Chapter 4. The Intensity-Dependent Refractive Index

- Third order nonlinear effect
- Mathematical description of the nonlinear refractive index
- Physical processes that give rise to this effect

Reference:
4.1 Description of the Intensity-Dependent Refractive Index

Refractive index of many materials can be described by

\[ n = n_0 + \bar{n}_2 \langle \tilde{E}^2(t) \rangle + \ldots \]

where, \( n_0 \) : weak-field refractive index

\( \bar{n}_2 \) : 2nd order index of refraction

\[ \tilde{E}(t) = E(\omega)e^{-i\omega t} + c.c. \quad \Rightarrow \quad \langle \tilde{E}^2(t) \rangle = 2E(\omega)E(\omega)^* = 2|E(\omega)|^2 \]

\[ n = n_0 + 2\bar{n}_2 |E(\omega)|^2 \quad : \text{optical Kerr effect (3rd order nonlinear effect)} \]
Polarization:

\[ P(\omega) = \chi^{(1)}E(\omega) + 3\chi^{(3)}|E(\omega)|^2 E(\omega) \equiv \chi_{\text{eff}} E(\omega) \]

In Gaussian units, \( n^2 = 1 + 4\pi\chi_{\text{eff}} \)

\[ \Rightarrow \quad \left[n_0 + 2\bar{n}_2|E(\omega)|^2\right]^2 = 1 + 4\pi\chi^{(1)} + 12\pi\chi^{(3)}|E(\omega)|^2 \]

\[ n_0^2 + 4n_0\bar{n}_2|E(\omega)|^2 + 4\bar{n}_2^2|E(\omega)|^4 = 1 + 4\pi\chi^{(1)} + 12\pi\chi^{(3)}|E(\omega)|^2 \]

\[ \therefore \quad n_0 = (1 + 4\pi\chi^{(1)})^{1/2} \]

\[ \bar{n}_2 = 3\pi\chi^{(3)}/n_0 \]
Appendix A. Systems of Units in Nonlinear Optics (Gaussian units and MKS units)

1) Gaussian units;

\[ \tilde{P}(t) = \chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \ldots \]

\[
\begin{align*}
[\tilde{P}] &= \text{statvolt} \\
[\tilde{E}] &= \text{cm} \\
\text{statcoulomb/cm}^2 \\
\end{align*}
\]

# \( \chi^{(1)} \equiv \text{dimensionless} \)

# \[
\left[ \chi^{(2)} \right] = \left[ \frac{1}{\tilde{E}} \right] = \frac{\text{cm}}{\text{statvolt}}
\]

# \[
\left[ \chi^{(3)} \right] = \left[ \frac{1}{\tilde{E}^2} \right] = \frac{\text{cm}^2}{\text{statvolt}^2}
\]

* The units of nonlinear susceptibilities are not usually stated explicitly; rather one simply states that the value is given in “esu” (electrostatic units).
2) MKS units ;

\[
[\tilde{P}] = \frac{C}{m^2} \quad [\tilde{E}] = \frac{V}{m}
\]

\[
\tilde{P}(t) = \varepsilon_0 \left[ \chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \ldots \right] : \text{MKS 1}
\]

\[
\tilde{P}(t) = \varepsilon_0 \chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \ldots : \text{MKS 2}
\]

# \( \varepsilon_0 = 8.85 \times 10^{-12} \text{F/m}, \ [\text{F}]=[\text{C/V}] \)

In MKS 1, \( \chi^{(1)} \equiv \text{dimensionless} \quad \left[ \chi^{(2)} \right] = \frac{1}{\tilde{E}} = \frac{m}{V} \quad \left[ \chi^{(3)} \right] = \frac{m^2}{V^2} \)

In MKS 2, \( \chi^{(1)} \equiv \text{dimensionless} \quad \left[ \chi^{(2)} \right] = \frac{C}{V^2} \quad \left[ \chi^{(3)} \right] = \frac{Cm}{V^3} \)
3) Conversion among the systems

(1) \( 1 \text{ statvolt} = 300 \text{ V} \Rightarrow \tilde{E} \quad (\text{MKS}) = 3 \times 10^4 \tilde{E} \quad (\text{Gaussian}) \)

(2) \( \tilde{D} = \tilde{E} + 4\pi \tilde{P} = \tilde{E}(1 + 4\pi \chi^{(1)}) \quad (\text{Gaussian}) \)
\[
\tilde{D} = \varepsilon_0 \tilde{E} + \tilde{P} = \varepsilon_0 \tilde{E}(1 + \chi^{(1)}) \quad (\text{MKS})
\Rightarrow \chi^{(1)} \quad (\text{MKS}) = 4\pi \chi^{(1)} \quad (\text{Gaussian})
\]

(3)
\[
\chi^{(2)} \quad (\text{MKS1}) = \frac{4\pi}{3 \times 10^4} \chi^{(2)} \quad (\text{Gaussian}) \quad \chi^{(3)} \quad (\text{MKS1}) = \frac{4\pi}{(3 \times 10^4)^2} \chi^{(3)} \quad (\text{Gaussian})
\]
\[
\chi^{(2)} \quad (\text{MKS2}) = \frac{4\pi \varepsilon_0}{3 \times 10^4} \chi^{(2)} \quad (\text{Gaussian}) \quad \chi^{(3)} \quad (\text{MKS2}) = \frac{4\pi \varepsilon_0}{(3 \times 10^4)^2} \chi^{(3)} \quad (\text{Gaussian})
\]
Alternative way of defining the intensity-dependent refractive index

\[ n = n_0 + n_2 I \]

\[ I = \frac{n_0 c}{2\pi} |E(\omega)|^2 \]

\[ n = n_0 + 2\bar{n}_2 |E(\omega)|^2 \quad (4.1.4) \]

\[ n_2 \leftrightarrow \chi^{(3)} ? \]

\[ n_2 \left( \frac{\text{cm}^2}{\text{W}} \right) = \frac{12\pi^2}{n_0 c} \times 10^7 \chi^{(3)} (\text{esu}) \approx \frac{0.0395}{n_0^2} \chi^{(3)} (\text{esu}) \]

Example) \( \text{CS}_2 (\chi^{(3)}: 1.9 \times 10^{-12} \text{ esu}), \quad n_0 = 1.58, \quad I = 1 \text{ MW/cm}^2, \quad \Delta n ? \)

\[ n_2 = \frac{0.0395}{n_0^2} \chi^{(3)} (\text{esu}) = \frac{0.0395}{(1.58)^2} 1.9 \times 10^{-12} \]

\[ \Delta n = n_2 I = 1 \times 10^6 \times 3 \times 10^{-14} = 3 \times 10^{-8} \]

\[ \approx 3 \times 10^{-14} \text{ cm}^2/\text{W} \]
<table>
<thead>
<tr>
<th>Material</th>
<th>$n_0$</th>
<th>$\chi^{(3)}$ (esu)</th>
<th>$n_2$ (cm$^2$/W)</th>
<th>Comments and references</th>
</tr>
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<tbody>
<tr>
<td>Crystals</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>1.8</td>
<td>$2.2 \times 10^{-14}$</td>
<td>$2.9 \times 10^{-16}$</td>
<td>1, 1.06 $\mu$m</td>
</tr>
<tr>
<td>CdS</td>
<td>2.34</td>
<td>$7.0 \times 10^{-12}$</td>
<td>$5.1 \times 10^{-14}$</td>
<td>1</td>
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<td>GaAs</td>
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<td>$3.3 \times 10^{-13}$</td>
<td>2, THG $</td>
</tr>
<tr>
<td>Ge</td>
<td>4.0</td>
<td>$4.0 \times 10^{-11}$</td>
<td>$9.9 \times 10^{-14}$</td>
<td>1</td>
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<td>LiF</td>
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<td>$2.7 \times 10^{-14}$</td>
<td>2, THG $</td>
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<td>ZnSe</td>
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<td>$4.4 \times 10^{-12}$</td>
<td>$3.0 \times 10^{-14}$</td>
<td>1, 1.06 $\mu$m</td>
</tr>
<tr>
<td>Glasses</td>
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<tr>
<td>Fused silica</td>
<td>1.47</td>
<td>$1.8 \times 10^{-14}$</td>
<td>$3.2 \times 10^{-16}$</td>
<td>1</td>
</tr>
<tr>
<td>As$_2$S$_3$ glass</td>
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<td>$2.9 \times 10^{-11}$</td>
<td>$2.0 \times 10^{-13}$</td>
<td>3</td>
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<td>Nanoparticles</td>
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<td>CdS$_2$Se in glass</td>
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<td>$1.0 \times 10^{-12}$</td>
<td>$1.8 \times 10^{-14}$</td>
<td>3, nonres.</td>
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<tr>
<td>CS-3-68 glass</td>
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<td>$1.3 \times 10^{-8}$</td>
<td>$2.3 \times 10^{-10}$</td>
<td>3, res.</td>
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<tr>
<td>Gold in glass</td>
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<td>$1.5 \times 10^{-10}$</td>
<td>$2.6 \times 10^{-11}$</td>
<td>3, res.</td>
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<tr>
<td>Polymers</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>Polymadiacetylenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTS</td>
<td>$6 \times 10^{-10}$</td>
<td></td>
<td>$3. \times 10^{-12}$</td>
<td>5, nonres.</td>
</tr>
<tr>
<td>PTS$_{\text{res}}$</td>
<td>$-4 \times 10^{-8}$</td>
<td></td>
<td>$-2 \times 10^{-10}$</td>
<td>6, res.</td>
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<tr>
<td>9BCMU</td>
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<td></td>
<td>$1.9 \times 10^{-10}$</td>
<td>7, $</td>
</tr>
<tr>
<td>4BCMU</td>
<td>$1.56 \times -9.2 \times 10^{-12}$</td>
<td>$-1.5 \times 10^{-13}$</td>
<td>8, nonres, $\beta = 0.01$ cm/MW</td>
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</tr>
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<td>Liquids</td>
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<td></td>
</tr>
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<td>Acetone</td>
<td>1.36</td>
<td>$1.1 \times 10^{-13}$</td>
<td>$2.4 \times 10^{-15}$</td>
<td>9</td>
</tr>
<tr>
<td>Benzene</td>
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<td>$6.8 \times 10^{-14}$</td>
<td>$1.2 \times 10^{-15}$</td>
<td>9</td>
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<td>Carbon disulfide</td>
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<td>$3.2 \times 10^{-14}$</td>
<td>9, $\tau = 2$ psec</td>
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<tr>
<td>Ethanol</td>
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<td>$3.6 \times 10^{-14}$</td>
<td>$7.7 \times 10^{-16}$</td>
<td>9</td>
</tr>
<tr>
<td>Methanol</td>
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<td>$3.1 \times 10^{-14}$</td>
<td>$6.9 \times 10^{-16}$</td>
<td>9</td>
</tr>
<tr>
<td>Nitrobenzene</td>
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<td>$4.1 \times 10^{-12}$</td>
<td>$6.7 \times 10^{-14}$</td>
<td>9</td>
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<tr>
<td>Water</td>
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<td>$1.8 \times 10^{-14}$</td>
<td>$4.1 \times 10^{-16}$</td>
<td>9</td>
</tr>
<tr>
<td>Other materials</td>
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<td></td>
<td></td>
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<tr>
<td>Air</td>
<td>1.0003</td>
<td>$1.2 \times 10^{-17}$</td>
<td>$5.0 \times 10^{-19}$</td>
<td>10</td>
</tr>
<tr>
<td>Ag</td>
<td>1.2</td>
<td>$5.1 \times 10^{-10}$</td>
<td>$0.2$</td>
<td>12, (EIT BEC)</td>
</tr>
<tr>
<td>Fluorescein dye in glass</td>
<td>1.5</td>
<td>$2 + 2i$</td>
<td>$0.035(1 + i)$</td>
<td>13, $\tau = 0.1s$</td>
</tr>
<tr>
<td>Vacuum</td>
<td>1</td>
<td>$2.4 \times 10^{-33}$</td>
<td>$1.0 \times 10^{-34}$</td>
<td>11</td>
</tr>
</tbody>
</table>

1. THG $|\chi^{(3)}|$  
2. THG $|\chi^{(3)}|$  
3. nonres.  
4. res.  
5. nonres.  
6. res.  
7. $|n_2|$, res.  
8. nonres, $\beta = 0.01$ cm/MW  
9. $\tau = 2$ psec  
10.  
11.  
12. (EIT BEC)  
13. $\tau = 0.1s$
Physical processes producing the nonlinear change in the refractive index

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>
<thead>
<tr>
<th>Mechanism</th>
<th>$n_2$ (cm$^2$/W)</th>
<th>$\chi_{1111}^{(3)}$ (esu)</th>
<th>Response time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic polarization</td>
<td>$10^{-16}$</td>
<td>$10^{-14}$</td>
<td>$10^{-15}$</td>
</tr>
<tr>
<td>Molecular orientation</td>
<td>$10^{-14}$</td>
<td>$10^{-12}$</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>Electrostriction</td>
<td>$10^{-14}$</td>
<td>$10^{-12}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Saturated atomic absorption</td>
<td>$10^{-10}$</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>Thermal effects</td>
<td>$10^{-6}$</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Photorefractive effect</td>
<td>(large)</td>
<td>(large)</td>
<td>(intensity-dependent)</td>
</tr>
</tbody>
</table>

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For linearly polarized light.

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.
4.2 Tensor Nature of the 3rd Susceptibility

Centrosymmetric media

\[ \tilde{F}_{\text{res}} = -m \omega_0^2 \tilde{r} + mb(\tilde{r} \cdot \tilde{r})\tilde{r} \]

Equation of motion:

\[ \ddot{\tilde{r}} + 2\gamma \dot{\tilde{r}} + \omega_0^2 \tilde{r} - b(\tilde{r} \cdot \tilde{r})\tilde{r} = -e\tilde{E}(t)/m \]

Solution:

\[ \tilde{E}(t) = E_1 e^{-i\omega t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t} + c.c = \sum_n E(\omega_n) e^{-i\omega_n t} \]

Perturbation expansion method:

\[ \tilde{r}(t) = \lambda \tilde{r}^{(1)}(t) + \lambda^2 \tilde{r}^{(2)}(t) + \lambda^3 \tilde{r}^{(3)}(t) + \ldots \]

\[ \Rightarrow \quad \ddot{\tilde{r}}^{(1)} + 2\gamma \dot{\tilde{r}}^{(1)} + \omega_0^2 \tilde{r}^{(1)} = -e\tilde{E}(t)/m \]

\[ \ddot{\tilde{r}}^{(2)} + 2\gamma \dot{\tilde{r}}^{(2)} + \omega_0^2 \tilde{r}^{(2)} = 0 \]

\[ \ddot{\tilde{r}}^{(3)} + 2\gamma \dot{\tilde{r}}^{(3)} + \omega_0^2 \tilde{r}^{(3)} - b(\tilde{r}^{(1)} \cdot \tilde{r}^{(1)})\tilde{r}^{(1)} = 0 \]
3\textsuperscript{rd} order polarization:

\[
P^{(3)}(\omega_q) = -N\epsilon^{(3)}(\omega_q)
\]

\[
\Rightarrow P_i^{(3)}(\omega_q) = \sum_{jkl} \sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)
\]

\[
= D \sum_{jkl} \chi_{ijkl}^{(3)}(\omega_q, \omega_m, \omega_n, \omega_p) E_j(\omega_m) E_k(\omega_n) E_l(\omega_p)
\]

where, D : Degeneracy factor
(The number of distinct permutations of the frequency \(\omega_m, \omega_n, \omega_p\))

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

\[
\chi_{1111} = \chi_{2222} = \chi_{3333} = \chi_{1122} = \chi_{1133} = \chi_{2211} = \chi_{2233} = \chi_{3311} = \chi_{3322} = \chi_{1212} = \chi_{1313} = \chi_{2323} = \chi_{2121} = \chi_{3131} = \chi_{3232}
\]

and, \(\chi_{1111} = \chi_{1122} + \chi_{1212} + \chi_{1221}\)

21 nonzero elements:

(Report)
Expression for the nonlinear susceptibility in the compact form:

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

Example) Third-harmonic generation: \( \chi_{ijkl}(3\omega=\omega+\omega+\omega) \)

\[ \chi_{1122}=\chi_{1212}=\chi_{1221} \]

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

Example) Intensity-dependent refractive index: \( \chi_{ijkl}(\omega=\omega+\omega-\omega) \)

\[ \chi_{1122}=\chi_{1212} \neq \chi_{1221} \]

\[ \Rightarrow \chi_{ijkl}(3\omega=\omega+\omega-\omega)=\chi_{1122}(\omega=\omega+\omega-\omega) \times (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl}) + \chi_{1221}(\omega=\omega+\omega-\omega) \delta_{il} \delta_{jk} \]
Nonlinear polarisation for Intensity-dependent refractive index

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

\[ \Rightarrow P_i(\omega) = 6 \chi_{1122} E_i(\mathbf{E} \cdot \mathbf{E}^*) + 3 \chi_{1221} E_i(\mathbf{E} \cdot \mathbf{E}) \quad \Rightarrow \quad P = 6 \chi_{1122} \mathbf{E} \cdot \mathbf{E}^* + 3 \chi_{1221} (\mathbf{E} \cdot \mathbf{E}) \mathbf{E}^* \quad \text{in vector form} \]

Defining the coefficients, A and B as

\[ A = 6 \chi_{1122}, \quad B = 6 \chi_{1221} \quad \text{(Maker and Terhune's notation)} \]

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

*Figure 4.2.1* Diagrams (a) and (b) represent the resonant contributions to the nonlinear coefficients A and B, respectively.
In some purpose, it is useful to describe the nonlinear polarization by in terms of an effective linear susceptibility, $\chi_{ij}$ as

$$P_i = \sum_j \chi_{ij} E_j$$

$$\Rightarrow \chi_{ij} = A'(E \cdot E^*) \delta_{ij} + \frac{1}{2} B' \left( E_i E_j^* + E_j E_i^* \right)$$

where, $A' = A - \frac{1}{2} B = 6 \chi_{122} - 3 \chi_{1221}$

$$B' = B = 6 \chi_{1221}$$

Physical mechanisms ;

$B/A=6, \quad B'/A'=-3$ : molecular orientation

$B/A=1, \quad B'/A'=2$ : nonresonant electronic response

$B/A=0, \quad B'/A'=0$ : electrostriction
4.3 Nonresonant Electronic Nonlinearities

# The most fast response: \( \tau = 2\pi a_0 / v \approx 10^{-16} \text{s} \quad [a_0 (\text{Bohr radius}) \sim 0.5 \times 10^{-8} \text{cm}, v (\text{electron velocity}) \sim c/137] \)

Classical, Anharmonic Oscillator Model of Electronic Nonlinearities

Approximated Potential: \( U(r) = \frac{1}{2} m \omega_0^2 |r|^2 - \frac{1}{4} mb |r|^4 \)

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

\[
\Rightarrow \chi_{ijkl}^{(3)}(\omega = \omega + \omega - \omega) = \frac{Nbe^4 [\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}]}{3m^3 D^3(\omega)D(-\omega)}
\]

where, \( D(\omega) = \omega_0^2 - \omega^2 - 2i\omega\gamma \)

According to the notation of Maker and Terhune,

\[
A = B = \frac{2Nbe^4}{m^3 D^3(\omega)D(-\omega)}
\]
Far off-resonant case, \( \omega < \omega_0 \Rightarrow D(\omega) \approx \omega_0^2, \ b \approx \omega_0^2/d^2 \)

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

**Typical value of \( \chi^{(3)} \)**

\( N=4 \times 10^{22} \text{ cm}^{-3}, \ d=3 \times 10^{-8} \text{ cm}, \ e=4.8 \times 10^{-10} \text{ esu} \)

\( \omega_0=7 \times 10^{15} \text{ rad/s}, \ m=9.1 \times 10^{-28} \text{ g} \)

\( \Rightarrow \chi^{(3)} \approx 2 \times 10^{-14} \text{ esu} \)
4.4 Nonlinearities due to Molecular Orientation

The torque exerted on the molecule when an electric field is applied:

\[ \tau = \mathbf{P} \times \mathbf{E} \]

induced dipole moment
Second order index of refraction

Change of potential energy :

\[ dU = -p \cdot d\mathbf{E} = -p_3 \ dE_3 - p_1 \ dE_1 = -\alpha_3 E_3 dE_3 - \alpha_1 E_1 dE_1 \]

\[ U = -\frac{1}{2} \left( \alpha_3 E_3^2 + \alpha_1 E_1^2 \right) = -\frac{1}{2} \left( \alpha_3 E^2 \cos^2 \theta + \alpha_1 E^2 \sin^2 \theta \right) \]

\[ = -\frac{1}{2} \alpha_1 E^2 - \frac{1}{2} (\alpha_3 - \alpha_1) E^2 \cos^2 \theta \]

* Optical field (orientational relaxation time ~ ps order) : \( E^2 \rightarrow \tilde{E}^2(t) \approx \tilde{E}^2 \)

* \( \langle U \rangle = -\frac{1}{2} \langle \alpha \rangle |E|^2 \)

1) With no local-field correction : \( n^2 = 1 + 4\pi N \langle \alpha \rangle \)

Mean polarization :

\[ \langle \alpha \rangle = \alpha_3 \langle \cos^2 \theta \rangle + \alpha_1 \langle \sin^2 \theta \rangle = \alpha_1 + (\alpha_3 - \alpha_1) \langle \cos^2 \theta \rangle \]
\begin{align*}
\langle \cos^2 \theta \rangle &= \frac{\int d\Omega \cos^2 \theta \exp[-U(\theta)/kT]}{\int d\Omega \exp[-U(\theta)/kT]} \\
\end{align*}

Defining intensity parameter, \(J = \frac{1}{2}(\alpha_3 - \alpha_1) \bar{E}^2 / kT\)

\begin{align*}
\langle \cos^2 \theta \rangle &= \frac{\int_0^\pi \cos^2 \theta \exp(J \cos^2 \theta) \sin \theta d\theta}{\int_0^\pi \exp(J \cos^2 \theta) \sin \theta d\theta} \\
\end{align*}

i) \(J \to 0\)

\begin{align*}
\langle \cos^2 \theta \rangle_0 &= \frac{\int_0^\pi \cos^2 \theta \sin \theta d\theta}{\int_0^\pi \sin \theta d\theta} = \frac{1}{3} \\
\Rightarrow \langle \alpha \rangle_0 &= \frac{1}{3} \alpha_3 + \frac{2}{3} \alpha_1 \\
\therefore \quad n_0^2 &= 1 + 4\pi N \left( \frac{1}{3} \alpha_3 + \frac{2}{3} \alpha_1 \right) \quad : \text{linear refractive index}
\end{align*}
ii) $J \neq 0$

\[
\begin{align*}
n^2 &= 1 + 4\pi N \left[ \alpha_1 + (\alpha_3 - \alpha_1) \right] \cos^2 \theta \\
\Rightarrow n^2 - n_0^2 &= 4\pi N \left[ \frac{1}{3} \alpha_1 + (\alpha_3 - \alpha_1) \right] \cos^2 \theta - \frac{1}{3} \alpha_3 \\
&= 4\pi N (\alpha_3 - \alpha_1) \left( \cos^2 \theta - \frac{1}{3} \right) \\
n^2 - n_0^2 &<< n_0^2 \\
\Rightarrow \delta_n = n - n_0 &= \frac{2\pi N}{n_0} (\alpha_3 - \alpha_1) \left( \cos^2 \theta - \frac{1}{3} \right)
\end{align*}
\]

**Figure 4.4.3** Variation of the quantity $(\cos^2 \theta - \frac{1}{3})$, which is proportional to the nonlinear change in refractive index $\delta n$, with the intensity parameter $J$. Note that for $J \lesssim 5$, $\delta n$ increases nearly linearly with $J$. 
\[
\langle \cos^2 \theta \rangle = \frac{\int_0^\pi \cos^2 \theta \exp(J \cos^2 \theta) \sin \theta d\theta}{\int_0^\pi \exp(J \cos^2 \theta) \sin \theta d\theta}
\]

\[
= \frac{1}{3} + \frac{4J^2}{45} + \frac{8J^2}{945} + ..., \\
\]

\[
\Rightarrow \delta_n \approx \frac{4\pi N}{2n_0} (\alpha_3 - \alpha_1) \frac{4J}{45} = \frac{4\pi N}{45 n_0} (\alpha_3 - \alpha_1)^2 \frac{\bar{E}^2}{kT} \equiv \bar{n}_2 \bar{E}^2
\]

Second-order index of refraction:

\[
\bar{n}_2 = \frac{4\pi N}{45n_0} \frac{(\alpha_3 - \alpha_1)^2}{kT}
\]
2) With local-field correction

\[ \tilde{E}_{loc} = \tilde{E} + \frac{4}{3} \pi \tilde{P} \]

\[ \tilde{P} = Np \quad \text{and} \quad \rho = \alpha \tilde{E}_{loc} \quad \Rightarrow \quad \tilde{P} = N\alpha \left( \tilde{E} + \frac{4\pi}{3} \tilde{P} \right) \]

\[ \therefore \quad \tilde{P} = \frac{N\alpha}{1 - \frac{4\pi}{3} N\alpha} \tilde{E} \equiv \chi^{(1)} \tilde{E} \quad \Rightarrow \quad \chi^{(1)} = \frac{N\alpha}{1 - \frac{4\pi}{3} N\alpha} \]

\[ \varepsilon^{(1)} = 1 + 4\pi\chi^{(1)} \quad \Rightarrow \quad \frac{\varepsilon^{(1)} - 1}{\varepsilon^{(1)} + 2} = \frac{4\pi N\alpha}{3} \quad \text{or} \quad \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N\langle \alpha \rangle}{3} : \text{Lorentz-Lorenz law} \]

\[ \Rightarrow \quad \overline{n}_2 = \frac{4\pi N}{45n_0} \left( \frac{n_0^2 + 2}{3} \right)^4 \left( \alpha_3 - \alpha_1 \right)^2 \frac{kT}{kT} \]
8.2 Electrostriction

: Tendency of materials to become compressed in the presence of an electric field

\[ U = -\int_0^E p \cdot dE' = -\int_0^E \alpha E' \cdot dE' = -\frac{1}{2} \alpha E \cdot E = -\frac{1}{2} \alpha E^2 \]

Force acting on the molecule:

\[ \mathbf{F} = -\nabla U = \frac{1}{2} \alpha \nabla (E^2) \]
Increase in electric permittivity due to the density change of the material:

\[ \Delta \varepsilon = \frac{\partial \varepsilon}{\partial \rho} \Delta \rho \]

Field energy density change in the material = Work density performed in compressing the material

\[ \Delta u = \frac{E^2}{8\pi} \Delta \varepsilon = \frac{E^2}{8\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right) \Delta \rho \equiv \Delta w = p_{st} \frac{\Delta V}{V} = -p_{st} \frac{\Delta \rho}{\rho} \]

So, electrostrictive pressure:

\[ p_{st} = -\rho \frac{\partial \varepsilon}{\partial \rho} \frac{E^2}{8\pi} = -\gamma_e \frac{E^2}{8\pi} \]

where, \( \gamma_e \equiv \rho \frac{\partial \varepsilon}{\partial \rho} \) : electrostrictive constant
Density change:

\[ \Delta \rho = -\rho \left( \frac{1}{\rho} \frac{\partial \rho}{\partial P} \right) P_{st} \equiv -\rho C P_{st} \quad \Rightarrow \quad \Delta \rho = \rho C \gamma_e \frac{E^2}{8\pi} \]

where, \( C \equiv \frac{1}{\rho} \frac{\partial \rho}{\partial P} \) : compressibility

For optical field, \( \Delta \rho = \rho C \gamma_e \frac{\langle \tilde{E}^2 \rangle}{8\pi} \)

\[ \Delta \chi = \frac{\Delta \varepsilon}{4\pi} = \frac{1}{4\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right) \Delta \rho \]

\[ \gamma_e \equiv \rho \frac{\partial \varepsilon}{\partial \rho} \]

\[ = \rho C \gamma_e \frac{\langle \tilde{E}^2 \rangle}{8\pi} \left( \frac{\partial \varepsilon}{\partial \rho} \right) \frac{1}{4\pi} = \frac{1}{32\pi^2} C \gamma_e \langle \tilde{E}^2 \rangle \]
\( \tilde{E}(t) = E e^{-i\omega t} + \text{c.c.} \Rightarrow \langle \tilde{E}^2 \rangle = 2E \cdot E^* \)

\[ \Delta \chi = \frac{1}{16\pi^2} C\gamma e^2 E \cdot E^* \]

\(<\text{Classification according to the Maker and Terhune’s notation}>\)

Nonlinear polarization : \( \mathbf{P} = \Delta \chi \mathbf{E} \)

\[ \mathbf{P} = \frac{1}{16\pi^2} C\gamma e^2 E^2 \mathbf{E} \equiv 3\chi^{(3)}(\omega = \omega + \omega - \omega) |\mathbf{E}|^2 \mathbf{E} \]

\[ \therefore \chi^{(3)}(\omega = \omega + \omega - \omega) = \frac{1}{48\pi^2} C\gamma e^2 \]

That is, \( A = \frac{C_T \gamma e^2}{16\pi^2}, \quad B = 0 \)
\[ \gamma_e = \rho \frac{\partial \varepsilon}{\partial \rho} \]

\[ \gamma_e = n^2 - 1 \quad \text{: For dilute gas} \]

\[ \gamma_e = \frac{(n^2 - 1)(n^2 + 2)}{3} \quad \text{: For condensed matter (Lorentz-Lorenz law)} \]

Example) Cs$_2$, \( C \sim 10^{-10} \text{ cm}^2/\text{dyne}, \gamma_e \sim 1 \Rightarrow \chi^{(3)} \sim 2 \times 10^{-13} \text{ esu} \)

Ideal gas, \( C \sim 10^{-6} \text{ cm}^2/\text{dyne} \) (1 atm), \( \gamma_e = n^2 - 1 \sim 6 \times 10^{-4} \Rightarrow \chi^{(3)} \sim 1 \times 10^{-15} \text{ esu} \)