Chapter 2
Third-Order Nonlinear Effects

2.1 Introduction

The book focuses on utilizing the third-order nonlinear effects (including nonlinear absorption and refraction) to break the diffraction limit and form super-resolution nanoscale spot. In this chapter, let us give a brief introduction to the characteristics of the third-order effects.

When a light beam with a frequency of \( \omega \) is incident on the isotropic nonlinear medium, the nonlinear effect occurs, and the second-order nonlinear susceptibility \( \chi^{(2)} \) can be neglectable. The whole polarization is expressed as [1]

\[
P[E(\omega)] = P^{(1)} + P^{(3)} = \varepsilon_0 \left[ \chi^{(1)} + 3 \chi^{(3)} |E(\omega)|^2 \right] E(\omega)
\]  

(2.1)

where \( P^{(1)} \) and \( P^{(3)} \) the linear and third-order nonlinear polarization. \( \chi^{(1)} \) and \( \chi^{(3)} \) are the linear and third-order nonlinear susceptibility, respectively. The polarizations are marked into the real and imaginary parts as follows

\[
\begin{align*}
P^{(1)} &= P^{(1)}_R + iP^{(1)}_I \\
P^{(3)} &= P^{(3)}_R + iP^{(3)}_I
\end{align*}
\]

(2.2)

The \( \chi^{(1)} \) and \( \chi^{(3)} \) can be also marked into real and imaginary parts as follows

\[
\begin{align*}
\chi^{(1)} &= \chi^{(1)}_R + i\chi^{(1)}_I \\
\chi^{(3)} &= \chi^{(3)}_R + i\chi^{(3)}_I
\end{align*}
\]

(2.3)

where \( \chi^{(1)}_R \) and \( \chi^{(3)}_R \) are real part and directly related with the refraction. \( \chi^{(1)}_I \) and \( \chi^{(3)}_I \) are imaginary parts and related with absorption.
2.2 Nonlinear Refraction

For isotropic (homogeneous) materials, the nonlinear refraction can be considered to be from a four-wave interaction and the third-order nonlinearity is mainly field dependent. Accordingly, the nonlinear polarization is written as $P^{(3)}[E(\omega)] = 3\varepsilon_0\chi^{(3)}_R|E(\omega)|^2E(\omega)$. Assuming that the refractive index is measured using a single laser beam method, such as single beam z-scan technique, the four-order and higher terms can be neglectable. Then, the total polarization of the material system is

$$P_R[E(\omega)] = P^{(1)}_R + P^{(3)}_R = \varepsilon_0 \left[ \chi^{(1)}_R + 3\chi^{(3)}_R|E(\omega)|^2 \right]E(\omega) \equiv \varepsilon_0 \chi^{\text{eff}}_R E(\omega) \quad (2.4)$$

where $\chi^{(1)}_R$ is the real part of linear susceptibility. Here, one defines the effective susceptibility as $\chi^{\text{eff}} = \chi^{\text{eff}}_R + i\chi^{\text{eff}}_I$, where the $\chi^{\text{eff}}_R$ and $\chi^{\text{eff}}_I$ are the real and imaginary parts of effective susceptibility, respectively. According to formula (2.4), the $\chi^{\text{eff}}_R$ is written as

$$\chi^{\text{eff}}_R = \chi^{(1)}_R + \chi^{(3)}_e |E(\omega)|^2 \quad (2.5)$$

with

$$\chi^{(3)}_e |E(\omega)|^2 = 3\chi^{(3)}_R|E(\omega)|^2 \quad (2.6)$$

If all of the nonlinear susceptibility is thought to be effective susceptibility, one can obtain

$$\chi^{(3)}_e |E(\omega)|^2 \sim \chi^{(3)}_R|E(\omega)|^2 \quad (2.7)$$

The electric displacement vector is

$$D = \varepsilon_0 E + P = \varepsilon_0 \left[ 1 + \chi^{(1)}_R + \chi^{(3)}_R|E(\omega)|^2 \right]E(\omega) \quad (2.8)$$

Based on $D = \varepsilon E$, the total permittivity is

$$\varepsilon = \varepsilon_0 \left[ 1 + \chi^{(1)}_R + \chi^{(3)}_R|E(\omega)|^2 \right] \quad (2.9)$$

The relative permittivity is

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = 1 + \chi^{(1)}_R + \chi^{(3)}_R|E(\omega)|^2 \quad (2.10)$$

The refractive index is defined as

$$n = \sqrt{\varepsilon_r \mu_r} \quad (2.11)$$
where $\mu_r$ is relative permeability and generally equals to 1 for non-magnetic materials. Thus

$$n = \sqrt{\epsilon_r} \quad (2.12)$$

Substituting formula (2.10) into formula (2.12), one has

$$n = \sqrt{1 + \chi^{(1)}_R + \chi^{(3)}_R |E(\omega)|^2} \quad (2.13)$$

The linear refractive index is defined as

$$n_0^2 = 1 + \chi^{(1)}_R \quad (2.14)$$

Thus, formula (2.13) is rewritten as

$$n = n_0 \left[ 1 + \frac{\chi^{(3)}_R |E(\omega)|^2}{n_0^2} \right]^{\frac{1}{2}} \quad (2.15)$$

Generally, the $\chi^{(3)}_R |E(\omega)|^2/n_0^2$ term is much smaller than 1. Using the Taylor series expansion, the formula (2.15) can be expressed as

$$n \approx n_0 + \frac{\chi^{(3)}_R |E(\omega)|^2}{2n_0} \quad (2.16)$$

Generally, the refractive index can also be written as

$$n = n_0 + \Delta n = n_0 + \gamma I \quad (2.17)$$

where $\Delta n$ is the third-order nonlinear susceptibility-induced refractive index change and $\gamma$ is nonlinear refraction coefficient. $I$ is light intensity and can be defined as

$$I = \frac{\nu \epsilon_r \epsilon_0}{2} \langle \tilde{E}(\omega, t)^2 \rangle \quad (2.18)$$

where $\nu = c/n_0$ is light speed in the medium. $\tilde{E}(\omega, t)$ is time-dependent optical field, and $\epsilon_r \sim n_0^2$, thus

$$I \approx \frac{1}{2} \epsilon_0 c n_0 \langle \tilde{E}(\omega, t)^2 \rangle \quad (2.19)$$

If the optical field is of the form [2]

$$\tilde{E}(\omega, t) = E(\omega) \exp(-i\omega t) + c.c., \quad (2.20)$$

one has

$$\langle \tilde{E}(\omega, t)^2 \rangle = 2E(\omega)E^*(\omega) = 2|E(\omega)|^2 \quad (2.21)$$

According to formulas (2.19) and (2.21), one has
Based on formulas (2.17) and (2.23), one can obtain the nonlinear refraction coefficient as

\[ \gamma = \frac{\chi_R^{(3)}}{2\epsilon_0cn_0^2} \]  

(2.24)

According to formula (2.24), one can obtain \( \gamma \) value. The different physical mechanisms can cause different \( \gamma \) values. The typical \( \gamma \) value and response time are listed in Table 2.1. In formula (2.24), \( \gamma < 0 \) corresponds to self-defocusing effect and \( \gamma > 0 \) can lead to self-focusing effect. The self-focusing effect can generate the nanoscale spot, which is very useful for nanolithography and high-resolving light imaging, etc.

### 2.3 Nonlinear Absorption

Similar to the real part of polarization, the imaginary part of polarization is

\[ P_I[E(\omega)] = P_I^{(1)} + P_I^{(3)} = i\epsilon_0 \left[ \chi_I^{(1)} + \chi_I^{(3)}|E(\omega)|^2 \right] E(\omega) \]  

(2.25)

For isotropic medium, on the basis of the *slowly varying-envelope approximation*, one has

\[ \frac{dE}{dz} = \frac{i\omega}{2\epsilon_0cn_0} P_I \]  

(2.26)

Substituting formulas (2.22) and (2.25) into formula (2.26), one has

### Table 2.1 Typical values of \( \gamma \) and response time for linearly polarized light \([2]\)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>( \gamma (m^2/W) )</th>
<th>Response time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic polarization</td>
<td>( \sim 10^{-20} )</td>
<td>( \sim 10^{-15} )</td>
</tr>
<tr>
<td>Molecular orientation</td>
<td>( \sim 10^{-18} )</td>
<td>( \sim 10^{-12} )</td>
</tr>
<tr>
<td>Electrostriction</td>
<td>( \sim 10^{-18} )</td>
<td>( \sim 10^{-9} )</td>
</tr>
<tr>
<td>Saturated atomic absorption</td>
<td>( \sim 10^{-14} )</td>
<td>( \sim 10^{-8} )</td>
</tr>
<tr>
<td>Thermal effects</td>
<td>( \sim 10^{-10} )</td>
<td>( \sim 10^{-3} )</td>
</tr>
<tr>
<td>Photorefractive effects(^a)</td>
<td>Large</td>
<td>Intensity dependent</td>
</tr>
</tbody>
</table>

\(^a\) The photorefractive effect can cause large nonlinear effect, which cannot usually be described with nonlinear susceptibility \( \chi^{(3)} \) (or \( \gamma \)). The nonlinear polarization process of the photorefractive effect is not the same as the other physical mechanisms listed.
One defines the following

\[
\frac{\alpha}{2} = \frac{\alpha_0}{2} + \Delta \alpha = \frac{\omega}{2cn_0} x_l^{(1)} + \frac{\omega}{2\varepsilon_0 c^2 n_0^2} x_l^{(3)} I
\]  

From the formula (2.28), the formula (2.27) is rewritten as

\[
\frac{dE}{dz} = -\frac{\alpha}{2} E
\]  

So

\[
E(L) = E_0 \exp \left( -\frac{\alpha}{2} L \right)
\]

where \(L\) is medium thickness. The intensity decaying accordingly is

\[
I(L) = I_0 e^{-\alpha L}
\]

Thus,

\[
\begin{cases}
\alpha_0 = \frac{\omega}{2cn_0} x_l^{(1)} \\
\Delta \alpha = \frac{\omega}{\varepsilon_0 c^2 n_0^2} x_l^{(3)} I
\end{cases}
\]

Thus, \(\alpha_0\) is defined as linear absorption coefficient, and \(\Delta \alpha\) is nonlinearity-induced intensity-dependent absorption coefficient change and is

\[
\Delta \alpha = \beta I
\]

where \(\beta\) is nonlinear absorption coefficient and is

\[
\beta = \frac{\omega}{\varepsilon_0 c^2 n_0^2} x_l^{(3)}
\]

For some materials, such as semiconductors, \(\beta < 0\) is saturation absorption, and \(\beta > 0\) means reverse saturation absorption or multi-photon absorption.

As described in formula (2.31), the light goes through the nonlinear materials, and the intensity changes with the traveling distance \(z\) inside the materials. The intensity decaying process can be rewritten as

\[
\frac{dI}{dz} = -\alpha_0 I - \beta I^2
\]

The exiting light intensity from the materials is [3]

\[
I_e = \frac{I_0 \exp(-\alpha_0 L)}{1 + \beta I_0 L_{eff}}
\]
with

\[ L_{\text{eff}} = \frac{1 - \exp(-\alpha_0 L)}{\alpha_0} \]

For \( \alpha_0 \to 0 \), the linear absorption of materials is neglectable, and the third-order nonlinear absorption is dominant. In this case, \( \exp(-\alpha_0 L) \sim (1 - \alpha_0 L) \), thus \( L_{\text{eff}} \sim L \). Based on formula (2.36), the exiting light intensity becomes

\[ I_e \sim \frac{I_0}{1 + \beta I_0 L} \]

(2.38)

An alternative way to obtain the exiting light intensity is through the formula (2.35) with \( \alpha_0 = 0 \), which yields

\[ \frac{\partial I}{\partial z} = -\beta I^2 \]

(2.39)

Formula (2.38) can be solved by the separation of variables, which yields

\[ I(z) = \frac{I_0}{1 + \beta I_0 z} \]

(2.40)

Formula (2.40) is consistent with formula (2.38) and can be used to calculate the light spot intensity profile after passing through the nonlinear absorption materials with weak linear absorption characteristics (\( \alpha_0 \to 0 \)).

The nonlinear refraction can induce self-focusing super-resolution effect (for \( \gamma > 0 \)), and the nonlinear absorption can lead to the generation of aperture-type super-resolution effect (for \( \beta < 0 \)), or subwavelength energy absorption region (for \( \beta > 0 \)), which can be applied to the nanolithography and nanoscale optical data storage, etc.

References

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