the absorption coefficient of the medium. This means that increased incident intensity linearly increases the output intensity. The polarization of a linear medium by an electric field \vec{E} is usually written as $\vec{P} = \epsilon_0 \chi \vec{E}$, where ϵ_0 is the vacuum permittivity and χ is the susceptibility of the medium.

Step 2- Introduction to nonlinear optics

Next, the student is introduced to nonlinear optical phenomena. The polarization of a nonlinear medium by an electric field \vec{E} is

$$P = \epsilon_0 (\chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \dots) = P_1 + (P_2 + P_3 + \dots)$$

where χ_1 is the linear susceptibility and χ_i (with $i > 1$) represent the nonlinear susceptibility coefficients of the medium. The first term P_1 represents the polarization of the linear medium (described by linear optics), while the higher order terms only appear in nonlinear optical media, when the intensity of incident light is very high. For this project we are interested in optical limiters for which the transmittance decreases with increased incident light intensity. This particular class of materials has potential applications for eye and sensor protection.² There are several mechanisms³ of achieving optical limiting, one of them being reverse saturable absorption (RSA), where the absorption of the material increases with light level. Reverse saturable absorption occurs when the excited states have absorption cross sections larger than that of the ground state. In order for the students to understand the reverse saturable absorption mechanism they use Mathcad to analyze the linear, the three level, and the five level model of an optical limiter.

Step 3 – Fullerene materials and basic properties related to OL (electron affinity, five level model reduced to three level model)

One class of materials that exhibit promising optical limiting properties is the fullerenes. Fullerenes represent a third allotropic form of carbon, besides graphite and diamond. Their existence was first demonstrated⁴ in 1985. Since then, other fullerene materials besides C_{60} have been created: higher cages (C_{70} , C_{76} , C_{84}), endohedral metallofullerenes, and various derivatives. The unique nonlinear optical properties of fullerenes are due to the highly polarizable conjugated π -electrons which are delocalized over the surface of the carbon cage. One of the properties of these materials that has been studied extensively is the optical limiting effect, first reported⁵ in C_{60} and C_{70} at 532 nm and later measured at longer wavelengths and demonstrated for other fullerene materials⁶. As in any other RSA materials, fullerene materials have the same requirements⁷: small, but finite ground state absorption and large excited state absorption; often these materials exhibit intersystem crossing to triplet manifold. To best describe the behavior of RSA materials under nanosecond pulses a five level model is usually employed.

The five levels include the ground state S_0 , the first excited singlet state S_1 , the next higher excited singlet state S_2 , the lowest T_0 and higher T_1 triplet states. The incident laser beam excites the molecules from the ground state S_0 to one of the many vibrational levels of state S_1 , which relaxes very fast (\sim ps) to the equilibrium singlet-state S_1 . From

this excited singlet state the molecules can relax to the ground state, with rate $1/\tau_0$, or, through a process called intersystem crossing (ISC) they can be transferred to a lower triplet state T_0 , from where they can undergo transitions to higher triplet state T_1 , upon absorption of another photon. The ISC crossing is fast (650 ps – 1.2 ns), with a quantum efficiency close to unity. Although by subsequent absorption of photons the molecules in S_1 and T_0 can be further excited to S_2 and T_1 , respectively, they relax rapidly (less than ps) back to S_1 and T_0 , and therefore there is no decrease in S_1 and T_0 populations during the duration of the nanosecond laser pulse. In addition, in RSA materials, the lifetime of T_0 is large ($\sim 100 \mu\text{s}$ to 100 ns) compared to the temporal width of the pulse. The rate equations that describe the above five-level model are:

$$\begin{aligned}\frac{dS_0}{dt} &= -\sigma_{01}S_0\phi + k_{10}S_1 + k_{30}T_0 \\ \frac{dS_1}{dt} &= \sigma_{01}S_0\phi - \sigma_{12}S_1\phi - (k_{10} + k_{13})S_1 + k_{21}S_2 \\ \frac{dS_2}{dt} &= \sigma_{12}S_1\phi - k_{21}S_2 \\ \frac{dT_0}{dt} &= -\sigma_{34}T_0\phi - k_{30}T_0 + k_{13}S_1 + k_{43}T_1 \\ \frac{d\phi}{dz} &= -\sigma_{01}S_0\phi - \sigma_{12}S_1\phi - \sigma_{34}T_0\phi\end{aligned}$$

When RSA is dominated by the excited triplet state absorption, the model can be reduced to a three level model which includes the ground state, the first excited singlet state, and the first excited triplet state, which has a long lifetime.

$$\begin{aligned}\frac{dS_0}{dt} &= -\sigma_{01}S_0\phi + k_{30}T_0 \\ \frac{dT_0}{dt} &= \sigma_{01}S_0\phi - k_{30}T_0 \\ \frac{d\phi}{dz} &= -\sigma_{01}S_0\phi - \sigma_{34}T_0\phi\end{aligned}$$

These are the three equations students use to model in Mathcad the OL behavior of the material, as described in the next section.

3. Mathcad modeling and computation

Step 4 – Set-up problem in Mathcad

Linear absorption can be described by the reduction of light intensity dI after an incident beam of photons I_0 crosses a linear dielectric of length l with absorption coefficient α and is given by

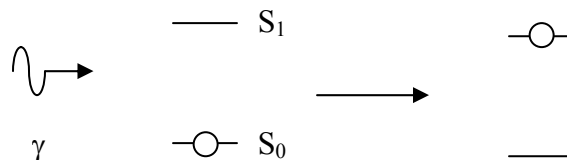
$$dI = -\alpha I dz$$

where the distance is integrated until l is reached. Likewise, the equation above can be turned into a time integral by noting that $dz = c dt$ and writing

$$dI = -\alpha I c dt = \alpha' I dt$$

where α' is a redefined absorption coefficient and we have assumed the velocity of light in the sample is the speed of light c . Simple integration yields, $I = I_0 e^{-\alpha' t}$. This equation simply states that the longer the beam takes to cross the sample, the greater the reduction in the incident intensity. The crossing time can be converted into a thickness by multiplication of the c but the point is clear enough that students can grasp this simple concept.

If asked to determine the transmitted intensity, the student will most likely solve the final equation above. If asked to graph the function, he/she will simply do so by having Mathcad compute the transmitted intensity I over a certain time domain t . However, if the student considers the problem from the atomic point of view and is asked to show how one arrives at linear absorption, he/she is likely to be befuddled and not know where to start. The best place to have him/her start is to consider a simple absorption process where an electron in the ground state absorbs a photon from the beam. In doing so the electron jumps to a higher energy state and does not return to populate the ground state. This is shown in the diagram below.



The student then reasons that the ground state will be depopulated at a certain rate and the excited state populated at the same rate. He/she should then reason that the ground state depopulation rate should depend on the incident intensity (or photon flux), the number of electrons in the state, and the ground state cross section. The rate equation for the ground state becomes

$$\frac{dS_0}{dt} = -\sigma_{01} S_0 \phi$$

where S_0 is the population of ground state, σ_{01} the ground state absorption cross section, and ϕ the incident photon flux. Next, the student has to reason that the excited state level is populated at the exact same rate (since we are not allowing for the possibility of the electron relaxing to the ground state). This lets him/her write a second equation as

$$\frac{dS_1}{dt} = \sigma_{01} S_0 \phi.$$

The third equation the student needs to reason out will be the reduction in the number of photons after the beam has crossed the material (or how many remain after a certain time period, which represents crossing the material). In terms of the rate at which photons are being removed from the beam, the reduction is simply,

$$\frac{d\phi}{dt} = -\sigma_{01} S_0 \phi$$

which shows that the photons are being absorbed at the same rate as electrons are being promoted to the excited state. This gives the student three equations which describe linear absorption. Now he/she is asked to determine the photon flux (which relates to I) using the three equations. This is where he/she uses Mathcad to solve this system of three linear first order differential equations.

In this Mathcad program the subscripted variable is x and it describes quantities S_0 , S_1 , and ϕ as follows: $x_0 \rightarrow S_0$, $x_1 \rightarrow S_1$, $x_2 \rightarrow \phi$. The first derivatives need to be written in the matrix form with these variables which means the student has to convert the equations as follows

$$\frac{dS_0}{dt} = -\sigma_{01} S_0 \phi = -\sigma_{01} x_0 x_2$$

$$\frac{dS_1}{dt} = \sigma_{01} S_0 \phi = \sigma_{01} x_0 x_2$$

$$\frac{d\phi}{dt} = -\sigma_{01} S_0 \phi = -\sigma_{01} x_0 x_2$$

A matrix $D(t,x)$ is defined that contains the three converted equations and in Mathcad is written as

$$D(t, x) := \begin{pmatrix} -x_0 x_2 \\ x_0 x_2 \\ -x_0 x_2 \end{pmatrix}$$

where the equations have been scaled by σ_{01} since it is contained in each term. This matrix is then passed to the Mathcad differential equation solver *rkfixed* which uses a fourth order Runge-Kutta method to solve the system of equations. It must also have the endpoints of the interval over which the equations are solved, the number of points the equations are solved at between those endpoints, and the initial conditions. Here the student chooses a time between 0 and 0.1 seconds with the initial conditions that $S_0 = Nm$, $S_1 = 0$ and $\phi = N\gamma$ where Nm is the number of molecules and $N\gamma$ is the number of incident photons. The output of *rkfixed* is a matrix that has 4 columns where the number of rows equal the number of steps specified in the call to *rkfixed*. The first column is the time interval with a step size equal to the difference between the two endpoints divided by the number of steps. The second, third, and fourth columns give the values of S_0 , S_1 , and ϕ respectively at those times.

The student then considers the transmitted flux at a certain point in time and runs the routine for an incident flux that doubles, that is $N\gamma = 2, 4, 8, \dots$ up to 512. He/she runs the program and plots the transmitted photon flux as a function of incident flux. The result is shown in the graph below (Figure 1) for $Nm = 100$. The result shows a linear behavior - as the incident flux increases so does the transmitted flux in direct proportion.

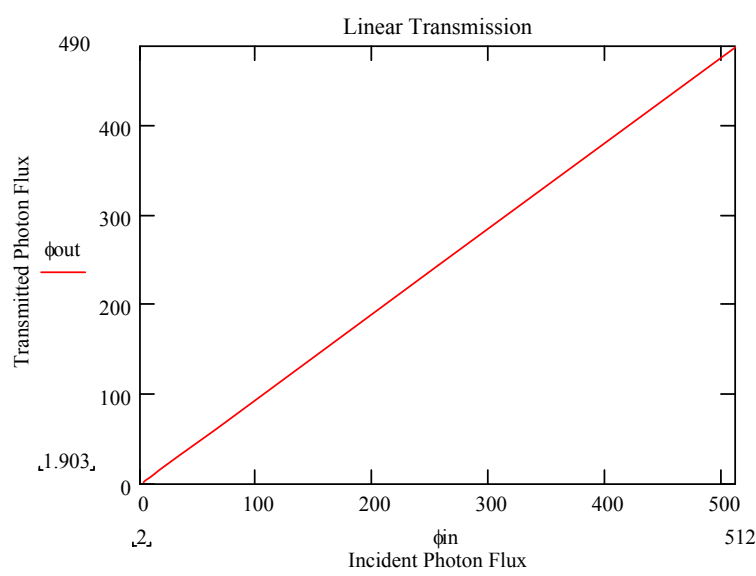


Figure 1. Linear dependence of transmittance.

Three level model.

Having learned how to model and solve the three equations for linear absorption the student is now ready to move on to the three level model for an optical limiter. Using the linear model explained above, the student now considers the possibility that the electron in the excited state can either return to the ground state by relaxation from the S_1 state, or by intersystem crossing it can go to the T_0 state and then return to the ground state. The equations that govern this process are converted into Mathcad as the following

$$D(t, x) := \begin{pmatrix} -\sigma_{01} S_0 \phi + k_{30} T_0 = -\sigma_{01} x_0 x_2 + k_{30} x_1 \\ \sigma_{01} S_0 \phi - k_{30} T_0 = \sigma_{01} x_0 x_2 - k_{30} x_1 \\ -\sigma_{01} c S_0 \phi - \sigma_{34} c T_0 \phi = -\sigma_{01} c x_0 x_2 - \sigma_{34} c x_1 x_2 \end{pmatrix}$$

where $x_0 \rightarrow S_0, x_1 \rightarrow T_0, x_2 \rightarrow \phi$. Similarly as before, the matrix is passed to a first order differential equation solver, but this time the Rkadapt routine is used. This method also uses the fourth order Runge-Kutta method, but allows the step size to vary in smaller steps where the solution is changing rapidly and larger steps where the change is smoother.

The student uses the ground state cross sections and rate constants for C_{60} from the literature⁸ and considers a 10 ns pulse with 500 iteration steps. He then considers the output a specific time and runs the model again for a series of

incident fluxes that doubles. The result is shown below (Figure 2) for $N_m = 10^{18}$ and where $N_\gamma = 2, 4, 8, \dots \times 10^{23}$ up to 512×10^{23} . The nonlinear behavior is clearly seen - as the number of incident photons increases, the transmitted flux does not double but starts to show optical limiting.

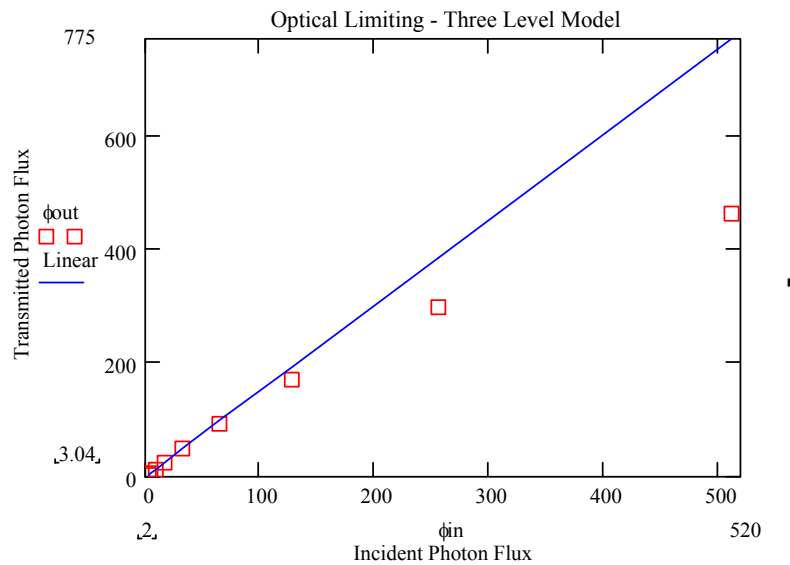


Figure 2. Optical limiting effect.

Step 5 – Future work related to modeling and experimental work

This project introduces students to numerical methods in nonlinear optics using Mathcad and forms a basis from which he/she can expand into future projects, specifically the incorporation of the five level model, numerical studies of C_{60} as well as other RSA materials, and experimental studies (including verifying the validity of the models) of C_{60} and other fullerenes (higher empty cages and endohedral metallofullerenes) using a pulsed nanosecond, Q-switched Nd:YAG laser.

4. Conclusion

This Mathcad exercise was aimed at introducing students to one aspect of the field of nonlinear optics through analyzing the three level model of an optical limiting material. The students use the knowledge learned in optics class and perform the computation with Mathcad.

5. References

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