Chapter 4

THE INTENSITY-DEPENDENT REFRACTIVE INDEX
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- 4.1. Descriptions of the Intensity-Dependent Refractive Index
- 4.2. Tensor Nature of the Third-Order Susceptibility
- 4.3. Nonresonant Electronic Nonlinearities
- 4.4. Nonlinearities Due to Molecular Orientation
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- 4.6. Semiconductor Nonlinearities
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4.1. Descriptions of the Intensity-Dependent Refractive Index

The refractive index of many materials can be described by the relation

\[ n = n_0 + \bar{n}_2 \langle \tilde{E}^2 \rangle, \]  \hspace{1cm} (4.1.1)

where \( n_0 \) represents the usual, weak-field refractive index and \( \bar{n}_2 \) is sometimes called the second-order index of refraction. The angular brackets surrounding the quantity \( \tilde{E}^2 \) represent a time average. Thus, if the optical field is of the form

\[ \tilde{E}(t) = E(\omega)e^{-i\omega t} + \text{c.c.} \] \hspace{1cm} (4.1.2)

\[ \langle \tilde{E}(t)^2 \rangle = 2E(\omega)E(\omega)^* = 2\left| E(\omega) \right|^2, \] \hspace{1cm} (4.1.3)
\[ n = n_0 + 2\overline{n_2}\left|E(\omega)\right|^2. \]  \hfill (4.1.4)

The change in refractive index described by Eq. (4.1.1) or (4.1.4) is sometimes called the **optical Kerr effect**.

The refractive index of a material changes by an amount that is proportional to the square of the strength of an applied static electric field.

The part of the nonlinear polarization that influences the propagation of a beam of frequency \( \omega \) is

\[ P^{NL}(\omega) = 3\varepsilon_0 \chi^{(3)}(\omega = \omega + \omega - \omega)\left|E(\omega)\right|^2 E(\omega). \]  \hfill (4.1.5)

For simplicity we are assuming here that the light is linearly polarized and are suppressing the tensor indices of \( \chi^{(3)} \); the tensor nature of \( \chi^{(3)} \) is addressed explicitly in the following sections. The total polarization of the material system is then described by

\[ P^{TOT}(\omega) = \varepsilon_0 \chi^{(1)}E(\omega) + 3\varepsilon_0 \chi^{(3)}\left|E(\omega)\right|^2 E(\omega) \equiv \varepsilon_0 \chi_{\text{eff}} E(\omega), \]  \hfill (4.1.6)
where we have introduced the effective susceptibility

$$\chi_{\text{eff}} = \chi^{(1)} + 3 \chi^{(3)} |E(\omega)|^2. \quad (4.1.7)$$

In order to relate the nonlinear susceptibility $\chi^{(3)}$ to the nonlinear refractive index $n_2$, we note that it is generally true that

$$n^2 = 1 + \chi_{\text{eff}}, \quad (4.1.8)$$

and by introducing Eq. (4.1.4) on the left-hand side and Eq. (4.1.7) on the right-hand side of this equation, we find that

$$\left[ n_0 + 2 \tilde{n}_2 |E(\omega)|^2 \right]^2 = 1 + \chi^{(1)} + 3 \chi^{(3)} |E(\omega)|^2. \quad (4.1.9)$$
Correct to terms of order $|E(\omega)|^2$, this expression when expanded becomes
\[ n_0^2 + 4n_0\bar{n}_2|E(\omega)|^2 = (1 + \chi^{(1)}) + [3\chi^{(3)}|E(\omega)|^2], \]
which shows that the linear and nonlinear refractive indices are related to the linear and nonlinear susceptibilities by
\[ n_0 = \left(1 + \chi^{(1)}\right)^{1/2} \quad \text{(4.1.10)} \]
and
\[ \bar{n}_2 = \frac{3\chi^{(3)}}{4n_0}. \quad \text{(4.1.11)} \]

**Figure 4.1.1** Two ways of measuring the intensity-dependent refractive index.

In part (a), a strong beam of light modifies its own propagation, whereas in part (b), a strong beam of light influences the propagation of a weak beam.
The nonlinear polarization affecting the probe wave is given by

\[
P^{\text{NL}}(\omega') = 6\varepsilon_0 \chi^{(3)}(\omega' = \omega' + \omega - \omega) \left| E(\omega) \right|^2 E(\omega').
\]  

(4.1.12)

The probe wave hence experiences a refractive index given by

\[
n = n_0 + 2\tilde{n}_2^{\text{(cross)}} \left| E(\omega) \right|^2,
\]  

(4.1.13)

Where

\[
\tilde{n}_2^{\text{(cross)}} = \frac{3 \chi^{(3)}}{2n_0}.
\]  

(4.1.14)

An alternative way of defining the intensity-dependent refractive index is by means of the equation

\[
n = n_0 + n_2 I,
\]  

(4.1.15)
where $I$ denotes the time-averaged intensity of the optical field, given by

$$I = 2n_0\varepsilon_0 c |E(\omega)|^2. \quad (4.1.16)$$

Since the total refractive index $n$ must be the same using either description of the nonlinear contribution, we see by comparing Eqs. (4.1.4) and (4.1.15) that

$$2\bar{n}_2 |E(\omega)|^2 = n_2 I, \quad (4.1.17)$$

and thus that $n_2$ and $n_2$ are related by

$$n_2 = \frac{\bar{n}_2}{n_0\varepsilon_0 c}, \quad (4.1.18)$$

we find that $n_2$ is related to $\chi^{(3)}$ by

$$n_2 = \frac{3}{4n_0^2\varepsilon_0 c} \chi^{(3)}. \quad (4.1.19)$$
This relation can be expressed numerically as

\[ n_2 = \frac{3}{4n_0^2 \epsilon_0 c} \chi^{(3)}. \]  \hspace{1cm} (4.1.19)

This relation can be expressed numerically as

\[ n_2 \left( \frac{m^2}{W} \right) = \frac{283}{n_0^2} \chi^{(3)} \left( \frac{m^2}{V^2} \right). \]  \hspace{1cm} (4.1.20)
Some of the physical processes that can produce a nonlinear change in the refractive index are listed here

1) Electronic polarization: **Electronic charge redistribution**

2) Molecular orientation: **Molecular alignment due to the induced dipole**

3) Electrostriction: **Density change by optical field**

4) Saturated absorption: **Intensity-dependent absorption**

5) Thermal effect: **Temperature change due to the optical field**

6) Photorefractive effect: **Induced redistribution of electrons and holes** ➔

   - **Refractive index change due to the local field inside the medium**
### Table 4.1.1 Typical values of the nonlinear refractive index \(^a\)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>(n_2) (cm(^2)/W)</th>
<th>(\chi^{(3)}_{1111}) (m(^2)/V(^2))</th>
<th>Response Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic polarization</td>
<td>(10^{-16})</td>
<td>(10^{-22})</td>
<td>(10^{-15})</td>
</tr>
<tr>
<td>Molecular orientation</td>
<td>(10^{-14})</td>
<td>(10^{-20})</td>
<td>(10^{-12})</td>
</tr>
<tr>
<td>Electrostriction</td>
<td>(10^{-14})</td>
<td>(10^{-20})</td>
<td>(10^{-9})</td>
</tr>
<tr>
<td>Saturated atomic absorption</td>
<td>(10^{-10})</td>
<td>(10^{-16})</td>
<td>(10^{-8})</td>
</tr>
<tr>
<td>Thermal effects</td>
<td>(10^{-6})</td>
<td>(10^{-12})</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>Photorefractive effect (^b)</td>
<td>(large)</td>
<td>(large)</td>
<td>(intensity-dependent)</td>
</tr>
</tbody>
</table>

\(^a\) For linearly polarized light.

\(^b\) The photorefractive effect often leads to a very strong nonlinear response. This response usually cannot be described in terms of a \(\chi^{(3)}\) (or an \(n_2\)) nonlinear susceptibility, because the nonlinear polarization does not depend on the applied field strength in the same manner as the other mechanisms listed.
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4.2. Tensor Nature of the Third-Order Susceptibility

The third-order susceptibility $\chi_{ijkl}^{(3)}$ is a **fourth-rank tensor**, and thus is described in terms of **81 separate elements**.

For **crystalline solids** with **low symmetry**, all 81 of these elements are independent and can be nonzero (Butcher, 1965).

For materials possessing a higher degree of spatial symmetry, the number of independent elements is very much reduced; As we show below, there are only **three independent elements** for an **isotropic material**.

Let’s consider the 3rd order susceptibility for the case of an isotropic material.

we represent the susceptibility as

$$\chi_{ijkl} \equiv \chi_{ijkl}^{(3)} (\omega_4 = \omega_1 + \omega_2 + \omega_3).$$

Since each of the coordinate axes must be **equivalent** in an isotropic material, it is clear that the susceptibility possesses the following symmetry properties:
we represent the susceptibility as

\[ \chi_{ijkl} = \chi_{ijkl}(\omega_4 = \omega_1 + \omega_2 + \omega_3). \]

Since each of the coordinate axes must be equivalent in an isotropic material, it is clear that the susceptibility possesses the following symmetry properties:

\[ \begin{align*}
\chi_{1111} & = \chi_{2222} = \chi_{3333}, \\
\chi_{1122} & = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322}, \\
\chi_{1212} & = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232}, \\
\chi_{1221} & = \chi_{1331} = \chi_{2112} = \chi_{2332} = \chi_{3113} = \chi_{3223}. 
\end{align*} \tag{4.2.1} \]

The four types of nonzero elements appearing in the four equations (4.2.1) are not independent of one another and, in fact, are related by the equation

\[ \chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221}. \tag{4.2.2} \]

The results given by Eqs. (4.2.1) and (4.2.2) can be used to express the nonlinear susceptibility in the compact form

\[ \chi_{ijkl} = \chi_{1122} \delta_{ij} \delta_{kl} + \chi_{1212} \delta_{ik} \delta_{jl} + \chi_{1221} \delta_{il} \delta_{jk}. \tag{4.2.3} \]
\[
\chi_{ijkl} = \chi_{122} \delta_{ij} \delta_{kl} + \chi_{1212} \delta_{ik} \delta_{jl} + \chi_{1221} \delta_{il} \delta_{jk}
\]

This form shows that the third-order susceptibility has three independent elements for the general case in which the field frequencies are arbitrary.

For the third-harmonic generation, where the frequency dependence of the susceptibility is taken as

\[
\chi_{ijkl}(3\omega = \omega + \omega + \omega)
\]

As a consequence of the intrinsic permutation symmetry of the nonlinear susceptibility, the elements of the susceptibility tensor are related by \(\chi_{1122} = \chi_{1212} = \chi_{1221}\) and thus Eq. (4.2.3) becomes

\[
\chi_{ijkl}(3\omega = \omega + \omega + \omega) = \chi_{1122}(3\omega = \omega + \omega + \omega)(\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}).
\]

(4.2.4)

there is only one independent element of the susceptibility tensor describing third-harmonic generation.
Now, we consider the choice of frequencies given
\[ \chi_{ijkl}(3\omega = \omega + \omega - \omega) \]

For this choice of frequencies, the condition of intrinsic permutation symmetry requires that \( \chi_{1122} \) be equal to \( \chi_{1212} \), and hence \( \chi_{ijkl} \) can be represented by

\[
\chi_{ijkl}(\omega = \omega + \omega - \omega) = \chi_{1122}(\omega = \omega + \omega - \omega) \\
\times (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl}) + \chi_{1221}(\omega = \omega + \omega - \omega)(\delta_{il}\delta_{jk}). \tag{4.2.5}
\]

The nonlinear polarization leading to the nonlinear refractive index is given in terms of the nonlinear susceptibility by

\[
P_i(\omega) = 3\varepsilon_0 \sum_{jkl} \chi_{ijkl}(\omega = \omega + \omega - \omega) E_j(\omega) E_k(\omega) E_l(-\omega). \tag{4.2.6}
\]

If we introduce Eq. (4.2.5) into this equation, we find that

\[
P_i = 6\varepsilon_0 \chi_{1122} E_i(\mathbf{E} \cdot \mathbf{E}^*) + 3\varepsilon_0 \chi_{1221} E_i^*(\mathbf{E} \cdot \mathbf{E}). \tag{4.2.7}
\]
This equation can be written entirely in vector form as

\[ \mathbf{P} = 6\varepsilon_0\chi_{1122}(\mathbf{E} \cdot \mathbf{E}^*)\mathbf{E} + 3\varepsilon_0\chi_{1221}(\mathbf{E} \cdot \mathbf{E})\mathbf{E}^*. \]  \hspace{1cm} (4.2.8)

Following the notation of Maker and Terhune (1965) (see also Maker \textit{et al.}, 1964), we introduce the coefficients

\[ A = 6\chi_{1122} \quad \text{(or} \quad A = 3\chi_{1122} + 3\chi_{1212}) \]  \hspace{1cm} (4.2.9a)

\[ B = 6\chi_{1221}, \]  \hspace{1cm} (4.2.9b)

in terms of which the nonlinear polarization of Eq. (4.2.8) can be written as

\[ \mathbf{P} = \varepsilon_0 A(\mathbf{E} \cdot \mathbf{E}^*)\mathbf{E} + \frac{1}{2}\varepsilon_0 B(\mathbf{E} \cdot \mathbf{E})\mathbf{E}^*. \]  \hspace{1cm} (4.2.10)
under certain circumstances, such as those described later in connection with Fig. 7.2.9, two-photon-resonant processes contribute only to the coefficient $B$

**Figure 4.2.1** Diagrams (a) and (b) represent the resonant contributions to the nonlinear coefficients $A$ and $B$, respectively.
For some purposes, it is useful to describe the nonlinear polarization not by Eq. (4.2.10) but rather in terms of an effective linear susceptibility defined by means of the relationship

$$P_i = \sum_j \varepsilon_0 \chi^{(\text{eff})}_{ij} E_j.$$  \hspace{1cm} (4.2.11)

Then, as can be verified by direct substitution, Eqs. (4.2.10) and (4.2.11) lead to identical predictions for the nonlinear polarization if the effective linear susceptibility is given by

$$\chi^{(\text{eff})}_{ij} = \varepsilon_0 A' (\mathbf{E} \cdot \mathbf{E}^*) \delta_{ij} + \frac{1}{2} \varepsilon_0 B' (E_i E_j^* + E_i^* E_j),$$ \hspace{1cm} (4.2.12a)

where

$$A' = A - \frac{1}{2} B = 6\chi_{1122} - 3\chi_{1221}$$ \hspace{1cm} (4.2.12b)

and

$$B' = B = 6\chi_{1221}.$$ \hspace{1cm} (4.2.12c)
The relative magnitude of these two coefficients depends on the nature of the physical process that produces the optical nonlinearity. For some of the physical mechanisms leading to a nonlinear refractive index, these ratios are given by

\[
\begin{align*}
B/A &= 6, \quad B'/A' = -3 \quad \text{for molecular orientation,} \\
B/A &= 1, \quad B'/A' = 2 \quad \text{for nonresonant electronic response,} \\
B/A &= 0, \quad B'/A' = 0 \quad \text{for electrostriction.}
\end{align*}
\]  

(4.2.13a) \hspace{1cm} (4.2.13b) \hspace{1cm} (4.2.13c)

The trace of the effective susceptibility is given by

\[
\text{Tr } \chi_{ij} = \sum_i \chi_{ii} = (3A' + B') \mathbf{E} \cdot \mathbf{E}^*. 
\]  

(4.2.14)
4.2.1. Propagation through Isotropic Nonlinear Media

The electric field vector of such a beam can always be decomposed into a linear combination of left- and right-hand circular components as

\[ \mathbf{E} = E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-, \quad (4.2.15) \]

\[ \hat{\sigma}_\pm = \frac{\hat{x} \pm i \hat{y}}{\sqrt{2}}. \quad (4.2.16) \]

We now introduce the decomposition (4.2.15) into Eq. (4.2.10). We find, using the identities

\[ \hat{\sigma}_\pm^* = \hat{\sigma}_\pm, \quad \hat{\sigma}_\pm \cdot \hat{\sigma}_\pm = 0, \quad \hat{\sigma}_\pm \cdot \hat{\sigma}_\mp = 1, \]
\[ \mathbf{E}^* \cdot \mathbf{E} = (E_+^* \hat{\sigma}_+^* + E_-^* \hat{\sigma}_-) \cdot (E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-) = E_+^* E_+ + E_-^* E_- \]
\[ = |E_+|^2 + |E_-|^2 \]
\[ \mathbf{E} \cdot \mathbf{E} = (E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-) \cdot (E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_-) = E_+ E_- + E_- E_+ = 2E_+ E_- , \]

so Eq. (4.2.10) can be written as

\[ \mathbf{P}_{\text{NL}} = \varepsilon_0 A(|E_+|^2 + |E_-|^2) \mathbf{E} + \varepsilon_0 B(E_+ E_-) \mathbf{E}^* . \]  

(4.2.17)

If we now represent \( \mathbf{P}_{\text{NL}} \) in terms of its circular components as

\[ \mathbf{P}_{\text{NL}} = P_+ \hat{\sigma}_+ + P_- \hat{\sigma}_- , \]  

(4.2.18)
we find that the coefficient $P_+$ is given by

$$P_+ = \epsilon_0 A \left( |E_+|^2 + |E_-|^2 \right) E_+ + \epsilon_0 B (E_+ E_-) E_-^*$$

$$= \epsilon_0 A \left( |E_+|^2 + |E_-|^2 \right) E_+ + \epsilon_0 B |E_-|^2 E_+$$

$$= \epsilon_0 A |E_+|^2 E_+ + \epsilon_0 (A + B) |E_-|^2 E_+ \quad (4.2.19a)$$

and similarly that

$$P_- = \epsilon_0 A |E_-|^2 E_- + \epsilon_0 (A + B) |E_+|^2 E_- \quad (4.2.19b)$$

These results can be summarized as

$$P_{\pm} \equiv \epsilon_0 \chi_{\pm}^{\text{NL}} E_{\pm}, \quad (4.2.20a)$$

where we have introduced the effective nonlinear susceptibilities

$$\chi_{\pm}^{\text{NL}} = A |E_{\pm}|^2 + (A + B) |E_{\mp}|^2 \quad (4.2.20b)$$
The expressions (4.2.15) and (4.2.18) for the field and nonlinear polarization are now introduced into the wave equation

\[ \nabla^2 \mathbf{E}(z, t) = \frac{\epsilon^{(1)}}{c^2} \frac{\partial^2 \mathbf{E}(z, t)}{\partial t^2} + \frac{1}{\epsilon_0 c^2} \frac{\partial^2}{\partial t^2} \mathbf{P}^{NL}, \quad (4.2.21) \]

Where \[ \tilde{\mathbf{E}}(z, t) = \mathbf{E} \exp(-i \omega t) + c.c. \]

and \[ \tilde{\mathbf{P}}(z, t) = \mathbf{P} \exp(-i \omega t) + c.c. \]

So the wave equation for each circular component becomes

\[ \nabla^2 \tilde{E}_\pm(z, t) = \frac{\epsilon_{\pm}^{(\text{eff})}}{c^2} \frac{\partial^2 \tilde{E}_\pm(z, t)}{\partial t^2}, \quad (4.2.22a) \]

where

\[ \epsilon_{\pm}^{(\text{eff})} = \epsilon^{(1)} + \chi_{\pm}^{NL}. \quad (4.2.22b) \]
This equation possesses solutions of the form of plane waves propagating with the phase velocity \( c/n^\pm \) where
\[
n^\pm = [\varepsilon_{\pm}^{\text{(eff)}}]^{1/2}
\]
\[
n_0^2 = \varepsilon^{(1)}
\]

\[
n^2 = n_0^2 + n_0^2 \chi_{\pm}^{\text{NL}} = n_0^2 + \left[ A |E_\pm|^2 + (A + B)|E_\mp|^2 \right]
\]
\[
= n_0^2 \left( 1 + \frac{1}{n_0^2} \left[ A |E_\pm|^2 + (A + B)|E_\mp|^2 \right] \right),
\]

and thus
\[
n_\pm \simeq n_0 + \frac{1}{2n_0} \left[ A |E_\pm|^2 + (A + B)|E_\mp|^2 \right]. \quad (4.2.23)
\]
We see that the left- and right-circular components of the beam propagate with different phase velocities. The difference in their refractive indices is given by

\[ \Delta n \equiv n_+ - n_- = \frac{B}{2n_0} (|E_-|^2 - |E_+|^2). \]  

In order to determine the angle of rotation, we express the field amplitude as

\[
E(z) = E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_- = A_+ e^{i(n_+ - n_-)z/c} \hat{\sigma}_+ + A_- e^{i(n_- - n_+)z/c} \hat{\sigma}_-
\]

\[
= (A_+ e^{i(1/2)\Delta n \omega z/c} \hat{\sigma}_+ + A_- e^{-i(1/2)\Delta n \omega z/c} \hat{\sigma}_-) e^{i(1/2)(n_+ + n_-)\omega z/c}.
\]

We now introduce the mean propagation constant and the angle

\[
k_m = \frac{1}{2}(n_+ + n_-)\omega/c \quad \theta = \frac{1}{2} \Delta n \frac{\omega}{c},
\]

in terms of which Eq. (4.2.25) becomes

\[
E(z) = \left( A_+ \hat{\sigma}_+ e^{i\theta} + A_- \hat{\sigma}_- e^{-i\theta} \right) e^{ik_m z}.
\]
\[ E(z) = E_+ \hat{\sigma}_+ + E_- \hat{\sigma}_- = A_+ e^{in_+ \omega z / c} \hat{\sigma}_+ + A_- e^{in_- \omega z / c} \hat{\sigma}_- = (A_+ e^{i(1/2) \Delta n \omega z / c} \hat{\sigma}_+ + A_- e^{-i(1/2) \Delta n \omega z / c} \hat{\sigma}_-) e^{i(1/2)(n_+ + n_-) \omega z / c}. \] (4.2.25)

In terms of which Eq. (4.2.25) becomes

\[ E(z) = (A_+ \hat{\sigma}_+ e^{i\theta} + A_- \hat{\sigma}_- e^{-i\theta}) e^{ik_m z}. \] (4.2.26b)

**Figure 4.2.3** Polarization ellipses of the incident and transmitted waves.
The conclusion can be demonstrated by noting that

$$\hat{\sigma} \pm e^{\pm i\theta} = \frac{\hat{x}' \pm i\hat{y}'}{\sqrt{2}}, \quad (4.2.27)$$

where $\hat{x}'$ and $\hat{y}'$ are polarization unit vectors in a new coordinate system—that is,

$$x' = x \cos \theta - y \sin \theta, \quad (4.2.28a)$$
$$y' = x \sin \theta + y \cos \theta. \quad (4.2.28b)$$

Measurement of the rotation angle $\theta$ provides a sensitive method for determining the nonlinear coefficient $B$ (see also Eqs. (4.2.24) and (4.2.26a)).

$$\Delta n \equiv n_+ - n_- = \frac{B}{2n_0}(|E_-|^2 - |E_+|^2). \quad (4.2.24)$$

$$\theta = \frac{1}{2} \Delta n \frac{\omega}{c}, \quad (4.2.26a)$$
we see from Eq. (4.2.23) that the change in refractive index is given by

$$
\delta n_{\text{circular}} = \frac{1}{2n_0} A |E|^2, \quad (4.2.29)
$$

which clearly depends on the coefficient $A$ but not on the coefficient $B$.

If we let $E$ denote the total field amplitude of the linearly polarized radiation, so that

$$
|E|^2 = 2|E_+|^2 = 2|E_-|^2
$$

we find from Eq. (4.2.23) that for linearly polarized light the change in refractive index is given by

$$
n_\pm \simeq n_0 + \frac{1}{2n_0} \left[ A |E_\pm|^2 + (A + B)|E_\mp|^2 \right]. \quad (4.2.23)
$$

$$
\delta n_{\text{linear}} = \frac{1}{2n_0} \left( A + \frac{1}{2} B \right) |E|^2. \quad (4.2.30)
$$
In general the relative change in refractive index, $\frac{\delta n_{\text{linear}}}{\delta n_{\text{circular}}}$, is equal to $1 + B/2A$, which for the mechanisms described after Eq. (4.2.10) becomes

$$\frac{\delta n_{\text{linear}}}{\delta n_{\text{circular}}} = \begin{cases} 
4 & \text{for molecular orientation}, \\
3 & \text{for nonresonant electronic nonlinearities}, \\
2 & \text{for electrostriction}.
\end{cases}$$
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4.3. Nonresonant Electronic Nonlinearities

4.3.1. Classical, Anharmonic Oscillator Model of Electronic Nonlinearities

We approximate the actual potential well as

\[ U(r) = \frac{1}{2}m\omega_0^2 |r|^2 - \frac{1}{4}mb |r|^4, \tag{4.3.1} \]

where \( b \) is a phenomenological nonlinear constant whose value is of the order of \( \frac{\omega_0^2}{d^2} \), where \( d \) is a typical atomic dimension.

By solving the equation of motion for an electron in such a potential well, we obtain expression (1.4.52) for the third-order susceptibility. When applied to the case of the nonlinear refractive index, this expression becomes

\[ \chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) = \frac{Nbe^4[\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}]}{3\varepsilon_0m^3D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}. \tag{1.4.52} \]

\[ \chi_{ijkl}^{(3)}(\omega = \omega + \omega - \omega) = \frac{Nbe^4[\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}]}{3\varepsilon_0m^3D(\omega)^3D(-\omega)}, \tag{4.3.2} \]
where

\[
D(\omega) = \omega_0^2 - \omega^2 - 2i\omega\gamma
\]

In the notation of Maker and Terhune (Eq. (4.2.10)), this result implies that

\[
P = \epsilon_0 A (E \cdot E^*) E + \frac{1}{2}\epsilon_0 B (E \cdot E) E^*.
\]

(4.2.10)

\[
A = B = \frac{2Nbe^4}{\epsilon_0 m^3 D(\omega)^3 D(-\omega)}.
\]

(4.3.3)

For the case of far-off-resonant excitation (i.e., \(\omega \ll \omega_0\)), we can replace \(D(\omega)\) by \(\omega_0^2\) in Eq. (4.3.2).

If in addition we set \(b\) equal to \(\frac{\omega_0^2}{d^2}\), we find that

\[
\chi^{(3)} \approx \frac{Ne^4}{\epsilon_0 m^3 \omega_0^6 d^2}.
\]

(4.3.4)
4.3.2. Quantum-Mechanical Model of Nonresonant Electronic Nonlinearities

In the case of nonresonant excitation, we make use of the expression for the nonlinear susceptibility in the form given by Eq. (3.2.33) – that is,

\[ \chi_{kijh}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P} \sum_{lmn} \left[ \frac{\mu_g^k \mu_m^j \mu_l^i \mu_l^h g}{(\omega_{ng} - \omega_\sigma)(\omega_{mg} - \omega_q - \omega_p)(\omega_{lg} - \omega_p)} \right], \]  

where \( \omega_\sigma = \omega_r + \omega_q + \omega_p \)

\[ \Rightarrow \chi_{ijkl}^{(3)}(\omega, \omega, \omega, -\omega) = \chi_{ijkl}^{(3)}(\omega = \omega + \omega - \omega) \quad \omega_{mg} - \omega_q - \omega_p \]

when the dummy index \( m \) is equal to \( g \) and when \( \omega_p = -\omega_q = \pm \omega \).

\[ \chi_{kijh}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P} \left[ \sum_{lmn} \left( \frac{\mu_g^k \mu_m^j \mu_l^i \mu_l^h g}{\omega_{ng} - \omega_\sigma}(\omega_{mg} - \omega_q - \omega_p)(\omega_{lg} - \omega_p) \right) 

- \sum_{ln} \left( \frac{\mu_g^k \mu_{ng}^l \mu_{lg}^h}{\omega_{ng} - \omega_\sigma}(\omega_q + \omega_p)(\omega_{lg} - \omega_p) \right) \right]. \]
The second summation, which appears to be divergent for $\omega_q = -\omega_p$, is now rearranged. We make use of the identity

$$\frac{1}{XY} = \frac{1}{(X + Y)Y} + \frac{1}{(X + Y)X},$$

(4.3.7)

with $X = \omega_q + \omega_p$ and $Y = \omega_{lg} - \omega_p$, to express Eq. (4.3.6) as

$$X_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_F \left[ \sum'_{lmn} \frac{\mu_{gn}^{k} \mu_{nm}^{j} \mu_{ml}^{i} \mu_{lg}^{h}}{(\omega_{ng} - \omega_\sigma)(\omega_{mg} - \omega_q - \omega_p)(\omega_{lg} - \omega_p)} \right. \right.

\left. \left. - \sum_{ln} \frac{\mu_{gn}^{k} \mu_{ng}^{j} \mu_{lg}^{i} \mu_{lg}^{h}}{(\omega_{ng} - \omega_\sigma)(\omega_{lg} + \omega_r)(\omega_{lg} - \omega_p)} \right] \right)

(4.3.8)
\[ \mathcal{P}_F \sum_{ln} \frac{\mu^k_{gn} \mu^j_{ng} \mu^i_{gl} \mu^h_{lg}}{(\omega_{ng} - \omega_\sigma)(\omega_{lg} + \omega_q)(\omega_q + \omega_p)} . \] (4.3.9)

However, this additional contribution vanishes, because for every term of the form

\[ \frac{\mu^k_{gn} \mu^j_{ng} \mu^i_{gl} \mu^h_{lg}}{(\omega_{ng} - \omega_\sigma)(\omega_{lg} + \omega_q)(\omega_q + \omega_p)} \] (4.3.10a)

there is another term with the dummy summation indices \(n\) and \(l\) interchanged, with the pair \((-\omega_\sigma, k)\) interchanged with \((\omega_q, i)\), and with the pair \((\omega_p, h)\) interchanged with \((\omega_r, j)\); this term is of the form

\[ \frac{\mu^i_{gl} \mu^h_{lg} \mu^j_{kn} \mu^j_{ng}}{(\omega_{lg} + \omega_q)(\omega_{ng} - \omega_\sigma)(\omega_r - \omega_\sigma)}. \] (4.3.10b)
Rather than considering all 48 terms of the expanded version of Eq. (4.3.8), let us consider only the nearly resonant terms, which would be expected to make the largest contributions to $\chi(3)$. After detailed analysis of Eq. (4.3.8), that the resonant contribution to the nonlinear susceptibility is given by

$$\chi_{kjih}^{(3)}(\omega, \omega, \omega, -\omega) = \chi_{kjih}^{(3)}(\omega = \omega + \omega - \omega) = \frac{N}{6 e_0 \hbar^3}$$

$$\times \left( \sum_{l \neq n} \frac{\mu_{k}^{h} \mu_{l}^{h} \mu_{l}^{j} + \mu_{k}^{h} \mu_{l}^{i} \mu_{l}^{j} + \mu_{l}^{h} \mu_{l}^{i} \mu_{l}^{j} + \mu_{l}^{h} \mu_{l}^{i} \mu_{l}^{j} + \mu_{l}^{h} \mu_{l}^{j} \mu_{l}^{i} + \mu_{l}^{h} \mu_{l}^{j} \mu_{l}^{i}}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)(\omega_{lg} - \omega)} \right)$$

$$- \sum_{l \neq n} \frac{\mu_{k}^{h} \mu_{l}^{h} \mu_{l}^{j} + \mu_{k}^{h} \mu_{l}^{i} \mu_{l}^{j} + \mu_{l}^{h} \mu_{l}^{i} \mu_{l}^{j} + \mu_{l}^{h} \mu_{l}^{i} \mu_{l}^{j} + \mu_{l}^{h} \mu_{l}^{j} \mu_{l}^{i} + \mu_{l}^{h} \mu_{l}^{j} \mu_{l}^{i}}{(\omega_{mg} - \omega)(\omega_{lg} - \omega)(\omega_{lg} - \omega)} \right).$$

(4.3.11)

Here the first summation represents two-photon-resonant processes and the second summation represents one-photon-resonant processes, in the sense illustrated in Fig. 4.3.1.
We find, for example, that $\chi_{1111}(\omega = \omega + \omega - \omega)$ is given by

$$\chi_{1111} = \frac{2N}{3\epsilon_0\hbar^3} \left[ \sum_{lmn} \left( \frac{\mu^x_{gn} \mu^x_{nm} \mu^x_{ml} \mu^x_{lg}}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)(\omega_{lg} - \omega)} - \frac{\mu^x_{gn} \mu^x_{ng} \mu^x_{gl} \mu^x_{lg}}{(\omega_{ng} - \omega)(\omega_{lg} - \omega)(\omega_{lg} - \omega)} \right) \right]. \quad (4.3.12)$$

Note that both one- and two-photon-resonant terms contribute to this expression. When $\omega$ is smaller than any resonant frequency of the material system, the two-photon contribution (the first term) tends to be positive.

**Figure 4.3.1** Resonance nature of the first (a) and second (b) summations of Eq. (4.3.11).
In a similar fashion, we find that the resonant contribution to $\chi_{1221}$ (or to $1/6B$ in the notation of Maker and Terhune) is given by

$$\chi_{1221} = \frac{2}{3} \frac{N}{e_0 \hbar^3} \sum_{lmn} \left[ \frac{\mu_{gm}^x \mu_{nm}^x \mu_{ml}^y \mu_{lg}^y}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)(\omega_{lg} - \omega)} \right].$$

(4.3.13)

The one-photon-resonant terms do not contribute to $\chi_{1221}$, since these terms involve the summation of the product of two matrix elements of the sort $\mu_{gl}^x \mu_{gl}^y$, and this contribution always vanishes.

**Figure 4.3.2** For $\omega < \omega_{lg}$ the ac Stark effect leads to an increase in the energy separation of the ground and excited states.
We also find that the resonant contribution to $\chi_{1122}$ (or to $1/64$) is given by

$$\chi_{1122} = \frac{N}{3\varepsilon_0 \hbar^3} \sum_{lmn} \left( \mu_{gn}^x \mu_{nm}^y \mu_{ml}^x \mu_{lg}^y + \mu_{gn}^x \mu_{nm}^y \mu_{ml}^x \mu_{lg}^y \right) \frac{1}{(\omega_{ng} - \omega)(\omega_{mg} - 2\omega)(\omega_{lg} - \omega)}$$

$$- \frac{N}{3\varepsilon_0 \hbar^3} \sum_{ln} \frac{\mu_{gn}^x \mu_{ng}^x \mu_{gl}^y \mu_{lg}^y}{(\omega_{ng} - \omega)(\omega_{mg} - \omega)(\omega_{lg} - \omega)}.$$

(4.3.14)
4.3.3. $\chi^{(3)}$ in the Low-Frequency Limit

If we assume that the optical frequency $\omega$ is much smaller than all atomic resonance frequencies, we find from Eq. (4.3.5) that the nonresonant value of the nonlinear optical susceptibility is given by

$$
\chi_{kjih}^{(3)}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3 P_F} \sum_{lmn} \left[ \frac{\mu_k^l \mu_{nml}^j \mu_{ml}^i \mu_{lgh}^h}{(\omega_{ng} - \omega_\sigma)(\omega_{mg} - \omega_q - \omega_p)(\omega_{lh} - \omega_p)} \right], \quad (4.3.5)
$$

where $\mu$ is a typical value of the dipole matrix element and $\omega_0$ is a typical value of the atomic resonance frequency.

If we identify $d$ with the Bohr radius $a_0 = 4\pi \epsilon_0 \hbar^2 / me^2$, $\mu$ with the atomic unit of electric dipole moment $-ea_0$, and $\omega_0$ with the Rydberg constant in angular frequency units, $\omega_0 = me^4 / 32\pi^2 \epsilon_0 \hbar^3$.

$$
\chi^{(3)} \simeq \frac{8N \mu^4}{\epsilon_0 \hbar^3 \omega_0^3}, \quad (4.3.15)
$$
The measured values of $\chi^{(3)}$ and $n_2$ for several materials that display nonresonant electronic nonlinearities are given in Table 4.3.1.

**TABLE 4.3.1 Nonlinear optical coefficient for materials showing electronic nonlinearities**

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_0$</th>
<th>$\chi_{1111}$ (m$^2$/V$^2$)</th>
<th>$n_2$ (m$^2$/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>2.42</td>
<td>$21 \times 10^{-22}$</td>
<td>$10 \times 10^{-20}$</td>
</tr>
<tr>
<td>Yttrium aluminum garnet</td>
<td>1.83</td>
<td>$8.4 \times 10^{-22}$</td>
<td>$8.4 \times 10^{-20}$</td>
</tr>
<tr>
<td>Sapphire</td>
<td>1.8</td>
<td>$4.2 \times 10^{-22}$</td>
<td>$3.7 \times 10^{-20}$</td>
</tr>
<tr>
<td>Borosilicate crown glass</td>
<td>1.5</td>
<td>$3.5 \times 10^{-22}$</td>
<td>$4.4 \times 10^{-20}$</td>
</tr>
<tr>
<td>Fused silica</td>
<td>1.47</td>
<td>$2.8 \times 10^{-22}$</td>
<td>$3.67 \times 10^{-20}$</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>1.43</td>
<td>$2.24 \times 10^{-22}$</td>
<td>$3.1 \times 10^{-20}$</td>
</tr>
<tr>
<td>LiF</td>
<td>1.4</td>
<td>$1.4 \times 10^{-22}$</td>
<td>$2.0 \times 10^{-20}$</td>
</tr>
</tbody>
</table>
THE INTENSITY-DEPENDENT REFRACTIVE INDEX

- 4.1. Descriptions of the Intensity-Dependent Refractive Index
- 4.2. Tensor Nature of the Third-Order Susceptibility
- 4.3. Nonresonant Electronic Nonlinearities
- 4.4. Nonlinearities Due to Molecular Orientation
- 4.5. Thermal Nonlinear Optical Effects
- 4.6. Semiconductor Nonlinearities
- 4.7. Concluding Remarks