The role of Kleinman Symmetry in the Simplified Bond Hyperpolarizability Model

Adalberto Alejo-Molina\textsuperscript{1*} and Hendradi Hardhienata\textsuperscript{2}

\textsuperscript{1} CONACYT Research Fellow - Center for Research in Engineering and Applied Science (CIICAp), Institute for Research in Pure and Applied Science (IICBA), UAEM Cuernavaca, Mor. 62209, Mexico
\textsuperscript{2} Theoretical Physics Division, Department of Physics, Bogor Agricultural University, Jl. Meranti, Gedung Wing S, Kampus IPB Darmaga, Bogor 16680, Jawa Barat, Indonesia

\textsuperscript{*}E-mail: adalberto.alejo@uaem.mx

Abstract. We have shown previously in [J. Opt. Soc. Am. 31, 526-533 (2014)] that Kleinman symmetry plays an important role when comparing the third rank tensor associated with Second Harmonic Generation (SHG) obtained from the Simplified Bond Hyperpolarizability Model (SBHM) and from group theory (GT) for diamond and zincblende lattice. In this work we show that the third rank tensor derived from the SBHM has inherently the assumption of Kleinman symmetry.

1. Introduction

In 2002 Powell \textit{et. al.} \cite{1} developed the phenomenological model first proposed by Sipe \textit{et. al.} \cite{2} to calculate the second harmonic susceptibilities of silicon surface layers. Their new approach, called the Simplified Bond Hyperpolarizability Model (SBHM) is based on the core assumption that the SHG susceptibility tensor can be obtained by direct product of the bond vector rather than using crystal group theory (GT). It has been shown by us in Ref. \cite{3} that there is a close connection between the third rank tensor obtained from SBHM and GT especially if Kleinman symmetry is assumed to hold and that this model can also be expanded for the case of third harmonic generation and electric field induced second harmonic generation \cite{4}. Very recently, SBHM was introduced in calculating the bulk dipolar SHG contribution in zincblende lattice yielding very good agreement with experiment \cite{5} and also successfully reproduced Rotational Anisotropy Spectroscopy (RAS) SHG intensity data using bulk quadrupolar and interface dipolar from a flat Si(111) facet \cite{6}. In this work we show how this symmetry is automatically included in SBHM.

In undergraduate textbooks \cite{7,8} it is assumed that the material has a susceptibility derived via an oscillator model and takes the form of a scalar because the focus is in obtaining its estimate strength of and its dependence to the frequency and damping. Thus the often oversimplified assumption is taken that the polarization vector and the driving field is the same which is however just a specific case. In reality, the tensorial nature of the susceptibility cannot be neglected because the polarization and the field can in general be pointing in a different direction depending on the symmetry of the crystal. The tensor indices used throughout this work is explained here for the case of one monochromatic incoming field $E(\omega)$. The tensor for a general field input is not discussed here.

In general when we consider nonlinear effects, $P(\omega)$ can be modeled in terms of power series
of the field $E(\omega)$:

$$P = \chi^{(1)} E(\omega) + \chi^{(2)} E(\omega) E(\omega) + \chi^{(3)} E(\omega) E(\omega) E(\omega) + \cdots \quad (2)$$

where $\chi^{(2)}$ and $\chi^{(3)}$ are respectively the second- and third-order susceptibilities. Eq. (2) can be rewritten in terms of the components:

$$P = \chi_{ij}^{(1)} E(\omega) + \chi_{ijk}^{(2)} E(\omega) E(\omega) + \chi_{ijkl}^{(3)} E(\omega) E(\omega) E(\omega) + \cdots \quad (3)$$

Eq. (3) contains the second-order nonlinear susceptibility and is a third rank tensor denoted by three subscripts “$i$”, “$j$”, and “$k$”.

2. Group Theory, Neumann principle, and Kleinman Symmetry

Group theory can be regarded as a general theory that can be applied to obtain the nonlinear susceptibility of a crystal. Three necessary properties must be fulfilled by a set of matrices to form a group under a particular operation, in this case the usual product of matrices. Neumann’s principle relates group theory and physics [9,10]:

"The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal."

In other words, after applying a symmetry operation belonging to a certain crystal, a particular property of this tensor should remain. These symmetry operations must preserve the crystal properties, which includes the optical ones.

Symmetry operations such as rotations and reflections can be represented mathematically by a matrix and for a particular crystal only rotation for specific angles are allowed for some specific existing mirror planes. Depending on the crystal symmetry various symmetry operation (rotation, reflection, etc.) belonging to the point group of the crystal to the susceptibility tensor can be applied. The tensorial elements of the material susceptibility which is indeed a physical property must fulfill this principle. After these transformations, Neumann’s principle implies that the two tensors must remain the same.

In addition, in nonlinear optics there is often a symmetry condition that is fulfilled for the case when anomalous dispersion can be ignored, then the susceptibility remains unchanged when the frequencies of the two input signals and the resulting beam are permuted. This has as a consequence that the indices in the susceptibility tensor must be invariant to all permutations [2]. Mathematically this can be stated as

$$d_{ij} = d_{ji} = d_{ij} = d_{ji} = d_{ij}.$$ (4)

This symmetry is known as Kleinman symmetry. As an example, for Second Harmonic Generation (SHG) only one input frequency is used, therefore Kleinman symmetry requires:

$$d_{ij}^{(2)}(2\omega = \omega + \omega) = d_{ji}^{(2)}(2\omega = \omega + \omega) = d_{ij}^{(2)}(\omega = 2\omega - \omega) =$$

$$d_{ij}^{(2)}(\omega = -\omega + 2\omega) = d_{ij}^{(2)}(\omega = 2\omega - \omega) = d_{ij}^{(2)}(\omega = -\omega + 2\omega) =$$

(5)

This kind of symmetry generally holds if the frequency of the laser is far below the resonance frequency $\omega_0$. Fortunately, many optical processes in material characterization applies an input frequency bandwidth that is far below the material resonant frequency. A more detailed discussion about the group theoretical properties of certain diamond lattice surfaces can be seen in Refs. [2,11].

3. Simplified Bond Hyperpolarizability Model (SBHM)

The main assumption of SBHM is to assume that the nonlinear polarization source produces an anharmonic dipole oscillation along the atomic bonds. This model is phenomenological in the sense that the hyperpolarizabilities must be derived from experiment fit. In addition it assigns different values for the polarizabilities and hyperpolarizabilities according to their
direction and is therefore affected by crystal symmetry. In its original formulation [1], SBHM assumes that the electron moves only along the bond which must be reconsidered if transversal motion is possible such as in third harmonic generation. Another additional view of SBHM is that the bond orientations in the surface have no molecular reconstruction, however such effects can also be incorporated in the extended model.

In SBHM the polarization up to the second order is calculated by [1,12]:

\[
P = \frac{1}{V} \sum_j [\alpha_{1,j} (R(x)(\phi) \cdot \hat{b}_j) \otimes (R(x)(\phi) \cdot \hat{b}_j)] \cdot E + \frac{1}{V} \sum_j [\alpha_{2,j} (R(x)(\phi) \cdot \hat{b}_j) \otimes (R(x)(\phi) \cdot \hat{b}_j) \otimes (R(x)(\phi) \cdot \hat{b}_j)] \cdot E \otimes E
\]

(6)

therefore, the susceptibility third rank tensor, is calculated by the formula:

\[
\chi^{(2)} = \frac{1}{V} \sum_j [\alpha_{2,j} (R(x)(\phi) \cdot \hat{b}_j) \otimes (R(x)(\phi) \cdot \hat{b}_j) \otimes (R(x)(\phi) \cdot \hat{b}_j)]
\]

(7)

where \( V \) is the volume, \( \alpha_{1,j} \) are the linear polarizabilities, \( \alpha_{2,j} \) are the hyperpolarizabilities and \( \hat{b}_j \) are the unit vectors in the direction of the atomic bonds. Note that the summation is going over all the bonds in the conventional cell. In the following we will show that Eq. (7) always obeys Kleinman symmetry if a monochromatic incoming field is applied. However there are also cases especially near the resonant frequency where this symmetry breaks down [13]

4. Results and Discussions

To prove that Eq (7) obey Kleinman symmetry for certain cases. Indeed it can be shown e.g. using brute force by applying the most general bond vector components and construct the tensor from SBHM that the final tensor always symmetric. This is due to the following fact: the tensor is generated by direct product of the same bonds \( \hat{b}_j \) and the hyperpolarizabilities in SBHM are just constants. Here we give a formal proof that this is indeed the case. Let us think that we have a number of vectors

\[
a = (a_1, a_2, a_3) \\
b = (b_1, b_2, b_3) \\
c = (c_1, c_2, c_3) \\
d = (d_1, d_2, d_3)
\]

(8)

and we want to calculate a tensor using direct product in the following way. We can generate a tensor of rank \( n \) doing the direct product

\[
P^\text{n}_{i=1} x_i
\]

(9)

where \( x_i \) represents any fixed vector, multiplied by itself \( n \) times, under the understanding that it is a direct product. In particular for the fourth rank tensor:

\[
b \otimes b \otimes b \otimes b
\]

(10)

or in terms of the components

\[
B_{ijkl} = b_i b_j b_k b_l
\]

(11)

If we permutated any two factors in Eq. (11), we get

\[
B_{ijkl} = b_i b_j b_k b_l
\]

(12)

but the subindices are free suffix and can be renamed
Moreover, there is nothing that forbids to repeat the same procedure, thus
\[ B_{ijkl} = b_{ij} b_{kl}, \]  
and as can be seen, the last expression Eq. (14) is identical to Eq. (11), so the permutation of whatever two factors generated exactly the same tensor:
\[ B_{ijkl} = B_{ijlk}. \]  
Therefore, the result is that any permutation of the subindices generates the same tensor and this is the equivalent to Kleinman symmetry. The result is that any permutation of the subindices generates the same tensor and this is the equivalent to Kleinman symmetry. In fact, for the summation in SBHM over the different bonds, also generates a tensor with Kleinman symmetry. We are going to show it only for two bonds but can be proved in general for any number of bonds and for a tensor of rank \( n \).

In a pedestrian way, we have two vectors and after generating the tensor doing the direct product four times, we can sum each other
\[ \Omega_{ijkl} = A_{ijkl} + B_{ijkl} \]  
the free suffix now are the same (dummy suffix) in both vectors because we are summing component to component in each tensor, or
\[ \Omega_{ijkl} = a_ia_ja_ka_l + b_ib_jb_kb_l \]  
and of course, it does not matter how we named the result of this sum, as tensors \( A_{ijkl} \) and \( B_{ijkl} \) have Kleinman symmetry, the sum also will have this symmetry, because the permutation of any two subindices will result on
\[ \Omega_{ijkl} = a_ia_ja_ka_l + b_ib_jb_kb_l = \Omega_{ijlk}. \]  
but for the reason explained above each term in the sum results in itself under the permutation of its indices. Then
\[ \Omega_{ijkl} = a_ia_ja_ka_l + b_ib_jb_kb_l = \Omega_{ijkl}. \]  
The same argumentation can be used to add more tensors generated by the direct product of any number of the remaining bonds:
\[ \Sigma_{ijkl} = a_ia_ja_ka_l + b_ib_jb_kb_l + c_ia_jc_ka_l + d_ia_jd_ka_l + ... \]  

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