Abstract

We derive the spectral dependence of the non-linear susceptibility of any order, generalizing the common form of Sellmeier equations. This dependence is fully defined by the knowledge of the linear dispersion of the medium. This finding generalizes the Miller formula to any order of non-linearity. In the frequency-degenerate case, it yields the spectral dependence of non-linear refractive indices of arbitrary order.
Generalized Miller Formulae

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Abstract: We derive the spectral dependence of the non-linear susceptibility of any order, generalizing the common form of Sellmeier equations. This dependence is fully defined by the knowledge of the linear dispersion of the medium. This finding generalizes the Miller formula to any order of non-linearity. In the frequency-degenerate case, it yields the spectral dependence of non-linear refractive indices of arbitrary order.

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References and links

1. Introduction

Non-linear optics [1] relies on the knowledge of the non-linear susceptibilities (or, alternatively, the non-linear indices) of the propagation media. This description is generally truncated to the
first term, i.e. the second-order susceptibility in non-centrosymmetric media, or the third-order susceptibility in centrosymmetric ones. However, the increase of the available laser powers as well as the investigation of systems like optical fibers [2] or photonic crystals [3] where the confinement of the light increases its intensity raise the need to consider higher-order processes. Recently, the non-linear refractive indices of O₂, N₂ were measured up to the second-order susceptibility in centrosymmetric ones. However, the increase of the available laser powers makes it necessary to consider higher-order processes. The Miller formula [Eq. (1)] [11] can be extended to any order of non-linearity. In the frequency-degenerate case, this finding yields the spectral dependence of non-linear refractive indices of arbitrary order, confirming and widely generalizing Mizrahi and Shelton’s statement about the Miller formula [11]

\[ \chi^{(2)}(\omega_1; \omega_2) = \chi^{(1)}(\omega_1)\chi^{(1)}(\omega_2) \]

Mizrahi and Shelton later suggested that the Miller formula could be extended to the non-linear indices of arbitrary order, confirming and widely generalizing Mizrahi and Shelton’s statement about the Miller formula [11].

### 2. Derivation of generalized Miller formulæ

#### 2.1. Electrons in an anharmonic oscillator

Elucidating the spectral dependence of the non-linear susceptibility requires to consider the equation of motion of an electron located at \( \vec{r} \) in a three-dimensional potential \( V(\vec{r}) \). V can be expanded as a 3-dimensional Taylor series around the equilibrium position \( \vec{r} = 0 \):

\[ V(\vec{r}) = V(0) + \sum_{i+j+k \geq 2} \frac{x^i y^j z^k}{i! j! k!} \left[ \frac{\partial^i V}{\partial x^i} \frac{\partial^j V}{\partial y^j} \frac{\partial^k V}{\partial z^k} \right] \bigg|_{\vec{r}=0} \]

where the summation begins at \( q \equiv i + j + k = 2 \) since \( \left[ \frac{\partial^i V}{\partial x^i} \right]_{x=0} = \left[ \frac{\partial^j V}{\partial y^j} \right]_{y=0} = \left[ \frac{\partial^k V}{\partial z^k} \right]_{z=0} = 0 \) by definition of the equilibrium position. As a consequence, the electron experiences a force equal to

\[ \vec{F}(\vec{r}) = -\vec{\nabla}V(\vec{r}) = -\sum_{q \geq 2} \frac{x^{i-1} y^{j-1} z^{k-1}}{i! j! k!} \left[ \frac{\partial^q V}{\partial x^i \partial y^j \partial z^k} \right] \bigg|_{\vec{r}=0} \]

The macroscopic polarization along the axes \( x, y, z \) is respectively \( P_x = -Ne_x, P_y = -Ne_y \) and \( P_z = -Ne_z \), \( N \) being the local density of electrons and \( -e \) their charge. Equation (3)
considered tensor element. As a consequence, the classical equation of motion of the electron \( \omega \) therefore rewrites:

\[
\vec{F}(\vec{r}) = -\sum_{q \geq 1} \left( \frac{1}{Ne} \right)^q \left( \frac{\partial^q V}{\partial x^i \partial y^j \partial z^k} \right) \left( \frac{\partial^{q+1} V}{\partial x^i \partial y^j \partial z^k} \right)_{\vec{r}=\vec{0}} \tag{4}
\]

or, equivalently:

\[
\vec{F}(\vec{r}) = -\sum_{q \geq 1} \left( \frac{1}{Ne} \right)^q \left( \frac{p^i_p^j p^k}{i! j! k!} \right) \left( \frac{\partial^{q+1} V}{\partial x^i \partial y^j \partial z^k} \right)_{\vec{r}=\vec{0}} \tag{5}
\]

We introduce the \((q + 1)^{th}\) rank tensor \( Q^{(q)} \), which elements are given by:

\[
\begin{pmatrix}
Q_{x^{(1)}Y^{(1)}Z^{(1)}}^{(q)} \\
Q_{y^{(1)}X^{(1)}Z^{(1)}}^{(q)} \\
Q_{z^{(1)}X^{(1)}Y^{(1)}}^{(q)}
\end{pmatrix} = (-1)^q \frac{m}{i! j! k!} \begin{pmatrix}
\frac{\partial^{q+1} V}{\partial x^i \partial y^j \partial z^k} \\
\frac{\partial^{q+1} V}{\partial x^i \partial y^j \partial z^k} \\
\frac{\partial^{q+1} V}{\partial x^i \partial y^j \partial z^k}
\end{pmatrix}_{\vec{r}=\vec{0}} \tag{6}
\]

where, for example, \( x^{(i)} \) indicates that the coordinate \( x \) appears \( i \) times in the index list of the considered tensor element. As a consequence, the classical equation of motion of the electron becomes:

\[
\frac{d^2 \vec{P}}{dt^2} + \gamma \frac{d \vec{P}}{dt} + \vec{\omega}_e^2 \vec{P} + Ne \sum_{q=1}^{\infty} Q^{(q)} : \bigotimes \frac{\vec{P}}{Ne} = \frac{Ne^2}{m} \vec{E}(t) \tag{7}
\]

where : denotes the contracted product and \( \bigotimes \) the tensorial product. \( \vec{E} \) is the driving electric field, \( \vec{\omega}_e^2 = \begin{pmatrix}
\omega_{e,x}^2 & 0 & 0 \\
0 & \omega_{e,y}^2 & 0 \\
0 & 0 & \omega_{e,z}^2
\end{pmatrix} \) is the eigenfrequency matrix of the considered medium, which is diagonal provided \( x, y, \) and \( z \) are the principal axes of the optical frame of the medium (\( \omega_{e,x} = \sqrt{\frac{1}{m} \frac{\partial^2 V}{\partial x^2}} \)), and the matrix \( \vec{\gamma} \) stands for the linear absorption. No multiphoton absorption is considered here. Note that a medium symmetry of at least \( K \times C_2 \) (\( i.e. \) a crystal with at least orthorhombic symmetry, or a statistically isotropic medium like air) allows to simultaneously diagonalize \( \vec{\omega}_e^2 \) and \( \vec{\gamma} \) in the optical frame [15].

A perturbative solution of Eq. (7) is searched as:

\[
\vec{P} = \sum_{l=1}^{\infty} \alpha^l \vec{P}^{(l)} \tag{8}
\]

where \( \alpha \in [0..1] \) is a free parameter. The series begins at 1, assuming \( \vec{P}^{(0)} = \vec{0} \). Inserting it in Eq. (7) and equating the terms in \( \alpha^q \) yields a set of equations

\[
\frac{d^2 \vec{P}^{(1)}}{dt^2} + \vec{\gamma} \frac{d \vec{P}^{(1)}}{dt} + \vec{\omega}_e^2 \vec{P}^{(1)} = \frac{Ne^2}{m} \vec{E}(t) \tag{9}
\]

and, \( \forall q \geq 2, 

\[
\frac{d^2 \vec{P}^{(q)}}{dt^2} + \vec{\gamma} \frac{d \vec{P}^{(q)}}{dt} + \vec{\omega}_e^2 \vec{P}^{(q)} = -Ne Q^{(q)} : \bigotimes \frac{\vec{P}^{(1)}}{Ne} \tag{10}
\]
2.2. Sellmeier equations

If the medium symmetry is at least $K \times C_2$ or absorption can be neglected, Eq. (9) can be reduced to a scalar form provided the polarization is excited along one principal axis. We will first focus on this case which simplifies the writing and thus helps focusing the discussion on the physical aspects, without altering the principle of the derivation. Omitting the index corresponding to the axis, the scalar form of Eq. (10) reads, for any $q \geq 2$:

$$\frac{d^2 P^{(q)}}{dt^2} + \gamma \frac{dP^{(q)}}{dt} + \omega^2 P^{(q)} = -Ne Q^{(q)} \left( \frac{P^{(1)}}{Ne} \right)^q$$

(14)

Since $P^{(q)}(t) = \int_{-\infty}^{+\infty} P^{(q)}(\omega)e^{i\omega t} d\omega$, Eq. (14) rewrites:

$$\int_{-\infty}^{+\infty} \sum_{q=0}^{\infty} \Omega^{(q)}(\omega) P^{(q)}(\omega) e^{i\omega t} d\omega = \frac{Q^{(q)}}{(Ne)^{q-1}} \left( \int_{-\infty}^{+\infty} P^{(1)}(\omega) e^{i\omega t} d\omega \right)^q$$

(15)

$$\int \cdots \int \prod_{i=1}^{q} \left( P^{(1)}(\omega_i) e^{i\omega_i t} d\omega_i \right)$$

(16)
2.4. Three-dimensionnal Miller formulæ

Identifying the terms at an arbitrary frequency \( \omega_0 \) on both sides of the equation, we obtain:

\[
P_0^{(q)}(\omega_0) = -\frac{Q^{(q)}}{\Omega(\omega_0)(Ne)^{q-1}} \iiint \delta \left( \sum_{l=0}^{q} \omega_l = 0 \right) \times \prod_{l=1}^{q} \left( P_0^{(1)}(\omega_l) d\omega_l \right)
\]

(17)

\[
P_0^{(q)}(\omega_0) = -Ne \left( \frac{e}{m} \right)^q \frac{Q^{(q)}}{\Omega(\omega_0)} \sum_{\sum_{l=0}^{q} \omega_l=0} \left( \prod_{l=1}^{q} E_0(\omega_l) \right)
\]

(18)

Let us now consider the construction of a wave at \( \omega_0 \) from a set of \( q' \leq q \) incident waves at frequencies \( \omega_1, \ldots, \omega_{q'} \), each algebraic frequency \( \omega_l \) being implied \( u_l \) times in the process: \( \sum_{l=1}^{q'} u_l = q \), while energy conservation imposes \( \sum_{l=1}^{q'} \omega_l = \omega_0 \). In this case,

\[
P_0^{(q)}(\omega_0) = -Ne \left( \frac{e}{m} \right)^q \frac{Q^{(q)}}{\Omega(\omega_0)} \sum_{\sum_{l=1}^{q'} \omega_l=\omega_0} \left( \prod_{l=1}^{q'} E_0(\omega_l) \right)^{u_l}
\]

(19)

where \( C_{q'\ldots u}' = q'! / (u_1! \times \ldots \times u_{q'}!) \) is the number of combinations achievable from \( q' \) sets of \( u_1, \ldots, u_{q'} \) objects, respectively. The terms of Eq. (18) corresponding to each combination of frequencies conserving energy can be identified with the expression of the non-linear polarization using the \((q+1)^{th}\) rank tensor:

\[
P_0^{(q)}(\omega_0) = e_0 C_q^{u_1\ldots u_{q'}} \chi(q)(\omega_0; \omega_1, \ldots, \omega_{q'}) \prod_{l=1}^{q'} E_0^{u_l}(\omega_l)
\]

(20)

As stated above, consistently with Eq. (14) we do not consider here the cascaded processes. Therefore, the identification yields:

\[
\chi(q)(\omega_0; \omega_1, \ldots, \omega_{q'}) = -Ne \left( \frac{e}{m} \right)^q \frac{Q^{(q)}}{e_0 \prod_{l=0}^{q} \Omega(\omega_l)}
\]

(21)

\[
= \frac{me_0^q}{N^q e^{q+1}} Q^{(q)} \prod_{l=0}^{q} \chi(1)(\omega_l)
\]

(22)

This expression provides a general description of the non-linear susceptibility of any order, provided the shape of the potential \( V \) is known. In practice, this potential is rarely known, but it is independent from the excitation frequency. The spectral dependence of the above expression is therefore only driven by \( \Omega \), i.e. the spectral dependence of the first-order susceptibilities. As a consequence, in a given medium, the knowledge of both the frequency dependence of the linear susceptibility and of the \( q^{th} \)-order susceptibility for a specific set of wavelengths is sufficient to extrapolate this susceptibility to any other set of wavelengths, through the relation:

\[
\frac{\chi(q)(\omega_0; \omega_1, \ldots, \omega_{q'})}{\chi(q)(\omega'_0; \omega'_1, \ldots, \omega'_{q'})} = \frac{\prod_{l=0}^{q'} \Omega(\omega'_l)}{\prod_{l=0}^{q} \Omega(\omega_l)} = \frac{\prod_{l=0}^{q'} \chi(1)(\omega'_l)}{\prod_{l=0}^{q} \chi(1)(\omega_l)}
\]

(23)

When applied to \( \chi^{(2)} \), this generalized Miller formula immediately reduces to the original one of Eq. (1) [11].

2.4. Three-dimensionnal Miller formulæ

While the one-dimensional treatment of Eqs. (14)–(23) provides an easy writing of the derivation, the same sequence can be applied to solve Eq. (10) in the general three-dimensional case.
Products simply have to be transposed to the adequate tensorial products. The identification of the spectral components of the Fourier expression of \( \tilde{P}^{(q)} \) and \( \otimes \tilde{P}^{(1)} \) yields a three-dimensional equivalent of Eq. (18):

\[
\tilde{\Omega}(\omega_0)P^{(q)}_0(\omega_0) = -Ne \left( \frac{e}{m} \right)^q Q^{(q)} : \left( \otimes_{l=1}^q \tilde{P}^{(1)}(\omega_l) \right)
\]  

(24)

In media with at least K\(\times\)C\(_2\) symmetry, or if absorption can be neglected, \(\tilde{\Omega}\) is diagonal so that this expression can easily be identified with the counterpart of Eq. (20) expressing the non-linear polarization in terms of non-linear susceptibility:

\[
\tilde{P}^{(q)}_0(\omega_0) = e_0 \chi^{(q)} : \otimes_{l=1}^q \tilde{E}(\omega_l)
\]  

(25)

where each index \(\nu_l\) denotes either the \(x\), \(y\), or \(z\) axis. The spectral dependence of \(\chi^{(q)}\) only depends on the product of the \(\Omega_{\nu_j}(\omega_l)\), meaning that all frequencies commute. This property, together with the fact that the \(\Omega_j(\omega_l)\) are even functions as soon as absorption can be neglected, provides a direct evidence and generalization to arbitrary orders of the ABDP relations. These relations state that as soon as \(\tilde{\Omega}\) can be diagonalized, \(\omega_0\) commutes with any \(\omega_l\) in the expression of \(\chi^{(2)}\) and \(\chi^{(3)}\) [16].

### 2.5. Application to non-linear refractive indices

In the case of frequency-degenerate interactions of odd order excited along one single principal axis, the susceptibility tensor reduces to \(\chi^{(2p+1)}(\omega_0) = \frac{2^{p+1}p!(p+1)!}{(2p+1)!} \left( \frac{n_0^2(\omega_0)\mu_0^2}{n_0(\omega_0)} \right)^p n_{2p}(\omega_0)\), which defines the \(p\)\(^{th}\)-order non-linear refractive index \(n_{2p}\). Therefore, the knowledge of the dispersion curve for the linear susceptibility and the measurement of \(\chi^{(2p+1)}\) at one single frequency \(\omega'_0\) are sufficient to provide \(\chi^{(2p+1)}\) at any frequency \(\omega_0\) thanks to Eq. (23):

\[
\frac{\chi^{(2p+1)}(\omega_0)}{\chi^{(2p+1)}(\omega'_0)} = \left( \frac{\Omega(\omega'_0)}{\Omega(\omega_0)} \right)^{2p+2} = \left( \frac{\chi^{(1)}(\omega'_0)}{\chi^{(1)}(\omega'_0)} \right)^{2p+2}
\]  

(28)

or equivalently, if absorption can be neglected, in terms of the real parts of the non-linear refractive indices:

\[
\frac{n_{2p}(\omega_0)}{n_{2p}(\omega'_0)} = \left( \frac{n_0^2(\omega_0) - 1}{n_0^2(\omega'_0) - 1} \right)^{2p+2}
\]  

(29)

As an illustration, Fig. 1 displays the values of \(n_2\) through \(n_8\) for N\(_2\), O\(_2\) and Ar, based on the measurements of Loriot et al. at 800 nm [4] as corrected by Béjot et al. [5], extrapolated to the whole spectrum using Eq. (28).
3. Generalization to mixes and multiple resonance frequencies

Up to now, we have only considered the case of a single type of oscillators. However, in actual media (e.g. in mixes like the air, where both N₂ and O₂ get polarized, or in crystals where several oscillation modes can be excited) several eigenfrequencies \( \omega_{l, i} \) may contribute. In this case, the polarization \( \vec{P} \) can be defined as \( \sum \vec{P}_l \), where \( l \) denotes the types of oscillators, or species. If the coupling between the oscillators can be neglected, the above derivation applies to each oscillator type independently, and the resulting refractive index will be given by the Lorentz-Lorenz model. For example the Sellmeier equation of air reads [14]:

\[
10^8 (n_0 - 1) = 8015.514 + \frac{2368616}{128.7459 - 1/\lambda^2} + \frac{19085.73}{50.01974 - 1/\lambda^2} \quad (30)
\]

where the wavelength \( \lambda \) is expressed in \( \mu \text{m} \). Obviously, the terms of Eq. (30) respectively correspond to N₂, with a resonance at \( 1/\lambda^2 \sim 128.7 \mu \text{m}^{-2} \) (i.e. \( \lambda = 88 \text{ nm} \)):

\[
10^8 (n_0, \text{N}_2 - 1) = 8736.28 + \frac{2398095.2}{128.7 - 1/\lambda^2} \quad (31)
\]

and to O₂, with \( 1/\lambda^2 \sim 50 \mu \text{m}^{-2} \) (i.e. \( \lambda = 141 \text{ nm} \)) [14]:

\[
10^8 (n_0, \text{O}_2 - 1) = 15532.45 + \frac{456402.97}{50.0 - 1/\lambda^2} \quad (32)
\]

In such cases, the generalized Miller formulæ of Eq. (23) cannot be applied to the material or the mix as a whole. Instead, they must be applied to each susceptibility-order of each oscillator type. The non-linear susceptibilities of the whole material will then be deduced from those of the individual oscillator types through the Lorentz-Lorenz model. Figure 1 displays the result of this treatment in the case of air.
4. Conclusion

In conclusion, we have explicitly derived the spectral dependence of the non-linear susceptibility of any order, generalizing the common form of Sellmeier equations, in both frequency-degenerate and non-degenerate systems. This spectral dependence is fully defined by the knowledge of the linear dispersion of the medium. As a consequence, the Miller formula [Eq. (1)] [11] can be generalized to any order of non-linearity and any tensor element of non-linear susceptibilities as soon as the material has at least $K \times C_2$ symmetry and negligible absorption. In particular, the spectral dependence of non-linear refractive indices of any order can be deduced from their value at one single frequency and the dispersion curve of the medium. Such knowledge is of particular value in nonlinear optics implying confined light leading to very-high intensities, as, e.g. in fiber optics [2] filamentation [7–10], or photonic crystals [3].

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