Theoretical Study of Optical Responses on Hydrogenated Graphene Structures

by

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to earn the degree of Doctor of Philosophy.

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"If you are receptive and humble, mathematics will lead you by the hand."

Paul Dirac

——— I dedicate this work to my wife, Paty,
and my two children, Samantha and Reinaldo. ———

Abstract

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Acknowledgements

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1 Introduction

Outline

1.1 Nonlinear Optics

Nonlinear optics studies the modifications of the optical properties of a material system as a result of its interaction with the electric field of light. Typically, only laser light is intense enough to produce a modification in the optical properties of a material system[1]. The nonlinearity of those phenomena came from the fact that their manifestation do not depend in a linear manner on the strength of the optical applied field. The field of nonlinear optics now extends from fundamental studies of the interaction of light with matter to applications such as laser frequency conversion, optical switching, and optical tests.

In 1917, Albert Einstein published the theoretical possibility of amplification of radiation through stimulated emission with coherence [1] and Valentin A. Fabrikat made the calculation of the conditions needed to produce radiation amplification by stimulated emission like the population inversion; he also proposed the resonant cavity [2]. This theory and calculations was not carried out to practice until 1952 when Joseph Weber started the development of masers but the first one was demonstrated by Charles H. Townes and his working team in 1953. The principal difficulty in the development of an *optical maser*, was the transition from centimeter to nanometer waves. In 1960 Theodore H. Maiman presented the first functional ruby laser [3]. One year later, second-harmonic generation (SHG) was the the first nonlinear effect observed by Peter Franken, et al. at University of Michigan [4]. Exciting a piece of crystalline quartz with a laser beam, they produced a second beam with

[1] Some nonlinear responses, like luminescence of dye molecules, were discovered previous to the development of the laser.

the double of frequency than the original but with less intensity than the original one. In 1962, Nicolaas Bloembergen et al. described the induced nonlinear electric dipole and higher moments in an atomic system using quantum-mechanical perturbation theory [5], and solved the Maxwell's equations in nonlinear dielectrics satisfying the boundary conditions at a plane interface between a linear and nonlinear medium [6]. The development of the first pulsed laser in 1964 by William B. Bridges [7], and the later works in this field, allowed the increase of laser intensities and then the induction of new nonlinear effects in nonlinear media. In 1988, Yuen-Ron Shen et al. studied the the bulk contribution to surface second-harmonic generation and presented a model for the bulk nonlinearity of molecular systems including the quadrupole bulk contribution [8]. Currently, chirped pulse amplification, developed by Gerard Morou and Donna Strickland [9], in Ti:Saphire lasers became the standard for high energy, ultrashort pulsed lasers.

1.1.1 Nonlinear polarization

To describe the optical nonlinearity we need to consider how the polarization of a material $P(\omega)$, defined as the dipole moment per unit volume, depends on the strength of an applied optical field $E(t)$. In the case of linear optics, the polarization dependence is lineal with respect to the strength of electric field and can be described as

$$P(\omega) = \epsilon_0 \chi^{(1)} E(\omega), \tag{1.1}$$

where ϵ_0 is the permittivity of free space and $\chi^{(1)}$ is the linear susceptibility. In nonlinear optics, the optical response of Eq. (1.1) is characterized by rewriting the polarization as a power series in the field strength as

$$\begin{aligned} P(\omega) =& \epsilon_0 [\chi^{(1)} E(\omega) + \chi^{(2)} E^2(\omega) + \chi^{(3)} E^3(\omega) + \cdots] \\ =& P^{(1)}(\omega) + P^{(2)}(\omega) + P^{(3)}(\omega) + \cdots . \end{aligned} \tag{1.2}$$

The $\chi^{(n)}$ expression is known as the n^{th} nonlinear optical susceptibility; the common linear effects presented in most media are described only by $P^{(1)}(\omega)$ that reduces the expression (1.2) to(1.1). The reason why the polarization has a determining role in the characterization of nonlinear optical phenomena comes from the fact that time-varying polarization can produce new components of the electromagnetic field. This can be shown using the wave equation in nonlinear media that is written as [10]

$$\nabla^2 E - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{1}{\epsilon_0 c^2} \frac{\partial^2 P^{NL}}{\partial t^2}, \tag{1.3}$$

where n is the usual linear refractive index and c is the speed of light in vacuum. This is an inhomogeneous wave equation in which the polarization P^{NL} related with the nonlinear response depends on the electric field E. The expression $\partial^2 P^{NL}/\partial t^2$ is a measure of the acceleration of the charges in the media that which generate new electromagnetic radiation.

Considering that the electric field E written here as a scalar must be considered a vector, then $\chi^{(1)}$ must be a second-rank tensor, $\chi^{(2)}$ a third-rank tensor and so on, and they depend on the frequencies of the applied fields [10]. The nonlinear polarization can also be described threating

the incident electric field as a superposition of plane waves. If we assume that the electric field is written as [11]

$$\mathbf{E}(\mathbf{r},\omega) = \sum_n \mathbf{E}_n(\mathbf{r},\omega) \tag{1.4}$$

where

$$\mathbf{E}_n(\mathbf{r},\omega) = \mathbf{E}_n(\mathbf{r})e^{-i\omega_n t} + c.c., \tag{1.5}$$

and then, from Eq. (1.2) we can write

$$\mathbf{P}(\mathbf{r},\omega) = \sum_n \mathbf{P}^{(n)}(\omega_n)e^{-i\omega_n t}. \tag{1.6}$$

Then, we can define the n^{th} order nonlinear polarization in terms of the n^{th} order susceptibility as

$$\mathbf{P}^{(n)}(\mathbf{r},\Omega) = \epsilon_0 \sum_{\text{bc}} \sum_{\Omega} \boldsymbol{\chi}^{(n)}\left(-\Omega;\omega_1,\omega_2,\ldots,\omega_n\right)\mathbf{E}(\mathbf{r},\omega_1)\mathbf{E}(\mathbf{r},\omega_2)(\cdots)\mathbf{E}(\mathbf{r},\omega_n), \tag{1.7}$$

where $\Omega = \omega_1 + \omega_2 + \ldots + \omega_n$. Making emphasys about we are interested in second order effects, we can analyze the case when we have two incoming fields, with frequencies ω_1 and ω_2, and write the total incident electric field as [12]

$$\mathbf{E}(\mathbf{r},\omega) = \mathbf{E}_1(\mathbf{r})e^{-i\omega_1 t} + \mathbf{E}_2(\mathbf{r})e^{-i\omega_2 t} + c.c.. \tag{1.8}$$

Then, from Eq. (1.2), the second order polarization can be written as

$$\mathbf{P}^{(2)}(\mathbf{r};\omega) = \epsilon_0 \boldsymbol{\chi}^{(2)}[\mathbf{E}(\mathbf{r},\omega)]^2, \tag{1.9}$$

and using Eq. (1.8) and omitting the $(\mathbf{r},\omega)$ dependence in the electric fields we can write

$$\begin{aligned}\mathbf{P}^{(2)}(\mathbf{r};\omega) = \epsilon_0\boldsymbol{\chi}^{(2)}[&\mathbf{E}_1^2 e^{-i2\omega_1 t} + \mathbf{E}_2^2 e^{-i2\omega_2 t} \\ &+ 2\mathbf{E}_1\mathbf{E}_2 e^{-i(\omega_1+\omega_2)t} + 2\mathbf{E}_1\mathbf{E}_2^* e^{-i(\omega_1-\omega_2)t} + c.c.] \\ &+ 2\epsilon_0\boldsymbol{\chi}^{(2)}[\mathbf{E}_1\mathbf{E}_1^* + \mathbf{E}_2\mathbf{E}_2^*].\end{aligned} \tag{1.10}$$

Separating this expression in its components and the nonlinear effect produced we have

$$\mathbf{P}(\mathbf{r};2\omega_1) = \epsilon_0\boldsymbol{\chi}^{(2)}\mathbf{E}_1^2 e^{-i2\omega_1 t} + c.c., \tag{1.11a}$$

$$\mathbf{P}(\mathbf{r};2\omega_1) = \epsilon_0\boldsymbol{\chi}^{(2)}\mathbf{E}_2^2 e^{-i2\omega_2 t} + c.c., \tag{1.11b}$$

$$\mathbf{P}(\mathbf{r};\omega_1+\omega_2) = 2\epsilon_0\boldsymbol{\chi}^{(2)}\mathbf{E}_1\mathbf{E}_2 e^{-i(\omega_1+\omega_2)t} + c.c, \tag{1.11c}$$

$$\mathbf{P}(\mathbf{r};\omega_1-\omega_2) = 2\epsilon_0\boldsymbol{\chi}^{(2)}\mathbf{E}_1\mathbf{E}_2^* e^{-i(\omega_1+\omega_2)t} + c.c., \tag{1.11d}$$

$$\mathbf{P}(\mathbf{r};0) = 2\epsilon_0\boldsymbol{\chi}^{(2)}(\mathbf{E}_1\mathbf{E}_1^* + \mathbf{E}_2\mathbf{E}_2^*) + c.c.. \tag{1.11e}$$

The expressions of Eq. (1.11) correspond to the following second order optical processes of light interacting with a nonlinear media:

- Second harmonic generation (SHG, Eqns. 1.11a and 1.11b) is a process in which photons with same frequency produce new photons with twice the energy and frequency and half the wavelength, respective to the initial photons.

Table 1.1: Optical processes described with $\boldsymbol{\chi}^{(n)}$.

$\boldsymbol{\chi}^{(n)}(-(\omega_1+\ldots+\omega_n);\omega_1,\ldots,\omega_n)$			**Process**	**Order**
$-\omega_1$	;	ω_1	Linear absorption / emission and refractive index	1
0	;	$\omega_1, -\omega_1$	Optical rectification (OR)	2
$-\omega_1$	;	$0, \omega_1$	Pockels effect	2
$-2\omega_1$	;	ω_1, ω_1	Second-harmonic generation (SHG)	2
$-(\omega_1+\omega_2)$	;	ω_1, ω_2	Sum-frequency generation (SFG)	2
$-(\omega_1-\omega_2)$	;	ω_1, ω_2	Difference-frequency generation (DFG) / Parametric amplification and oscillation	2
$-\omega_1$	;	$0, 0, \omega_1$	d.c. Kerr effect	3
$-2\omega_1$	;	$0, \omega_1, \omega_1$	Electric Field induced SHG (EFISH)	3
$-3\omega_1$	;	$\omega_1, \omega_1, \omega_1$	Third-harmonic generation (THG)	3
$-\omega_1$	;	$\omega_1, -\omega_1, \omega_1$	Degenerate four-wave mixing (DFWM)	3
$-\omega_1$	;	$-\omega_2, \omega_2, \omega_1$	Two-photon absorption (TPA) / ionization / emission	3

- Sum frequency generation (SFG, Eq. 1.11c) is a process in which photons with different frequency generate photons with frequency equal to the sum of the frequencies of the originals.
- Difference frequency generation (DFG, Eq. 1.11d) is a process in which the frequency of the generated photons is the difference between two other photon frequencies.
- Optical rectification (OR, Eq. 1.11e) is a process that consists of the generation of a quasi-DC polarization.

In table 1.1 are presented the most common optical processes of low order [11].

1.2 Symmetry consequences in nonlinear media

The symmetry of each them plays a very important role in nonlinear optics. As mentioned in the beginning of this section, $\boldsymbol{\chi}^{(2)}$ is a third rank tensor, and it has 27 elements. The number of non-zero or independent elements depends on the symmetry properties of the nonlinear media in question. In crystallography, there are 32 crystal classes and we can find two big groups, centrosymmetric and non-centrosymmetric. A centrosymmetric media is a system with an inversion of symmetry center. It means that the structure has a point (x, y, z) in the unit cell that is equivalent at $(-x, -y, -z)$. Then, if we are in a centrosymmetric media, the second order nonlinear polarization can be written as Eq. (1.9). If the system presents inversion of symmetry, a inversion in the coordinates will change both, the electric field and the polarization, since they are polar vectors [12, 13], and so

$$\begin{aligned} -\mathbf{P}^{(2)}(\mathbf{r},\omega) &= \epsilon_0 \boldsymbol{\chi}^{(2)}[\mathbf{E}(-\mathbf{r},\omega)]^2, \\ &= \epsilon_0 \boldsymbol{\chi}^{(2)}[-\mathbf{E}(\mathbf{r},\omega)]^2, \\ &= \epsilon_0 \boldsymbol{\chi}^{(2)}[\mathbf{E}(\mathbf{r},\omega)]^2. \end{aligned} \tag{1.12}$$

So we have that $-\mathbf{P}^{(2)}(\mathbf{r},\omega) = \mathbf{P}^{(2)}(\mathbf{r},\omega)$, and since we assume that $\mathbf{E}(\mathbf{r},\omega) \neq 0$, then we conclude that

$$\boldsymbol{\chi}^{(2)} = 0. \tag{1.13}$$

In table 1.2 we present the the form of the second order susceptibility tensor for each of the 32 crystal classes with each element denoted by Cartesian indices [10].

Table 1.2: Form of the second order susceptibility tensor for each of the 32 crystal classes. Each element is denoted by its Cartesian indices.

Crystal system	**Crystal class**	**Nonvanishing Tensor Elements**
Triclinic	$1 = C_1$	All elements are independent and nonzero
	$\overline{1} = S_2$	Each element vanishes
Monoclinic	$2 = C_2$	xyz, xzy, xxy, xyx, yxx, yyy, yzz, yzx, yxz, zyz, zzy, zxy, zyx (twofold axis parallel to $\hat{y}$)
	$m = C_{1h}$	xxx, xyy, xzz, xzx, xxz, yyz, yzy, yxy, yyx, zxx, zyy, zzz, zzx, zxz (mirror plane perpendicular to $\hat{y}$)
	$2/m = C_{2h}$	Each element vanishes
Orthorhombic	$222 = D_2$	xyz, xzy, yzx, yxz, zxy, zyx
	$mm2 = C_{2v}$	Each element vanishes
Tetragonal	$4 = C_4$	$xyz = -yxz$, $xzy = -yzx$, $xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz, $zxy = -zyx$
	$\overline{4} = S_4$	$xyz = yxz$, $xzy = yzx$, $xzx = -yzy$, $xxz = -yyz$, $zxx = -zyy$, $zxy = zyx$
	$422 = D_4$	$xyz = -yxz$, $xzy = -yzx$, $zxy = -zyx$
	$4mm = C_{4v}$	$xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz
	$\overline{4}2m = D_{2d}$	$xyz = yxz$, $xzy = yzx$, $zxy = zyx$
	$4/m = C_{4h}$	Each element vanishes
	$4/mmm = D_{4h}$	Each element vanishes
Cubic	$432 = O$	$xyz = -xzy = yzx = -yxz = zxy = -zyx$
	$\overline{4}3m = T_d$	$xyz = xzy = yzx = yxz = zxy = zyx$
	$23 = T$	$xyz = yzx = zxy$, $xzy = yxz = zyx$
	$m3 = T_h$, $m3m = O_h$	Each element vanishes
Trigonal	$3 = C_3$	$xxx = -xyy = -yyz = -yxy$, $xyz = -yxz$, $xzy = -yzx$, $xzx = yzy$, $xxz = yyz$, $yyy = -yxx = -xxy = -xyx$, $zxx = zyy$, zzz, $zxy = -zyx$
	$32 = D_3$	$xxx = -xyy = -yyx = -yxy$, $xyz = -yxz$, $xzy = -yzx$, $zxy = -zyx$
	$3m = C_{3v}$	$xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz, $yyy = -yxx = -xxy = -xyx$ (mirror plane perpendicular to $\hat{x}$)
	$\overline{3} = S_6$, $\overline{3}m = D_{3d}$	Each element vanishes
Hexagonal	$6 = C_6$	$xyz = -yxz$, $xzy = -yzx$, $xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz, $zxy = -zyx$
	$\overline{6} = C_{3h}$	$xxx = -xyy = -yxy = -yyx$, $yyy = -yxx = -xyx = -xxy$
	$622 = D_6$	$xyz = -yxz$, $xzy = -yxz$, $zxy = -zyx$
	$6mm = C_{6v}$	$xzx = yzy$, $xxz = yyz$, $zxx = zyy$, zzz
	$\overline{6}m2 = D_{3h}$	$yyy = -yxx = -xxy = -xyx$
	$6/m = C_{6h}$	Each element vanishes
	$6/mmm = D_{6h}$	Each element vanishes

1.3 Graphene and Hydrogenated Graphene

Graphene is an allotrope of carbon consisting of planar mono-atomic sheets of sp^2 bonded carbon atoms. This synthetic structure is a densely packed two-dimensional equilateral triangular crystal lattice [14] with a carbon-carbon chemical bond length of 0.142 nm [15]. In 2010 the Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their breaking new work about graphene[2].

1.3.1 Graphene properties

Due to the properties that the structure presents, graphene became one of the most relevant research topics in condensed matter physics and material science for the last eight years [14–18] since its first synthesis in 2004.

[2]Nobel Foundation announcement of Nobel Price, 2010.

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