PHYS2202 Nonlinear Optics
Problem Set 6 solutions

1. **(20 points)**

Context: Except for the final equation, this contextual information is not needed to solve the problem; it is just to explain why we would consider such a problem.

Throughout the course, we have used the electric-dipole approximation. Namely, we have assumed that the interaction Hamiltonian between the optical fields and the medium is given by

$$\hat{H}_I = \hat{H}_{\mathrm{ED}} = -\sum_j q_j \hat{\vec{r}}_j \cdot \vec{E}(\vec{r}_j), \tag{1}$$

where q_j is the charge of particle j located at position $\vec{r}_j$. This approximation is reasonable since the wavelengths of optical fields are long compared to the size of an atom, molecule, or crystal lattice period. We have seen, though, that for a crystal of given symmetry, there are certain combinations of input and output electric field polarizations for which the n^{th} order nonlinear response *in the electric-dipole approximation* (ED) is zero because $\hat{u} \cdot \overset{\leftrightarrow}{\chi}{}^{(n)}_{\mathrm{ED}} : \hat{a}\hat{b} \cdots \hat{n} = \chi^{(n)}_{\mathrm{ED},uab\ldots n} = 0$. For such combinations of polarizations, we might still see a non-zero n^{th} order nonlinear optical response (i.e., a response that depends on n interactions with the electric field), but this response will be due to typically weak but non-zero non-dipolar contributions.

The leading order non-dipolar contributions to the optical response of a material are typically the electric quadrupole response and the magnetic dipole response. Let us consider the electric quadrupole response. Our elementary model for an electric quadrupole is two oppositely aligned electric dipoles of equal magnitude next to one another. To *induce* an electric quadrupole, the electric field cannot be constant across the material; the electric field must be spatially varying on a short enough timescale to push like charges in opposite directions. We can write the quadrupolar interaction Hamiltonian as

$$\hat{H}_{\mathrm{EQ}} = -\frac{1}{6}\sum_{i,j} Q_{ij} \frac{\partial}{\partial x_i} \vec{E}_j(\vec{r}), \tag{2}$$

where the "molecular" (here we use the term in an extended sense to mean a microscopic object: atom, molecule, or unit cell) quadrupole operator $\overset{\leftrightarrow}{Q}$ for a collection of point charges is

$$\overset{\leftrightarrow}{Q}_{ij} = \frac{1}{6}\sum_n \left(3x_{n,i}x_{n,j} - r^2\delta_{ij}\right) q_n \tag{3}$$

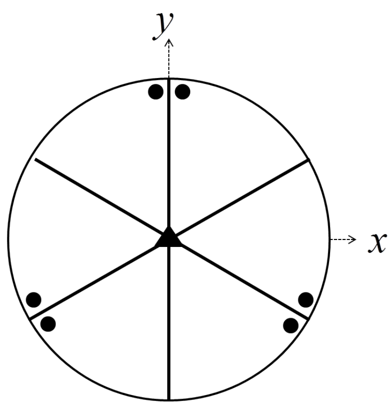
Just as we saw that we can express the dipolar response in terms of a *local* susceptibility $\overset{\leftrightarrow}{\chi}^{(n)}$, the *nonlocal* electric quadrupole response (nonlocal because the response depends on the fact that the electric field has a spatial variation; there is a difference in electric field between two locations) can be expressed in terms of an n^{th} order nonlocal susceptibility $\overset{\leftrightarrow}{\chi}^{(n)}_{\text{EQ}}$. For example, the second-order electric quadrupole response can be written

$$P_u^{(2)}(\omega) = \sum_{a,b,c} \chi^{(2)}_{\text{EQ},uabc}(-\omega;\omega_1,\omega_2) E_a(\omega_1) \frac{d}{dx_b} E_c(\omega_2). \tag{4}$$

Note that the n^{th} order electric quadrupole contribution to the susceptibility is characterized by four indices instead of the three indices characterizing the dipolar $\overset{\leftrightarrow}{\chi}^{(2)}$, so although they are both labeled here by a (2) superscript they tensors are not the same rank.

Question: Consider the 3m crystal class whose stereogram is illustrated below. The filled circles represent atoms above the plane of the page. The only symmetry operations of this system are a three fold rotation about the z axis (out of the page), i.e., rotations of $2\pi/3$ and $4\pi/3$, and a mirror plane perpendicular to the x axis (in the yz plane). Note that the three-fold symmetry means that there must then be three mirror reflection planes. Find all combinations of input and output polarizations that could yield a non-zero polarization; that is, find all the non-zero quadrupole susceptibility elements $\chi^{(2)}_{\text{EQ},ijkl}$. Identify the dependences between elements that are not independent.

Note: You must demonstrate which elements are potentially non-zero and their dependencies. You cannot just give the result.



Solution:
We begin by summarizing the result. A list of the 37 tensor elements (identified by just their indices) not required by symmetry to be equal to zero and their dependencies (there are only 14 unique elements) is

$$\begin{aligned}
&zzzz;\\
&zzyy = zzxx, \quad zyzy = zxzx, \quad zyyz = zxxz,\\
&yzzy = xzzx, \quad yzyz = xzxz, \quad yyzz = xxzz;\\
&xxxx = yyyy = xxyy + xyxy + xyyx, \quad yxxy = xyyx, \quad yxyx = xyxy, \quad yyxx = xxyy;\\
&yyyz = -xxyz = -xyxz = -yxxz, \quad yyzy = -xxzy = -xyzx = -yxzx\\
&yzyy = -xzxy = -xzyx = -yzxx, \quad zyyy = -zxxy = -zxyx = -zyxx
\end{aligned}$$

The 44 zero elements that must be equal to zero are then

$$\begin{aligned}
&zzzy, \quad zzyz, \quad zyzz, \quad yzzz;\\
&xyyy, \quad xyyz, \quad xyzy, \quad xzyy, \quad xzzy, \quad xzyz, \quad xyzz, \quad xzzz,\\
&yxyy, \quad yxyz, \quad yxzy, \quad zxyy, \quad zxzy, \quad zxyz, \quad yxzz, \quad zxzz,\\
&yyxy, \quad yyxz, \quad yzxy, \quad zyxy, \quad zzxy, \quad zyxz, \quad yzxz, \quad zzxz,\\
&yyyx, \quad yyzx, \quad yzyx, \quad zyyx, \quad zzyx, \quad zyzx, \quad yzzx, \quad zzzx,\\
&xxxy, \quad xxxz, \quad xxyx, \quad xxzx, \quad xyxx, \quad xzxx, \quad yxxx, \quad zxxx
\end{aligned}$$

The first thing to realize is that there is nothing fundamentally different going on here than when if we treat a third order dipolar nonlinear process:

$$P_u^{(3)}(\omega) = \sum_{a,b,c} \chi^{(2)}_{\mathrm{ED}}(-\omega; \omega_1, \omega_2, \omega_3) E_a(\omega_1) E_b(\omega_2) E_c(\omega_3). \tag{5}$$

In each case we have a fourth rank tensor, and in each case, each component of the tensor is associated with a component of a polar vector or, in the current problem, an operator (∇) that transforms like a polar vector. What is different in the two cases is the microscopic manner in which the signal is generated and so the magnitudes of the non-zero susceptibility elements and perhaps the atomic selection rules but not the overall structural symmetry. Therefore, we can still use our previous analysis of the transformation of the susceptibility elements under rotations:

$$\chi^{(2)}_{\mathrm{EQ},\mu\alpha\beta\gamma} = R_{\mu u} R_{\alpha a} R_{\beta b} R_{\gamma c} \chi^{(2)}_{\mathrm{EQ},uabc}, \tag{6}$$

where the Einstein summation convention is used (multiplication of terms with repeated indices implies a sum over all the values of that index). We just need to be able to analyze $3^4 = 81$ tensor elements!

To implement the last equation, we need to identify the rotation operations corresponding to the symmetries of our system. For a $\pm 120^\circ$ rotation about the z axis, the matrix is

$$R(120^\circ) = -\frac{1}{2}\begin{pmatrix} 1 & \sqrt{3} & 0 \\ -\sqrt{3} & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \qquad R(-120^\circ) = -\frac{1}{2}\begin{pmatrix} 1 & -\sqrt{3} & 0 \\ \sqrt{3} & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \tag{7}$$

For reflection about the yz plane, the matrix is

$$R(m_x) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{8}$$

The fact that the rotation matrices are characterized by $R_{z\alpha} = R_{\alpha z} = 0$ unless $\alpha = z$ means that right away we can conclude that

$$\boxed{\chi^{(2)}_{\mathrm{EQ},zzzz}} \tag{9}$$

is independent and not required to be zero.

Reflection:

Let's first see what we can learn from the reflection m_x. We begin with the susceptibility element $\chi^{(2)}_{\mathrm{EQ},xxxx}$. It must be the case that

$$\chi^{(2)}_{\mathrm{EQ},xxxx} = R_{xu}(m_x)R_{xa}(m_x)R_{xb}(m_x)R_{xc}(m_x)\chi^{(2)}_{\mathrm{EQ},uabc}. \tag{10}$$

Since the only non-zero element $R_{xa}(m_x)$ is $R_{xx}(m_x) = -1$, we find

$$\chi^{(2)}_{\mathrm{EQ},xxxx} = (-1)^4\chi^{(2)}_{\mathrm{EQ},xxxx} = \chi^{(2)}_{\mathrm{EQ},xxxx}. \tag{11}$$

So we learn nothing about the element $\chi^{(2)}_{\mathrm{EQ},xxxx}$ from the operation $\hat{m}_x$.

Let us now look at $\chi^{(2)}_{\mathrm{EQ},xxxy}$ under the reflection $\hat{m}_x$:

$$\begin{aligned} \chi^{(2)}_{\mathrm{EQ},xxxy} &= R_{xu}(m_x)R_{xa}(m_x)R_{xb}(m_x)R_{yc}(m_x)\chi^{(2)}_{\mathrm{EQ},uabc} \\ &= (-1)^3R_{yc}(m_x)\chi^{(2)}_{\mathrm{EQ},xxxc} \\ &= -R_{yc}(m_x)\chi^{(2)}_{\mathrm{EQ},xxxc}. \end{aligned} \tag{12}$$

The only non-zero element $R_{yy}(m_x) = 1$, so

$$\chi^{(2)}_{\mathrm{EQ},xxxy} = -\chi^{(2)}_{\mathrm{EQ},xxxy}. \tag{13}$$

Therefore, it must be the case that

$$\chi^{(2)}_{\mathrm{EQ},xxxy} = 0. \tag{14}$$

Only 80 elements to go! However, it should now be evident that the reflection m_x will similarly lead to the conclusion that all $\chi^{(2)}_{\mathrm{EQ},uabc}$ with an odd number of x indices must be zero due to the reflection symmetry of the system. For a single x index, there are four positions where the x could appear, and for each of these four cases, there are then 2 options (y or z) for each of the three remaining indices, so this takes care of $4(2^3) = 32$ elements. Similarly, for three x indices, there are four locations for the remaining index, which can take one of two values. This takes care of $4(2) = 8$ susceptibility tensor elements. So we have determined that 40 elements must be zero based on the reflection m_x:

$$\boxed{\begin{aligned} xyyy &= xyyz = xyzy = xzyy = xzzy = xzyz = xyzz = xzzz \\ &= yxyy = yxyz = yxzy = zxyy = zxzy = zxyz = yxzz = zxzz \\ &= yyxy = yyxz = yzxy = zyxy = zzxy = zyxz = yzxz = zzxz \\ &= yyyx = yyzx = yzyx = zyyx = zzyx = zyzx = yzzx = zzzx \\ &= xxxy = xxxz = xxyx = xxzx = xyxx = xzxx = yxxx = zxxx = 0. \end{aligned}}$$

Rotation

Let us now turn to the 120° rotation. Consider the $\chi^{(2)}_{\mathrm{EQ},zzzy}$ tensor element:

$$\chi^{(2)}_{\mathrm{EQ},zzzy} = R_{zu}(120^\circ)R_{za}(120^\circ)R_{zb}(120^\circ)R_{yc}(120^\circ)\chi^{(2)}_{\mathrm{EQ},uabc}. \tag{15}$$

Again, the only non-zero $R_{z\alpha}(120^\circ)$ is $R_{zz}(120^\circ) = 1$, but in the case of $R_{y\alpha}(120^\circ)$ we find two non-zero elements $R_{yx}(120^\circ) = \sqrt{3}/2$ and $R_{yy}(120^\circ) = -1/2$. Therefore,

$$\chi^{(2)}_{\mathrm{EQ},zzzy} = R_{yx}(120^\circ)\chi^{(2)}_{\mathrm{EQ},zzzx} + R_{yy}(120^\circ)\chi^{(2)}_{\mathrm{EQ},zzzy}, \tag{16}$$

but we already found that $\chi^{(2)}_{\mathrm{EQ},zzzx} = 0$. We then conclude that

$$\chi^{(2)}_{\mathrm{EQ},zzzy} = -\frac{1}{2}\chi^{(2)}_{\mathrm{EQ},zzzy}. \tag{17}$$

The 120° rotational symmetry then requires that

$$\chi^{(2)}_{\mathrm{EQ},zzzy} = 0. \tag{18}$$

Again, it should be clear that this result is independent of the position of the y index, so

$$\boxed{zzzy = zzyz = zyzz = yzzz = 0}. \tag{19}$$

(For simplicity, from here on, we will just represent $\chi^{(2)}_{\mathrm{EQ},uabc}$ by $uabc$.)

Now let's look at $\chi^{(2)}_{\mathrm{EQ},zzyy}$:

$$\begin{aligned}
zzyy &= R_{yb}(120^\circ)R_{yc}zzbc \\
&= R_{yx}R_{yx}zzxx + R_{yx}R_{yy}zzxy + R_{yy}R_{yx}zzyx + R_{yy}R_{yy}zzyy \\
&= \frac{3}{4}zzxx - \frac{\sqrt{3}}{4}zzxy - \frac{\sqrt{3}}{4}zzyx + \frac{1}{4}zzyy \\
&= \frac{3}{4}zzxx + \frac{1}{4}zzyy. \qquad (20)
\end{aligned}$$

We conclude that

$$\boxed{\chi^{(2)}_{\mathrm{EQ},zzyy} = \chi^{(2)}_{\mathrm{EQ},zzxx}}. \qquad (21)$$

Again, there is nothing special about the order of the specific indices, so it will be the case that

$$\boxed{\begin{array}{lll} zzyy = zzxx, & zyzy = zxzx, & zyyz = zxxz \\ yzzy = xzzx, & yzyz = xzxz, & yyzz = xxzz. \end{array}} \qquad (22)$$

Consider now $\chi^{(2)}_{\mathrm{EQ},yyxx}$:

$$yyxx = R_{yu}R_{ya}R_{xb}R_{xc}R_{xb}\chi^{(2)}_{\mathrm{EQ},uabc}. \qquad (23)$$

Since we have already seen that an odd number of x indices implies that the susceptibility tensor is zero

$$\begin{aligned}
yyxx &= R_{yx}R_{yx}R_{xx}R_{xx}xxxx + R_{yx}R_{yx}R_{xy}R_{xy}xxyy + R_{yx}R_{yy}R_{xx}R_{xy}xyxy \\
&+ R_{yx}R_{yy}R_{xy}R_{xx}xyyx + R_{yy}R_{yx}R_{xx}R_{xy}yxxy + R_{yy}R_{yx}R_{xy}R_{xx}yxyx \\
&+ R_{yy}R_{yy}R_{xx}R_{xx}yyxx \\
&= \frac{1}{16}\left[3xxxx + 9xxyy - 3(xyxy + xyyx + yxxy + yxyx) + yyxx + 3yyyy\right]. \qquad (24)
\end{aligned}$$

We see that the 8 elements $yyxx$, $xxxx$, $xxyy$, $xyxy$, $xyyx$, $yxxy$, $yxyx$, $yyxx$, and $yyyy$ are dependent. To determine the exact relations, we must repeat this process for each of the elements on the right-hand side of the last equation.

Repeating this procedure for $xxxx$ and again excluding terms with an odd number of x indices,

$$\begin{aligned}
xxxx &= R^4_{xx}xxxx + R^2_{xx}R^2_{xy}\left(xxyy + xyxy + xyyx + yxxy + yxyx + yyxx\right) + R^4_{xy}yyyy \\
&= \frac{1}{16}\left[xxxx + 3\left(xxyy + xyxy + xyyx + yxxy + yxyx + yyxx\right) + 9yyyy\right]. \qquad (25)
\end{aligned}$$

$$\begin{aligned}
xyxy &= R^2_{xx}R^2_{yx}xxxx + R_{xx}R_{yx}R_{xy}R_{yy}(xxyy + yyxx + xyyx + yxxy) + R^2_{xx}R^2_{yy}xyxy \\
&+ R^2_{xy}R^2_{yx}yxyx + R^2_{xy}R^2_{yy}yyyy \qquad (26) \\
&= \frac{1}{16}\left[3xxxx - 3(xxyy + yyxx + xyyx + yxxy) + xyxy + 9yxyx + 3yyyy\right] \qquad (27)
\end{aligned}$$

$$
\begin{aligned}
xyyx &= R_{xx}^2 R_{yx}^2 xxxx + R_{xx}R_{yx}R_{yy}R_{xy}(xxyy + yyxx + xyxy + yxyx) + R_{xx}^2 R_{yy}^2 xyyx \\
&\quad + R_{xy}^2 R_{yx}^2 yxxy + R_{xy}^2 R_{yy}^2 yyyy && (28)\\
&= \frac{1}{16}\left[3xxxx - 3(xxyy + yyxx + xyxy + yxyx) + xyyx + 9yxxy + 3yyyy\right] && (29)
\end{aligned}
$$

Since for the 120° rotation, $R_{xy} = -R_{yx}$ and $R_{xx} = R_{yy}$, we can obtain the elements $xxyy$, $yxyx$, $yxxy$, and $yyyy$ by simply switching x and y in the formulas for $yyxx$, $yxyx$, $xyyx$, and $xxxx$ respectively:

$$
\begin{aligned}
xxyy &= \frac{1}{16}\left[3xxxx + xxyy - 3(xyxy + xyyx + yxxy + yxyx) + 9yyxx + 3yyyy\right] && (30)\\
yxyx &= \frac{1}{16}\left[3xxxx - 3(xxyy + yyxx + xyyx + yxxy) + 9xyxy + yxyx + 3yyyy\right] && (31)\\
yxxy &= \frac{1}{16}\left[3xxxx - 3(xxyy + yyxx + xyxy + yxyx) + 9xyyx + yxxy + 3yyyy\right] && (32)\\
yyyy &= \frac{1}{16}\left[9xxxx + 3\left(xxyy + xyxy + xyyx + yxxy + yxyx + yyxx\right) + yyyy\right]. && (33)
\end{aligned}
$$

From the equations for $xxxx$ and $yyyy$, we see that $16yyyy = 16xxxx + 8xxxx - 8yyyy$ or

$$\boxed{yyyy = xxxx}. \tag{34}$$

From the equations for $xyyx$ and $yxxy$, we see that $yxxy = xyyx + 8xyyx - 8yxxy$ or

$$\boxed{yxxy = xyyx}. \tag{35}$$

Similarly, from the equations for $xyxy$ and $yxyx$ and for $yyxx$ and $xxyy$, we find

$$\boxed{yxyx = xyxy, \quad yyxx = xxyy}. \tag{36}$$

Plugging the last three equalities into the equation for $yyyy$ yields

$$\boxed{xxxx = yyyy = xxyy + xyxy + xyyx}. \tag{37}$$

We are left with the tensor elements involving a single z index. These must have zero or two x indices based on our earlier results, so we are left with the the four elements with one z and three y coefficients and the 12 elements with one z index, one y index, and two x indices.

Consider for example, $yyyz$. Since the only non-zero element of the rotation matrix that involves z is $R_{zz} = 1$, the z index must remain in the same spot on both sides of the equation:

$$
\begin{aligned}
yyyz &= R_{yx}^2 R_{yy} R_{zz}(xxyz + xyxz + yxxz) + R_{yy}^3 R_{zz} yyyz && (38)\\
&= -\frac{1}{8}\left[3(xxyz + xyxz + yxxz) + yyyz\right], && (39)
\end{aligned}
$$

or

$$yyyz = -\frac{1}{3}(xxyz + xyxz + yxxz). \tag{40}$$

The elements $yyzy$, $yzyy$, and $zyyy$ are obtained just by corresponding cycling of the indices on the right-hand side of the equation:

$$yyzy = -\frac{1}{3}(xxzy + xyzx + yxzx) \tag{41}$$

$$yzyy = -\frac{1}{3}(xzxy + xzyx + yzxx) \tag{42}$$

$$zyyy = -\frac{1}{3}(zxxy + zxyx + zyxx) \tag{43}$$

Turning to $xxyz$:

$$\begin{aligned} xxyz &= R_{zz}\left[R_{xx}^2 R_{yy} xxyz + R_{xx}R_{xy}R_{yx}(xyxz + yxxz) + R_{xy}^2 R_{yy} yyyz\right] \\ &= \frac{1}{8}\left[-xxyz + 3(xyxz + yxxz) - 3yyyz\right]. \end{aligned} \tag{44}$$

Substituting the result for $yyyz$,

$$xxyz = \frac{1}{2}(xyxz + yxxz). \tag{45}$$

We now look at $xyxz$:

$$xyxz = \frac{1}{8}\left[-xyxz + 3(xxyz + yxxz) - 3yyyz\right] \tag{46}$$

Using the result for $yyyz$ again,

$$xyxz = \frac{1}{2}(xxyz + yxxz). \tag{47}$$

Subracting this equation for $xyxz$ from the preceding equation for $xxyz$, we find that

$$xxyz = xyxz, \tag{48}$$

which when plugged into the equation for $xyxz$ or $xxyz$ in turn yields

$$xxyz = xyxz = yxxz, \tag{49}$$

which then implies that

$$\boxed{yyyz = -xxyz = -xyxz = -yxxz}. \tag{50}$$

The procedure yielding the last result can be repeated for all the same tensor elements but where z is cycled through the different positions. We end up with

$$\boxed{\begin{aligned} yyyz &= -xxyz = -xyxz = -yxxz \\ yyzy &= -xxzy = -xyzx = -yxzx \\ yzyy &= -xzxy = -xzyx = -yzxx \\ zyyy &= -zxxy = -zxyx = -zyxx \end{aligned}}$$