Solution to Problem Set 6
Nonlinear Optics (NLO)

1) Crystal Symmetry Classes and Susceptibility

In crystallography, by means of group theory, all crystals can be classified according to their point group. A crystallographic point group is a set of symmetry operations, such as rotations or reflections, that leave a central point fixed while moving atoms into position previously occupied by another atom of the same kind, therefore leaving the crystal unchanged.

For crystals in 3-dimensional space, there are 32 possible point groups. Each of them corresponds to one of the 32 "crystal classes". An example of a point group is the so-called tetragonal-trapezoidal group, also called D_4 in the Schoenflies notation, or 422 in the international (Hermann–Mauguin) notation. This point group belongs to the tetragonal crystal system and therefore the crystal's Bravais lattice is a cuboid with two equal dimensions whereas the third dimension is shorter or longer than the other two. The D_4 point group of symmetry operations comprises rotation by 2π/4 about one axis (z) and rotations by 2π/2 about the other two axes (x and y), see Fig. 1.

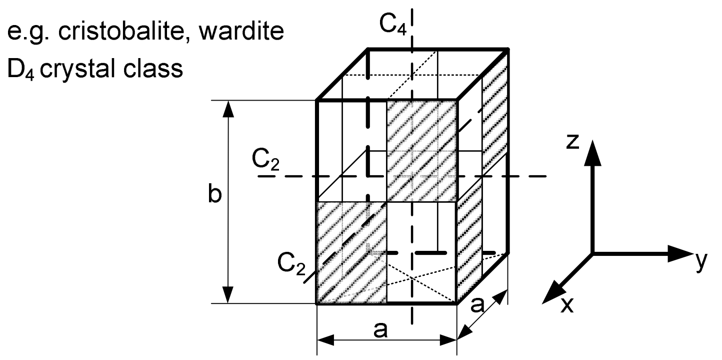

Figure 1: Schematic representation of the D_4 symmetry class with its three angles and two- and four-fold axes of rotation (C_2, C_4).

In this exercise, we are going to look at the restrictions that the D_4 point group imposes on the form of the second-order nonlinear susceptibility tensor. For simplicity, we are going to analyze the case of second-harmonic generation (SHG).

Let us consider a material with a second-order nonlinear susceptibility tensor χ_{qrs}, where the subscripts $q, r, s \in \{1,2,3\}$ denote the vector component of the polarization and the electric field. The component q of the polarization is then given by

$$P_q = \frac{1}{2}\epsilon_0 \chi_{qrs} E_r E_s, \tag{1}$$

where Einstein summation convention is used so that index repetition on the right hand side of the equation indicates sum over these indices.

Now apply a symmetry operation T to the entire configuration (E, P and the material), for example a π/2 rotation. In general, the tensor describing the new material has now changed. However, because of crystal symmetry, T leaves the material physically unchanged. The susceptibility tensor can therefore be replaced by the original susceptibility tensor elements:

$$T_{qq'} P_{q'} = \frac{1}{2}\epsilon_0 \chi_{qrs} (T_{rr'} E_{r'})(T_{ss'} E_{s'}). \tag{2}$$

Equation (2) can be further simplified by using the contracted notation, $\underline{\chi}^{(2)}_{\text{qrs}} \mapsto d_{\text{ql}} = \underline{\chi}^{(2)}_{\text{qrs}} / 2$, with the matrix components d_{ij} instead of the susceptibility tensor components:

$$\begin{bmatrix} P_{x,2\omega} \\ P_{y,2\omega} \\ P_{z,2\omega} \end{bmatrix} = \epsilon_0 \begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix} \begin{bmatrix} E^2_{x,\omega} \\ E^2_{y,\omega} \\ E^2_{z,\omega} \\ 2E_{y,\omega}E_{z,\omega} \\ 2E_{x,\omega}E_{z,\omega} \\ 2E_{x,\omega}E_{y,\omega} \end{bmatrix} \tag{3}$$

For finding the implications of the symmetry on the form of the matrix d_{ij} proceed as follows:

1. Complete the following tables that describe how the elements in Eq. (3) change for each of the three rotations described above. In the table, "2π/2, *x*" denotes a rotation by 2π/2 about the *x*-axis. The second column of the first table has been already completed. (Hint: Use the matrix expression for the rotation operations).

	$\frac{2\pi}{2}, x$	$\frac{2\pi}{2}, y$	$\frac{2\pi}{4}, z$
$P'_{x,2\omega}$		$-P_{x,2\omega}$	
$P'_{y,2\omega}$		$P_{y,2\omega}$	
$P'_{z,2\omega}$		$-P_{z,2\omega}$	

(4)

	$\frac{2\pi}{2}, x$	$\frac{2\pi}{2}, y$	$\frac{2\pi}{4}, z$
$E'^2_{x,\omega}$			
$E'^2_{y,\omega}$			
$E'^2_{z,\omega}$			
$2E'_{y,\omega}E'_{z,\omega}$			
$2E'_{x,\omega}E'_{z,\omega}$			
$2E'_{x,\omega}E'_{y,\omega}$			

(5)

Use Eq. (3), (4) and (5) to derive expressions for the $P'_{x,2\omega}$, $P'_{y,2\omega}$ and $P'_{z,2\omega}$ components of the polarization after the various rotations and compare them to the original expressions before rotation. Use the concept express by Eq. (2) to compare the coefficients associated with the various products of the electric fields and find the constraints on the matrix components d_{ij}. Identify the non-zero elements of the matrix.

Solution

1. Operation of rotation about the *x*, *y* and *z* axes by an angle of θ can be expressed by the following rotation matrices.

$$R_x(\theta)=\begin{bmatrix}1&0&0\\0&\cos(\theta)&-\sin(\theta)\\0&\sin(\theta)&\cos(\theta)\end{bmatrix};R_y(\theta)=\begin{bmatrix}\cos(\theta)&0&-\sin(\theta)\\0&1&0\\\sin(\theta)&0&\cos(\theta)\end{bmatrix};$$

$$R_z(\theta)=\begin{bmatrix}\cos(\theta)&-\sin(\theta)&0\\\sin(\theta)&\cos(\theta)&0\\0&0&1\end{bmatrix}.$$

For the given rotation angles $\left(\frac{2\pi}{2},x\right)$, $\left(\frac{2\pi}{2},y\right)$ and $\left(\frac{2\pi}{4},z\right)$, the rotation matrices are:

$$R_x(\theta)=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{bmatrix};R_y(\theta)=\begin{bmatrix}-1&0&0\\0&1&0\\0&0&-1\end{bmatrix};R_z(\theta)=\begin{bmatrix}0&-1&0\\1&0&0\\0&0&1\end{bmatrix}.$$

The rotation of the nonlinear polarization about the *x* axis can be represented by:

$$R_x\left(\frac{2\pi}{2}\right)\cdot\begin{bmatrix}P_{x,2\omega}\\P_{y,2\omega}\\P_{z,2\omega}\end{bmatrix}=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&-1\end{bmatrix}\cdot\begin{bmatrix}P_{x,2\omega}\\P_{y,2\omega}\\P_{z,2\omega}\end{bmatrix}=\begin{bmatrix}P_{x,2\omega}\\-P_{y,2\omega}\\-P_{z,2\omega}\end{bmatrix}=\begin{bmatrix}P'_{x,2\omega}\\P'_{y,2\omega}\\P'_{z,2\omega}\end{bmatrix}$$

Analogous relations hold for the electric field. In a similar way, using rotation matrices, we can get the other missing relations and fill in the tables (4) and (5).

	$\frac{2\pi}{2},x$	$\frac{2\pi}{2},y$	$\frac{2\pi}{4},z$
$P'_{x,2\omega}$	$P_{x,2\omega}$	$-P_{x,2\omega}$	$-P_{y,2\omega}$
$P'_{y,2\omega}$	$-P_{y,2\omega}$	$P_{y,2\omega}$	$P_{x,2\omega}$
$P'_{z,2\omega}$	$-P_{z,2\omega}$	$-P_{z,2\omega}$	$P_{z,2\omega}$

(6)

	$\frac{2\pi}{2},x$	$\frac{2\pi}{2},y$	$\frac{2\pi}{4},z$
$E'^2_{x,\omega}$	$E^2_{x,\omega}$	$E^2_{x,\omega}$	$E^2_{y,\omega}$
$E'^2_{y,\omega}$	$E^2_{y,\omega}$	$E^2_{y,\omega}$	$E^2_{x,\omega}$
$E'^2_{z,\omega}$	$E^2_{z,\omega}$	$E^2_{z,\omega}$	$E^2_{z,\omega}$
$2E'_{y,\omega}E'_{z,\omega}$	$2E_{y,\omega}E_{z,\omega}$	$-2E_{y,\omega}E_{z,\omega}$	$2E_{x,\omega}E_{z,\omega}$
$2E'_{x,\omega}E'_{z,\omega}$	$-2E_{x,\omega}E_{z,\omega}$	$2E_{x,\omega}E_{z,\omega}$	$-2E_{y,\omega}E_{z,\omega}$
$2E'_{x,\omega}E'_{y,\omega}$	$-2E_{x,\omega}E_{y,\omega}$	$-2E_{x,\omega}E_{y,\omega}$	$-2E_{x,\omega}E_{y,\omega}$

(7)

2. Let us first consider the rotation about the *x* axis. Before the rotation, the following relation holds:

$$P_{x,2\omega} = \varepsilon_0 \left(d_{11} E_{x,\omega}^2 + d_{12} E_{y,\omega}^2 + d_{13} E_{z,\omega}^2 + 2d_{14} E_{y,\omega} E_{z,\omega} + 2d_{15} E_{x,\omega} E_{z,\omega} + 2d_{16} E_{x,\omega} E_{y,\omega} \right) \quad (8)$$

After the rotation, we get:

$$P'_{x,2\omega} = \varepsilon_0 \left(d_{11} E'^2_{x,\omega} + d_{12} E'^2_{y,\omega} + d_{13} E'^2_{z,\omega} + 2d_{14} E'_{y,\omega} E'_{z,\omega} + 2d_{15} E'_{x,\omega} E'_{z,\omega} + 2d_{16} E'_{x,\omega} E'_{y,\omega} \right)$$

$$P_{x,2\omega} = \varepsilon_0 \left(d_{11} E_{x,\omega}^2 + d_{12} E_{y,\omega}^2 + d_{13} E_{z,\omega}^2 + 2d_{14} E_{y,\omega} E_{z,\omega} - 2d_{15} E_{x,\omega} E_{z,\omega} - 2d_{16} E_{x,\omega} E_{y,\omega} \right) \quad (9)$$

Since the right-hand parts of Eqs. (8) and (9) must be equal, we conclude that:

$$d_{15} = d_{16} = 0 .$$

In a similar fashion, we get the following:

$$P_{y,2\omega} = \varepsilon_0 \left(d_{21} E_{x,\omega}^2 + d_{22} E_{y,\omega}^2 + d_{23} E_{z,\omega}^2 + 2d_{24} E_{y,\omega} E_{z,\omega} + 2d_{25} E_{x,\omega} E_{z,\omega} + 2d_{26} E_{x,\omega} E_{y,\omega} \right)$$

$$P'_{y,2\omega} = \varepsilon_0 \left(d_{21} E'^2_{x,\omega} + d_{22} E'^2_{y,\omega} + d_{23} E'^2_{z,\omega} + 2d_{24} E'_{y,\omega} E'_{z,\omega} + 2d_{25} E'_{x,\omega} E'_{z,\omega} + 2d_{26} E'_{x,\omega} E'_{y,\omega} \right)$$

$$-P_{y,2\omega} = \varepsilon_0 \left(d_{21} E_{x,\omega}^2 + d_{22} E_{y,\omega}^2 + d_{23} E_{z,\omega}^2 + 2d_{24} E_{y,\omega} E_{z,\omega} - 2d_{25} E_{x,\omega} E_{z,\omega} - 2d_{26} E_{x,\omega} E_{y,\omega} \right)$$

$$P_{y,2\omega} = \varepsilon_0 \left(-d_{21} E_{x,\omega}^2 - d_{22} E_{y,\omega}^2 - d_{23} E_{z,\omega}^2 - 2d_{24} E_{y,\omega} E_{z,\omega} + 2d_{25} E_{x,\omega} E_{z,\omega} + 2d_{26} E_{x,\omega} E_{y,\omega} \right)$$

$$\Rightarrow \quad d_{21} = d_{22} = d_{23} = d_{24} = 0 .$$

Doing the same thing for the *z* component of the nonlinear polarization, we get:

$$P_{z,2\omega} = \varepsilon_0 \left(d_{31} E_{x,\omega}^2 + d_{32} E_{y,\omega}^2 + d_{33} E_{z,\omega}^2 + 2d_{34} E_{y,\omega} E_{z,\omega} + 2d_{35} E_{x,\omega} E_{z,\omega} + 2d_{36} E_{x,\omega} E_{y,\omega} \right)$$

$$P'_{z,2\omega} = \varepsilon_0 \left(d_{31} E'^2_{x,\omega} + d_{32} E'^2_{y,\omega} + d_{33} E'^2_{z,\omega} + 2d_{34} E'_{y,\omega} E'_{z,\omega} + 2d_{35} E'_{x,\omega} E'_{z,\omega} + 2d_{36} E'_{x,\omega} E'_{y,\omega} \right)$$

$$-P_{z,2\omega} = \varepsilon_0 \left(d_{31} E_{x,\omega}^2 + d_{32} E_{y,\omega}^2 + d_{33} E_{z,\omega}^2 + 2d_{34} E_{y,\omega} E_{z,\omega} - 2d_{35} E_{x,\omega} E_{z,\omega} - 2d_{36} E_{x,\omega} E_{y,\omega} \right)$$

$$P_{z,2\omega} = \varepsilon_0 \left(-d_{31} E_{x,\omega}^2 - d_{32} E_{y,\omega}^2 - d_{33} E_{z,\omega}^2 - 2d_{34} E_{y,\omega} E_{z,\omega} + 2d_{35} E_{x,\omega} E_{z,\omega} + 2d_{36} E_{x,\omega} E_{y,\omega} \right)$$

$$\Rightarrow \quad d_{31} = d_{32} = d_{33} = d_{34} = 0$$

Considering the rotation about the *y* axis and analyzing the *x*, *y* and *z* components of the nonlinear polarization in the way we did it for the rotation about the *x* axis, we will get:

$$\begin{aligned} P'_{x,2\omega} &= -P_{x,2\omega} \;\Rightarrow\; d_{11} = d_{12} = d_{13} = d_{15} = 0 \\ P'_{y,2\omega} &= P_{y,2\omega} \;\Rightarrow\; d_{24} = d_{26} = 0 \\ P'_{z,2\omega} &= -P_{z,2\omega} \;\Rightarrow\; d_{31} = d_{32} = d_{33} = d_{35} = 0 \end{aligned}$$

So far we have shown that from 18 elements of d_{ij} matrix, only 3 are non-zero $d_{14} \neq 0, d_{25} \neq 0, d_{36} \neq 0$. Thus, the Eq. (3) is now simplified:

$$\begin{bmatrix} P_{x,2\omega} \\ P_{y,2\omega} \\ P_{z,2\omega} \end{bmatrix} = \epsilon_0 \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix} \begin{bmatrix} E_{x,\omega}^2 \\ E_{y,\omega}^2 \\ E_{z,\omega}^2 \\ 2E_{y,\omega}E_{z,\omega} \\ 2E_{x,\omega}E_{z,\omega} \\ 2E_{x,\omega}E_{y,\omega} \end{bmatrix} \Rightarrow \begin{aligned} P_{x,2\omega} &= \epsilon_0 d_{14} 2E_{y,\omega}E_{z,\omega} \\ P_{y,2\omega} &= \epsilon_0 d_{25} 2E_{x,\omega}E_{z,\omega} \\ P_{z,2\omega} &= \epsilon_0 d_{36} 2E_{x,\omega}E_{y,\omega} \end{aligned} .$$

If we now consider the rotation about the *z* axis, we will get $d_{36} = 0$ and $d_{25} = -d_{14} \neq 0$.

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