6

Second- and Higher-Order Harmonic Generation

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6.1 INTRODUCTION

Second-harmonic generation is the prototypical nonlinear optical process. Its discovery by Franken et al. (1961) is often taken as the birth of the field of nonlinear optics. Even today, this process is extremely important for various applications, including shifting the output frequency of lasers, as a diagnostic tool to determine the surface properties of various materials, and for use in nonlinear optical microscopy.

The process of second-harmonic generation is illustrated in Figure 6.1. A laser beam at frequency ω illuminates a nonlinear optical material and a beam of light at frequency 2ω is created. Under proper circumstances, the efficiency of this process can exceed 50% (Seka et al., 1980). The transfer of energy from the input field to the output field can be visualized in terms of the energy-level diagram shown on the right-hand side of the figure. One visualizes the process as one in which two photons from the input beam are lost and one photon in the output beam is created. The process of second-harmonic generation generalizes straightforwardly to direct third- and higher-order harmonic generation. The process of N-th harmonic generation, for arbitrary order N, is illustrated in Figure 6.2. Here N photons are lost to the input beam and one photon at frequency $N\omega$ is created. These intuitive descriptions of the nature of harmonic generation can be justified more formally by means of the Manley-Rowe relations (Manley & Rowe, 1959).

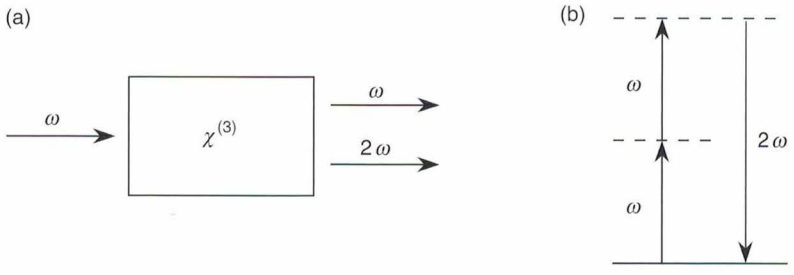

Figure 6.1. The process of second-harmonic generation.

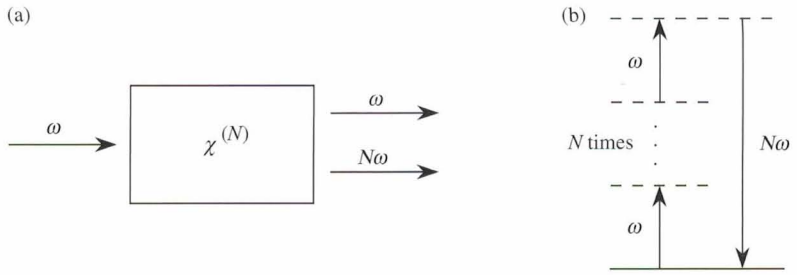

Figure 6.2. The process of direct N-th harmonic generation.

6.2 THEORY OF THE NONLINEAR OPTICAL SUSCEPTIBILITY

Theoretical treatments of harmonic generation can be found both in the early research papers (Armstrong et al. 1962) and in various textbook accounts (Boyd, 2003; Butcher & Cotter, 1990; Shen, 1984; Zernike & Midwinter, 1973). These treatments usually begin by considering how the response of the material medium, specified by means of the polarization P (dipole moment per unit volume), depends on the amplitude E of the electric field of the applied optical wave. Under the simplest circumstances, this relationship can be expressed in the time domain as

$$\tilde{P}(t) = \epsilon_0 \left[\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \cdots \right], \tag{6.1}$$

where the presence of a tilde over a quantity indicates that that quantity is a rapidly varying function of time. Here $\chi^{(1)}$ is the linear susceptibility, $\chi^{(2)}$ is the second-order susceptibility, $\chi^{(3)}$ is the third-order susceptibility, etc.

Second-harmonic generation occurs as a result of the second-order response described by $\chi^{(2)}$. A slight variant of this process is sum-frequency generation, which is illustrated in Figure 6.3. The situation is a bit more complicated for third-harmonic generation, which can occur either directly as a consequence of the third-order response $\chi^{(3)}$, or indirectly as a two-step process involving two second-order processes. In this latter case, the first step involves second-harmonic generation involving $\chi^{(2)}$ and the second step involves sum-frequency mixing, also involving $\chi^{(2)}$, of frequencies ω and 2ω to produce 3ω. This circumstance is illustrated in Figure 6.4. In well-designed optical systems, the sequential process can be far more efficient than the direct process, although in situations involving biological materials the direct process usually dominates. Similar considerations regarding direct and indirect processes apply to higher-order harmonic generation.

A more complete description of the nonlinear response requires that the vector nature of the electric field and polarization be taken into account. Also, if the various orders of the nonlinear susceptibility are frequency dependent, the relationship between the electric field and polarization is best expressed in the frequency domain. For example, the second-order polarization can be expressed more generally as:

$$P_i(\omega_n + \omega_m) = \epsilon_0 \sum_{jk} \sum_{(nm)} \chi^{(2)}_{ijk}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m). \tag{6.2}$$

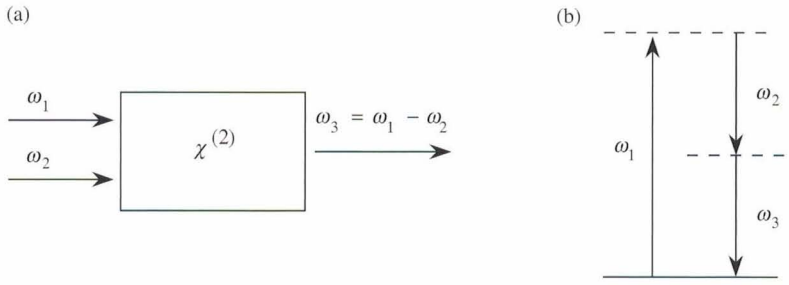

Figure 6.3. The process of sum-frequency generation.

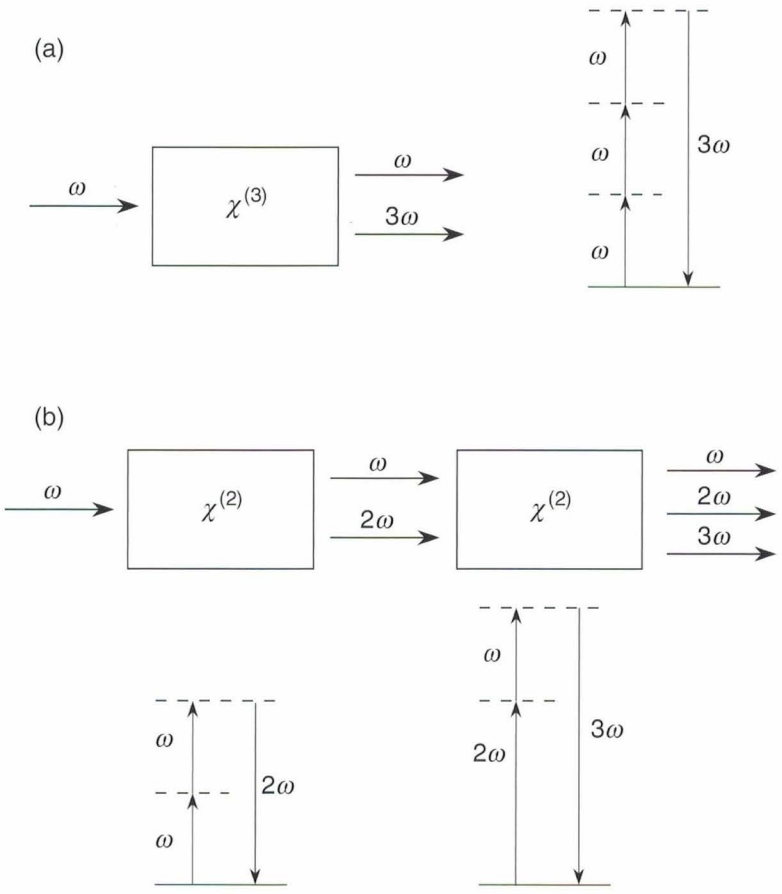

Figure 6.4. (a) Direct third-harmonic generation. (b) The process of sequential third-harmonic generation.

Here i, j, and k represent various cartesian components of the field vectors and the notation (n, m) implies that the expression is to be summed over ω_n and ω_m but only those contributions that lead to the particular frequency $\omega_n + \omega_m$ given in the argument on the left-hand side of the equation are to be retained. Likewise, the third-order polarization can be expressed as:

$$P_i(\omega_o + \omega_n + \omega_m) = \epsilon_0 \sum_{jkl} \sum_{(mno)} \chi^{(3)}_{ijkl}(\omega_0 + \omega_n + \omega_m, \omega_o, \omega_n, \omega_m) \times E_j(\omega_o) E_k(\omega_n) E_l(\omega_m). \tag{6.3}$$

These relations generalize in obvious ways to higher-order contributions to the nonlinear polarization.

The values of the nonlinear susceptibility elements can be obtained either by measurement or, in principle, by calculation. Extensive tables of values of the nonlinear susceptibility can be found in the scientific literature (Cleveland Crystals, 2005; Smith, 2005; Sutherland, 1996). Even when explicit calculation of the nonlinear susceptibility is hopelessly difficult, as it is for many biological materials, theoretical models of the nonlinear response are still very useful as they provide insight into the nature of the nonlinear response and show how the magnitude of the response depends on physical properties of the material system.

6.3 SIMPLE MODEL OF THE NONLINEAR SUSCEPTIBILITY

Considerable insight can be obtained by considering the form of the potential energy function that binds the electron to the atomic core. Two different possibilities are shown in Figure 6.5. According to linear reponse theory, the potential well would have the form of a perfect parabola, and the restoring force would be described by Hooke's law. In a real material, the force law need not obey Hooke's law and the potential well need not be a parabola. For a material that possesses a center of inversion symmetry, illustrated on the right-hand side of the figure, the potential well must be a symmetric function of the displacement x. Such a nonlinear response can produce only even

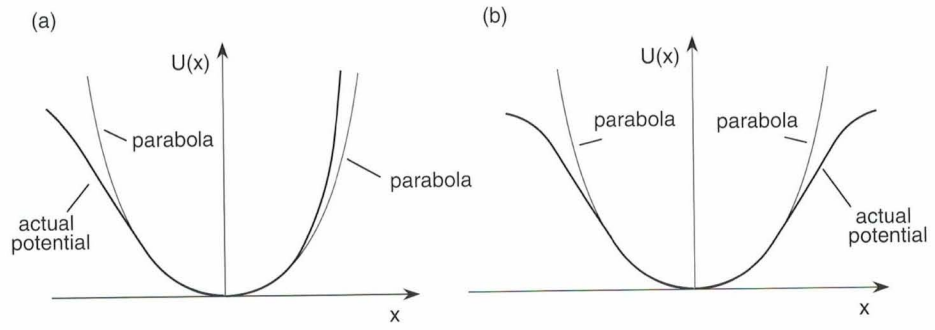

Figure 6.5. (a) The potential well for a material that lacks a center of inversion symmetry. Both even- and odd-order nonlinearities can occur for such a material. (b) The potential well for a material that possesses a center of inversion symmetry. Only even-order nonlinearities can occur for such a material.

harmonics of the applied optical frequency. However, a material that lacks a center of inversion symmetry will have a potential function of the sort shown on the left-hand side of the figure. A potential function of this form can produce both even and odd harmonics of an applied field frequency. This argument leads to the important conclusion that second-harmonic generation can occur only in materials that lack a center of inversion symmetry. Most biological materials lack a center of inversion and thus in principle can produce second-harmonic generation. But it should be noted that a material must be non-centrosymmetric over macroscopic distances in order to produce appreciable radiation at the second-harmonic frequency. Thus, for example, a liquid sample of biological molecules, each of which lacks a center of inversion symmetry, cannot produce second-harmonic generation.

6.4 QUANTUM MECHANICAL TREATMENT OF THE NONLINEAR SUSCEPTIBILITY*

More exacting models of the nonlinear optical response are provided by quantum mechanical calculation (Armstrong et al., 1962; Boyd, 2003; Butcher & Cotter, 1990; Hanna et al., 1979; Shen, 1984; Zernike & Midwinter, 1973). For example, for the case of usual interest in which the applied and generated fields are detuned by at least several line widths from the closest material resonance, the second-order susceptibility can be expressed as:

$$\chi^{(2)}_{ijk}(\omega_\sigma, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^2} \mathcal{P}_F \sum_{mn} \frac{\mu^i_{gn} \mu^j_{nm} \mu^k_{mg}}{(\omega_{ng} - \omega_\sigma)(\omega_{mg} - \omega_p)}, \tag{6.4}$$

where $\omega_\sigma = \omega_p + \omega_q$, N is the number density of molecules, μ^j_{nm} represents the j-th cartesian component of the electric-dipole moment matrix element connecting levels n and m, and ω_{mg} is the energy separation of levels m and g divided by $\hbar$. The symbol $\mathcal{P}_F$ is the full permutation operator, defined such that the expression that follows it is to be summed over all permutations of the frequencies ω_p, ω_q, and $-\omega_\sigma$.

The cartesian indices are to be permuted along with the related frequencies, and the final result is to be divided by the number of distinct permutations of the input frequencies ω_p and ω_q. In the general case in which ω_p and ω_q are distinct, this equation thus expands to six separate terms. Three of these six terms are illustrated in Figure 6.6; the other six terms result from simply interchanging ω_p and ω_q in these figures.

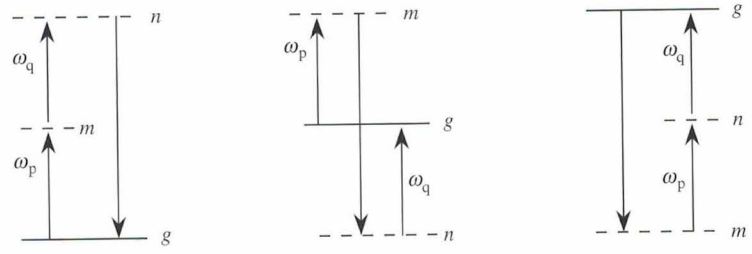

Figure 6.6. Various quantum-mechanical contributions to the second-order nonlinear optical response.

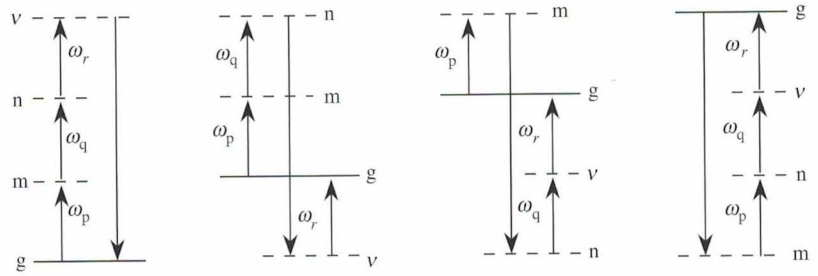

Figure 6.7. Various quantum-mechanical contributions to the third-order nonlinear optical response.

Similarly, the expression for the third-order susceptibility can be expressed in the limit of nonresonant interaction as:

$$\chi^{(3)}_{kjih}(\omega_\sigma, \omega_r, \omega_q, \omega_p) = \frac{N}{\epsilon_0 \hbar^3} \mathcal{P}_F \sum_{mnv} \frac{\mu^k_{gv} \mu^j_{vn} \mu^i_{nm} \mu^h_{mg}}{(\omega_{vg} - \omega_\sigma)(\omega_{ng} - \omega_q - \omega_p)(\omega_{mg} - \omega_p)}, \tag{6.5}$$

where $\omega_\sigma = \omega_p + \omega_q + \omega_r$.

When expanded, this expression represents 24 separate terms. Four of these terms are represented in the diagrams shown in Figure 6.7. The other terms can be found from the six interchanges of the frequencies ω_p, ω_q, and ω_r. The quantum mechanical expressions given here describe the nonlinear response of bound electrons. Even free electrons can produce a nonlinear response, for instance, by means of relativistic effects (Park et al., 2002). Also, it has been found that extremely large harmonic orders can be generated under conditions such that the laser field is sufficiently large to nearly remove the electron from the atomic core. For example, harmonic orders as large as 221 have been observed by Chang et al. (1997).

6.5 WAVE EQUATION DESCRIPTION OF HARMONIC GENERATION*

The intensity of the radiation emitted in the harmonic generation process can be predicted by means of a propagation calculation. We begin with the wave equation in the form:

$$\nabla^2 \tilde{E} - \frac{n^2}{c^2} \frac{\partial^2 \tilde{E}}{\partial \tilde{p}^{\mathrm{NL}} t^2} = \mu_0 \frac{\partial^2 \tilde{p}^{\mathrm{NL}}}{\partial t^2}, \tag{6.6}$$

where μ_0 denotes the magnetic permeability of free space.

For the present, we take the fundamental- and second-harmonic waves to be plane waves of the form:

$$\tilde{E}_j(z,t) = E_j(z) e^{-i\omega_j t} + \text{c.c.} = A_j(z) e^{i(k_j z - \omega_j t)} + \text{c.c.} \tag{6.7}$$

where $j = 1, 2$, with $\omega_1 = \omega$ and $\omega_2 = 2\omega$, and where c.c. stands for complex conjugate. Here $E_j(z)$ represents the complex amplitude of field j, and $A_j(z)$ represents the spatially slowly varying field amplitude of this wave.

to obtain:

$$J_N(\Delta k, z_0, z) = \begin{cases} 0, & \Delta k \leq 0, \\ \dfrac{b}{2}\dfrac{2\pi}{(N-2)!}\left(\dfrac{b\Delta k}{2}\right)^{N-2} e^{-b\Delta k/2}, & \Delta k > 0. \end{cases} \tag{6.17}$$

This result shows that harmonic generation vanishes whenever Δk is negative, which it is for the usual case of normal dispersion. The vanishing of the harmonic generation is a result of destructive interference between the contributions to the harmonic field from both sides of the beam waist.

6.8 SURFACE NONLINEAR OPTICS

One important application of second-harmonic generation is as an exacting diagnostic of the surface properties of optical materials. As noted above, second-harmonic generation is a forbidden process for a material that possesses a center of inversion symmetry. The surface of a material clearly lacks inversion symmetry, and thus second-harmonic generation can occur at the surface of a material of any symmetry. For the same reason, the intensity and angular distribution of surface second-harmonic generation depends critically on the morphology of a surface and on the presence of impurities on the surface of the material. Good reviews of the early work in this area are given by Shen (1985, 1989), and procedures for calculating the intensity of the second-harmonic light are given by Mizrahi and Sipe (1988).

6.9 NONLINEAR OPTICAL MICROSCOPY

Another application of harmonic generation is its use in nonlinear microscopy. Since this topic is developed in considerable detail in succeeding chapters, only a few comments of a general nature will be made here. One motivation for using nonlinear effects and in particular harmonic generation in microscopy is to provide enhanced transverse and longitudinal resolution. The resolution is enhanced because nonlinear effects are excited most efficiently only in the region of maximum intensity of a focused laser beam. Microscopy based on harmonic generation also offers the advantage that the signal is far removed in frequency from the unwanted background light that results from linear scattering of the incident laser beam. Also, light at a wavelength sufficiently long that it will not damage biological materials can be used to achieve a resolution that would normally require a much shorter wavelength. Harmonic-generation microscopy can either make use of the intrinsic nonlinear response of biological materials or can be used with materials that are labeled with nonlinear optical chromophores. Also, harmonic-generation microscopy can be used to form images of transparent (phase) objects, because the phase-matching condition of nonlinear optics depends sensitively on the refractive index variation within the sample being imaged (Muller et al., 1998).

Gao et al. (1997) have used tomography based on second-harmonic generation to characterize biological materials. Gauderon et al. (1998) have demonstrated three-dimensional imaging based on second-harmonic generation with fs laser pulses.

The nonlinear polarization is then given by:

$$\tilde{P}_2(z,t) = P_2(z)e^{i(2k_1 z - 2\omega t)} + \text{c.c.}, \tag{6.8}$$

where $P_2 = P(\omega_2) = \epsilon_0 \chi^{(2)} E_1^2$ represents the complex amplitude of the nonlinear polarization.

If these expressions are introduced into the wave equation (6.6), we find that:

$$\frac{d^2A_2}{dz^2} + 2ik_2\frac{dA_2}{dz} - k_2^2 A_2 - \frac{(2\omega)^2 n_2^2}{c^2}A_2 = -(2\omega)^2 \epsilon_0 \mu_0 \chi^{(2)} A_1^2 \, e^{i(2k_1 - k_2)z} \tag{6.9}$$

This expression can be simplified by omitting the first term on the basis of the argument that it is much smaller than the second term. This simplification is known as the slowly varying amplitude approximation. We also see that the third and fourth terms cancel exactly. We are thus left with the equation:

$$\frac{dA_2}{dz} = \frac{2i\omega}{n_2 c}\chi^{(2)} A_1^2 \, e^{i(2k_1 - k_2)z}. \tag{6.10}$$

Under the assumption that A_1 is not appreciably modified by the nonlinear interaction, we can take A_1 to be a constant and solve this equation by direct integration. We find that after propagation through a distance L the amplitude of the second-harmonic field is given by:

$$A_2(L) = \frac{2i\omega\chi^{(2)} A_1^2}{n_2 c} \, \frac{e^{i\Delta k} - 1}{i\Delta k \, L}, \tag{6.11}$$

where $\Delta k = 2k_1 - k_2$.

Since the intensity is related to the field strength according to $I = 2n\sqrt{\epsilon_0/\mu_0}\,|A|^2$, we find that the intensity of the generated radiation is given by:

$$I_2(L) = \sqrt{\frac{\mu_0}{\epsilon_0}}\frac{2\omega^2}{n_1^2 n_2 c^2}\,[\chi^{(2)}]^2 I_1^2 L^2\,[\text{sinc}^2(\Delta k\, L/2)]. \tag{6.12}$$

The condition $\Delta k = 0$ is known as the condition of perfect phase matching and is a requirement for efficient gereration of second-harmonic radiation. When this condition is fulfilled, the last factor in this equation is equal to unity, and one sees that the intensity of the second-harmonic radiation scales with the square of the length L of the interaction region. For technological applications of nonlinear optics, the phase-matching condition is often fulfilled by making use of a birefringent material. When using such a material, the fundamental and harmonic fields are chosen to have orthogonal polarizations, and the difference in refractive index for the two polarization directions can compensate for the intrinsic wavelength dependence of the refractive index. The phase-matching condition can also be mimicked by using quasi–phase-matching in structured materials, in which a periodic variation of the sign of $\chi^{(2)}$ is used to compensate for wave vector mismatch (Lim et al., 1989). Furthermore, structured materials in the form of photonic crystals and photonic bandgap materials can lead to phase matching by means of the large contribution to the refractive index associated with the periodic arrangement of

constituent particles (Markowicz et al., 2004). However, these methods are generally not suitable for utilization with most biological materials, and harmonic generation must therefore occur in the presence of a large wave vector mismatch, leading to greatly reduced efficiency of the harmonic generation process. Nonetheless, the conversion efficiency is typically sufficiently large to produce a measurable signal at the harmonic frequency, and thus harmonic generation is useful as a method to study certain biological structures such as collagen fibrils.

6.6 N-TH HARMONIC GENERATION*

For definiteness, the discussion of the previous paragraph was restricted to the case of second-harmonic generation, but this discussion is readily extended to direct harmonic generation of arbitrary order N. In this case, the amplitude of the nonlinear polarization is given by $P_N = P(N\omega) = \epsilon_0 \chi^{(N)} E_1^N$ and equation (6.11) is replaced by:

$$A_N(L) = \frac{2i\omega\chi^{(N)} A_1^N}{n_N c} \frac{e^{i\Delta k} - 1}{i\Delta k\, L}. \tag{6.13}$$

Also, equation (6.14) for the intensity of the emitted radiated intensity is replaced by:

$$I_N(L) = (\mu_0/\epsilon_0)^{(N-1)/2} \frac{N^4\omega^2}{2^{N+1} n_1^N n_N c^2} [\chi^{(N)}]^2 I_1^N L^2 [\mathrm{sinc}^2(\Delta k\, L/2)]. \tag{6.14}$$

In this case, the wave vector mismatch is given by $\Delta k = Nk_1 - k_N$.

6.7 HARMONIC GENERATION WITH FOCUSED LASER BEAMS*

Harmonic generation can display quite different behavior when excited by a focused laser beam. In such a situation, the peak amplitude $\mathcal{A}_N$ (that is, the amplitude on axis at the beam waist) of the generated N-th harmonic wave is related to the peak amplitude $\mathcal{A}_1$ of the fundamental wave by:

$$\mathcal{A}_N(z) = \frac{iN\omega}{2nc} \chi^{(N)} \mathcal{A}_1^N J_N(\Delta k, z_0, z), \tag{6.15}$$

where $J_N(\Delta k, z_0, z)$ represents the integral

$$J_N(\Delta k, z_0, z) = \int_{z_0}^{z} \frac{e^{i\Delta k z'} dz'}{(1 + 2iz'/b)^{N-1}}. \tag{6.16}$$

Here z_0 represents the value of z at the entrance to the nonlinear medium, $b = 2\pi w_0^2/\lambda_1$ is the confocal parameter of the fundamental laser beam, and w_0 is its beam radius measured to the $1/e$ amplitude point.

For the case of a beam that is tightly focused into the bulk of the interaction region, the limits of integration can be replaced by $\pm\infty$, and the integral can be evaluated

They used this method to characterize the microcrystal structure of lithium triborate. Campagnola et al. (1999) have used second-harmonic generation to produce images of live cells. Moreaux et al. (2000) have used styrl dyes as labels to image membranes using second-harmonic generation microscopy.

Third-harmonic generation has also been used for imaging applications. Muller et al. (1998) have demonstrated imaging of transparent objects using microscopy based on third-harmonic generation. Yelin and Silbenberg (1999) have constructed a scanning microscope based on third-harmonic generation and have used it for the imaging of biological materials.

6.10 HARMONIC GENERATION AS A PROBE OF MEMBRANE POTENTIALS

Second-harmonic generation can also be used to probe potential differences across biological membranes. Bouevitch et al. (1993) observed that the second-harmonic signal shows a pronounced dependence on this potential difference. Styrl dyes imbedded into membranes also show a strong dependence on the potential difference (Millard et al., 2004). Similar effects have been observed in mammalian brain tissue (Dombeck et al., 2005).

In summary, harmonic generation is a well-established physical process that holds considerable promise for applications in nonlinear microscopy.

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