4 A quantum mechanical system is described by the Hamiltonian H_0, and is the set of eigenfunctions $\{|\psi_n\rangle\}$. It is subjected to a perturbation of the form

$$V(t) = v_1 e^{-i(\omega_1 + i\eta)t} + v_1^+ e^{+i(\omega_1 - i\eta)t} + v_2 e^{-i(\omega_2 + i\eta)t} + v_2^+ e^{+i(\omega_2 - i\eta)t},$$

which we may write in the form

$$V(t) = \sum_{\sigma = +,-} \sum_{j=1}^{2} v_j(\sigma) e^{-i\sigma\omega_j t} e^{\eta t},$$

where $v_1(+) = v_1$, $v_1(-) = v_1^+$, etc.

Calculate the expectation value $\langle\psi|0|\psi\rangle$ correct through terms second order $V(t)$, i.e., extend (A.23) in Appendix A to the second order of perturbation theory.

This result can be used as the basis for microscopic calculation of $\chi_\gamma(\boldsymbol{k}_1\omega_1; \boldsymbol{k}_2\omega_2)$ after the appropriate choices are made for the operators O, v_1, v_1^+, etc. Notice your expression contains resonant denominators that are singular when $\omega_1 = \omega_{n0}$, $\omega_2 = \omega_{n0}$, and the output frequency $\sigma_i\omega_i + \sigma_j\omega_j = \omega_{n0}$, where ω_{n0} is an excitation energy of the system.

4. Basic Principles of Nonlinear Wave Interactions: Second Harmonic Generation and Four Wave Mixing

We now turn from our discussion of the nature of a material's linear and nonlinear response to an external electric field, to the consequences of the latter. We have seen that we can decompose the electric dipole moment per unit volume into a linear portion, and a nonlinear portion, as in (1.7 a). When we Fourier transform all quantities with respect to time by writing

$$E_\alpha(\boldsymbol{r}, t) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} E_\alpha(\boldsymbol{r}, \omega) e^{-i\omega t}, \tag{4.1}$$

then introduce the frequency dependent dielectric tensor, (1.3 a,b) become

$$\nabla \cdot [\boldsymbol{\varepsilon}(\omega) \cdot \boldsymbol{E}(\boldsymbol{r}, \omega)] = -4\pi \nabla \cdot \boldsymbol{P}^{(\mathrm{NL})}(\boldsymbol{r}, \omega) \tag{4.2 a}$$

and

$$\nabla^2 \boldsymbol{E}(\boldsymbol{r}, \omega) - \nabla(\nabla \cdot \boldsymbol{E}(\boldsymbol{r}, \omega)) + \frac{\omega^2}{c^2} \boldsymbol{\varepsilon}(\omega) \cdot \boldsymbol{E}(\boldsymbol{r}, \omega) = -\frac{4\pi\omega^2}{c^2} \boldsymbol{P}^{(\mathrm{NL})}(\boldsymbol{r}, \omega). \tag{4.2 b}$$

We shall ignore the influence of the wave vector dependence of the dielectric tensor in what follows.

Quite clearly, the nonlinear polarization present at the frequency ω can be viewed as a source of electromagnetic radiation at that frequency. We shall focus our attention on the theory of second harmonic generation, treated first within a perturbation theoretic framework. We shall then turn to a nonperturbative analysis of the process which, as we shall come to appreciate, is required in certain circumstances.

4.1 Perturbation Theoretic Analysis of Second-Harmonic Generation

Suppose the material is illuminated with a laser beam, here taken to be a simple plane wave, of frequency ω_1 and wave vector $\boldsymbol{k}_1$. If we assume the intensity

of the second harmonic radiation is very weak, then we can ignore the depletion of the primary wave due to a conversion of a portion of its energy into second harmonic. We may then calculate $\boldsymbol{P}^{(\mathrm{NL})}(\boldsymbol{r}, \omega)$ by simply inserting the expression for the amplitude of the initial wave into the appropriate terms in the power series expansion of the dipole moment per unit volume in powers of electric field. Let the incident field be given by

$$\boldsymbol{E}(z, t) = \hat{\mathbf{e}} E(\omega_1) e^{ik_1 z} e^{-i\omega_1 t} + \hat{\mathbf{e}} E^*(\omega_1) e^{-ik_1 z} e^{+i\omega_1 t} , \tag{4.3}$$

where we orient the z axis along the propagation direction of the beam. The components of the dipole moment with the frequency $2\omega_1$ are

$$P_\alpha^{(\mathrm{NL})} = E^2(\omega_1) \sum_{\beta\gamma} \chi^{(2)}_{\alpha\beta\gamma} \hat{e}_\beta \hat{e}_\gamma e^{i2k_1 z} e^{-i2\omega_1 t} + \text{c.c.} . \tag{4.4}$$

If we suppose the dielectric is a simple isotropic dielectric, or if we suppose the propagation direction of the incident wave is aligned with a principal axis of the dielectric tensor in the more general case, the electric field of the incident wave will lie in the xy plane. The incident wave is then transverse. However, in general, even in such a simple case the nonlinear polarization in (4.4) may have a component parallel to the z axis, as well as in the xy plane, because of the tensor character of $\chi^{(2)}_{\alpha\beta\gamma}$. It is convenient to break $\boldsymbol{P}^{(\mathrm{NL})}$ into two pieces, one parallel to $\hat{\mathbf{z}}$ and one in the xy plane:

$$\boldsymbol{P}^{(\mathrm{NL})} = \hat{\mathbf{z}} P_\parallel^{(\mathrm{NL})} + \boldsymbol{P}_\perp^{(\mathrm{NL})} . \tag{4.5}$$

The amplitude of the second harmonic field will have amplitude dependent on only z, for an incident wave of plane wave character. We write, for the second harmonic field at the frequency $\omega_2 = 2\omega_1$

$$\boldsymbol{E}(z, \omega_2) = \hat{\mathbf{z}} E_\parallel(z, \omega_2) + \boldsymbol{E}_\perp(z, \omega_2) . \tag{4.6}$$

One may show rather easily that $\nabla^2 \boldsymbol{E} - \nabla(\nabla \cdot \boldsymbol{E}) = \partial^2 \boldsymbol{E}_\perp / \partial z^2$. Furthermore, it will simplify our discussion to assume the z direction is a principal axis, and in fact that the dielectric material is isotropic in its response to electric fields in the xy plane. The discussion would then be applicable to second harmonic generation in a crystal such as quartz, for the case where the incident beam propagates parallel to the optic axis.

We combine the decompositions described above with the model, (4.2 a) and (4.2 b) become

$$\frac{\partial^2}{\partial z^2} \boldsymbol{E}_\perp + \omega_2^2 \frac{\varepsilon_\perp(\omega_2)}{c^2} \boldsymbol{E}_\perp + \frac{4\pi\omega_2^2}{c^2} \boldsymbol{P}_\perp^{(\mathrm{NL})} + \left[\frac{\omega_2^2 \varepsilon_\parallel(\omega_2)}{c^2} E_\parallel + \frac{4\pi\omega_2^2}{c^2} P_\parallel^{(\mathrm{NL})} \right] \hat{\mathbf{z}} = 0 \tag{4.6a}$$

and

$$\frac{\partial}{\partial z} [\varepsilon_\parallel(\omega_2) E_\parallel + 4\pi P_\parallel^{(\mathrm{NL})}] = 0 , \tag{4.6b}$$

where $\varepsilon_\perp$ and $\varepsilon_\parallel$ describe the dielectric response perpendicular and parallel to the optic axis, respectively.

Satisfaction of (4.6 a) requires the two conditions:

$$E_\parallel(\omega_2, z) = -\frac{4\pi}{\varepsilon_\parallel(\omega_2)} P_\parallel^{(\mathrm{NL})}(\omega_2, z) \tag{4.7a}$$

and

$$\left(\frac{\partial}{\partial z^2} + k_2^2 \right) \boldsymbol{E}_\perp(\omega_2, z) = -\frac{4\pi\omega_2^2}{c^2} \boldsymbol{P}_\perp^{(\mathrm{NL})}(\omega_2, z) . \tag{4.7b}$$

Note that satisfaction of (4.7 a) insures that (4.6 b) is obeyed. We have introduced

$$k_2 = \frac{\omega_2}{c} \sqrt{\varepsilon_\perp(\omega_2)} \equiv \frac{2\omega_1}{c} \sqrt{\varepsilon_\perp(2\omega_1)} , \tag{4.8}$$

which is the wave vector of a wave of frequency $\omega_2 = 2\omega_1$, as it propagates freely in the medium.

The component of the second harmonic wave parallel to the optic axis, and to the direction of propagation of the second harmonic wave, is given by the simple expression in (4.7 a).

The analysis of $\boldsymbol{E}_\perp$ will prove of more interest. While it is not a difficult matter to solve (4.7 b) as it stands, in fact we can turn to an approximate treatment based on a scheme used commonly in situations such as the present. As one progresses along the propagation direction, the amplitude of the second harmonic builds up very slowly, as a consequence of the smallness of $\chi^{(2)}_{\alpha\beta\gamma}$. The amplitude changes very little, if we move just one wavelength. Thus, for the amplitude of the second harmonic wave, we write

$$\boldsymbol{E}_\perp(\omega_2, z) = \boldsymbol{E}(\omega_2, z) e^{ik_2 z} , \tag{4.9}$$

where the spatial variation of $\exp(ik_2 z)$ is assumed rapid compared to that of $\boldsymbol{E}(\omega_2, z)$. Then we have

$$\frac{\partial^2 \boldsymbol{E}_\perp}{\partial z^2} = -\left(k_2^2 \boldsymbol{E} - 2ik_2 \frac{\partial \boldsymbol{E}}{\partial z} - \frac{\partial^2 \boldsymbol{E}}{\partial z^2} \right) e^{ik_2 z} \cong -\left(k_2^2 \boldsymbol{E} - 2ik_2 \frac{\partial \boldsymbol{E}}{\partial z} \right) e^{ik_2 z} . \tag{4.10}$$

When this is inserted into (4.7 b), and we write $\boldsymbol{E} = \hat{\boldsymbol{e}}^{(2)}E(\omega_2, z)$ where $\hat{\boldsymbol{e}}^{(2)}$ is a unit vector parallel to $\boldsymbol{P}_\perp^{(\mathrm{NL})}$, we may write (4.7 b) in the form

$$\frac{\partial E(\omega_2, z)}{\partial z} = \frac{2\pi i\omega_2^2}{c^2 k_2}\bar{\chi}^{(2)}E^2(\omega_1)e^{i(2k_1-k_2)z}, \tag{4.11}$$

where

$$\bar{\chi}^{(2)} = \sum_{\alpha\beta\gamma}\chi^{(2)}_{\alpha\beta\gamma}\hat{e}^{(2)}_\alpha\hat{e}_\beta\hat{e}_\gamma . \tag{4.12}$$

The scheme used to obtain (4.11) is called the slowly varying envelope approximation.

It is an elementary matter to integrate (4.11). We shall assume the surface of the material is at $z = 0$. The second harmonic field vanishes there, and builds in intensity as one moves into the material. We thus integrate (4.11) subject to the boundary condition $E(\omega_2, 0) = 0$. The result may be arranged to read, with $\Delta k = 2k_1 - k_2$,

$$E(\omega_2, z) = \frac{4\pi i\omega_2^2\bar{\chi}^{(2)}E^2(\omega_1)}{c^2 k_2}e^{i\Delta kz/2}\frac{\sin(\Delta kz/2)}{\Delta k} . \tag{4.13}$$

The energy per unit area per unit time carried by the second harmonic is found by evaluating the Poynting vector. In the slowly varying envelope approximation, we have for the magnitude S of the Poynting vector $S = c^2k_2|E(\omega_2, z)|^2/2\pi\omega_2$, or

$$S = \frac{8\pi\omega_2^3|\bar{\chi}^{(2)}|^2}{c^3 k_2}|E(\omega_1)|^4\frac{\sin^2(\Delta kz/2)}{(\Delta k)^2} . \tag{4.14}$$

The crucial parameter which controls the intensity of the second harmonic output is Δk. Recall that $k_1 = \omega_1\sqrt{\varepsilon(\omega_1)}/c$ is the wave vector of the primary wave of frequency ω_1, while $k_2 = 2\omega_1\sqrt{\varepsilon(2\omega_2)}/c$ is that of a freely propagating wave with frequency $2\omega_1$. If the dielectric constant were to be independent of frequency, then $\varepsilon(2\omega_1) = \varepsilon(\omega_1)$, and we have $\Delta k = 0$. Upon noting that

$$\lim_{\Delta k\to 0}\frac{\sin(\Delta kz/2)}{\Delta k} = \frac{z}{2} , \tag{4.15}$$

in this limit the field envelope $E_\perp(\omega_2, z)$ grows linearly with z, and the power flow in the second harmonic increases as z^2. Clearly, at large values of z our perturbation theory which ignores depletion of the first harmonic, breaks down, though it is quite clear that we wish to achieve the condition $\Delta k = 0$ to generate an intense second harmonic wave. As we have seen earlier, the dielectric constant of any medium depends on frequency, unfortunately. Thus, in general, the condition $\Delta k = 0$ is not realized. We shall discuss shortly how one may arrange to satisfy this condition.

A direct experimental test of the predictions of (4.14) can be found in the work of *Maker* et al. [4.1]. For example, as the path length z is varied, one expects oscillations with distance of travel in the second harmonic output, for $\Delta k \neq 0$. In [4.1], the path length is varied by using a thin film to generate the second harmonic, and rotating the film. The path length in the medium is then $d/\cos\theta$, where d is the film thickness and θ the angle between the pump beam (in the crystal) and the normal to the film. In Fig. 4.1, we show the comparison between theory (solid line) and experiment (dots), taken from [4.1].

When the condition $\Delta k = 0$ is obeyed, the interaction which leads to second harmonic generation is said to be phase matched. Physically, the reason why a phase matched interaction leads to intense output is the following: The nonlinear dipole moment exhibits the spatial variation $\exp(i2k_1z)$, as we have seen. If we consider two small regions of space separated by the distance d, the phase difference between the dipoles in each responsible for generating the second harmonic radiation is thus $2k_1d$. The radiation emitted by each set of dipoles has the frequency $\omega_2 = 2\omega_1$, and will propagate through the medium with the wave vector k_2. If $k_2 = 2k_1$, the radiation field emitted from the set of dipoles in the first volume is exactly in phase with that emitted by the dipoles in the second. The fields reinforce coherently. If we add up the fields radiated by all the dipoles in the strip which lies between 0 and z, since all the dipole fields reinforce coherently, the amplitude of the second harmonic is linear with z, and its intensity varies as z^2.

If $\Delta k \neq 0$, the length $\ell_c = 1/|\Delta k|$ has the following interpretation: A strip of "second harmonic" dipoles with width ℓ_c radiate second harmonic fields which reinforce constructively. Thus, for $z \ll \ell_c$, the second harmonic fields grow linearly with z. As z increases beyond ℓ_c, we encounter destructive interference, the field no longer grows monotonically, and in fact the combined effects of constructive and destructive interference lead to the oscillatory behavior for the field envelope displayed in (4.13). The length ℓ_c is called the coherence length of the nonlinear interaction.

Some comments follow from the above remarks. First notice that if the process of second harmonic generation is phase matched, then no matter how small $\bar{\chi}^{(2)}$ is, our perturbation theoretic treatment of the phenomenon breaks

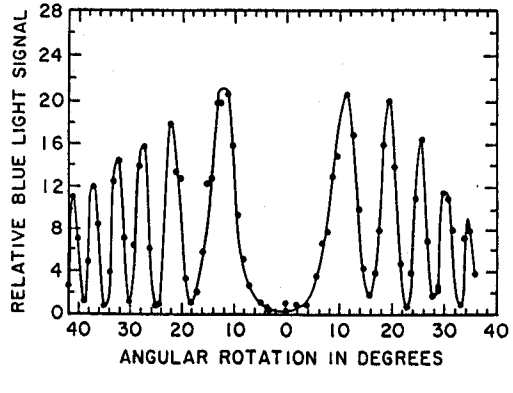

Fig. 4.1. The intensity of the second harmonic, as a function of rotation angle for a laser beam incident on a film of KDP. The experimental data (dots) is compared with theoretical prediction of (4.14) (solid line). This tests the dependence of the intensity of the second harmonic signal with path length in the medium; in (4.41), $z = d/\cos\theta$, with θ the angle between the pump beam inside the crystal, and the normal to the film. The figure has been reproduced from [4.1]

down if the optical path length in the medium is sufficiently long. Validity of the perturbation treatment requires the path length L be shorter than $L_c = c^2 k_2/[2\pi\omega_2^2|\bar{\chi}^{(2)}E(\omega_1)|]$, a criterion which follows upon comparing the intensity of the second harmonic wave with that of the first harmonic, if $L \gtrsim L_c$, the intensity of the second harmonic is comparable to that of the pump beam, even though $\bar{\chi}^{(2)}$ is small, and $\boldsymbol{P}^{(NL)}$ is everywhere small compared to the contribution to the dipole moment per unit volume linear in the external field.

It follows also from the above that if we have a medium whose thickness is small compared to the coherence length ℓ_c, then we need not be concerned about the question of phase matching. The second harmonic intensity is then independent of ℓ_c, and the wavevector mismatch Δk.

There is another means of understanding the phenomenon of phase matching. While our treatment here is based entirely on classical physics, we may also adopt a quantum mechanical view point, which treats the incident beam as a collection of photons, each of energy $\hbar\omega_1$. When $\chi^{(2)}_{\alpha\beta\gamma} \neq 0$, the photons may interact with each other. This may be appreciated by noting that the presence of $\chi^{(2)}_{\alpha\beta\gamma}$ leads to a term in the energy density of the medium proportional to $\Sigma_{\alpha\beta\gamma}\chi^{(2)}_{\alpha\beta\gamma}E_\alpha E_\beta E_\gamma$ (these remarks assume $\chi^{(2)}_{\alpha\beta\gamma}$ is real, and ignore complications which arise from its frequency dependence). When the electric field is expressed in terms of the photon annihilation and creation operators, one sees this term leads to three photon interactions. Two photons may "fuse" to form a third. Thus, two quanta in the pump beam may fuse to form a single quantum of energy $2\hbar\omega_1$. While such an interaction clearly conserves energy, a photon of wave vector $\boldsymbol{k}$ also carries momentum $\hbar\boldsymbol{k}$. Thus, unless $k_2 = 2k_1$, momentum is not conserved in the interaction. The full classical treatment given below of the problem of phase matched second harmonic generation will show that under such conditions, all the pump beam is converted to second harmonic. Thus the photons of frequency ω_1 fuse until the supply is exhausted.

It is quite possible to give a theoretical treatment of second harmonic generation, with use of the photon annihilation and creation operators; of course the final answer must agree with that provided by our classical theory, when the occupation numbers of the states involved are large compared to unity. This is insured by the correspondence principle of quantum theory. Full quantum theoretical treatments are to be found in the literature. In the experience of the present author, the classical approach to such problems is far more flexible and powerful. It is very tricky to incorporate the influence of absorption on the nonlinear interactions, within quantum theory, for example. Most such treatments ignore its role as a consequence, though in fact it is important in practice. The treatment presented here, while very simple, in fact is valid in the presence of absorption as it stands, though in our discussion we regarded both $\varepsilon(\omega_1)$ and $\varepsilon(2\omega_1)$ as real. All we need to do is realize that in the presence of absorption, these are complex. Also, the classical treatment is extended rather easily to incorporated boundary conditions and finite size effects (within the perturbation theoretic framework), while full quantum treatments of such influences are much more cumbersome, in the view of this writer.

While we have encountered the notion of phase matching in the context of second harmonic generation, in fact the concept enters crucially into a diverse array of nonlinear interactions. A key ingredient critical to achieving an intense output is the realization of phase matching in a nonlinear interaction of interest. We next turn to a discussion of the means of achieving phase matching, in the specific case of second harmonic generation.

4.2 Methods of Achieving the Phase Matching Condition

In general, second harmonic generation experiments are carried out in crystalline media since, as we have seen, for $\chi^{(2)}_{\alpha\beta\gamma}$ to be nonzero, we require a material within which inversion symmetry is lacking. Gasses and liquids are isotropic, of course, and this third rank tensor thus vanishes in the limit of zero-wave vector. It should be remarked that $\chi^{(2)}_{\alpha\beta\gamma}$ is nonzero in the near vicinity of the surface of any medium, since atoms in the surface occupy positions that lack inversion symmetry. Since such a small fraction of the total number of atoms reside in the surface, the intensity of second harmonic radiation generated from the surface region is quite small. We explore surface nonlinear effects in Chap. 8.

We need a long optical path length for intense second harmonic signals to be generated; one must thus operate well below the absorption edge of the medium. We have seen in Chap. 2 that $\varepsilon_1(\omega)$ increases with frequency in this spectral range, for dielectric materials, so $\varepsilon_1(2\omega) > \varepsilon_1(\omega)$ and one cannot achieve phase matching.

However, in anisotropic crystals, by means of a trick, the condition can be realized. In Sect. 2.3, we discussed the electromagnetic modes of a uniaxial crystal, with dielectric constant $\varepsilon_\parallel(\omega)$ for electric fields applied parallel to the optic axis, and $\varepsilon_\perp(\omega)$ applied in the basal plane. There is the ordinary wave, with index of refraction $n_o(\theta,\omega) = \sqrt{\varepsilon_\perp(\omega)}$ independent of propagation angle, and the extraordinary wave with index of refraction $n_e(\theta,\omega)$ that does depend on the angle between the wave vector of the wave, and the optic axis. The expression for $n_e(\theta,\omega)$ is given in (2.65).

If the input wave is an ordinary wave, and the output wave is an extraordinary wave, then there is one particular angle θ where precise phase matching may be achieved, provided the inequality $\varepsilon_\parallel(2\omega) < \varepsilon_\perp(\omega)$ is satisfied. The situation is illustrated in Fig. 4.2. The crystal KDP satisfies the required condition, and *Maker* et al. [4.1] verified the critical role played by the phase matching condition. We reproduce their data in Fig. 4.3; one sees the dramatic variation of the intensity of the second harmonic output (blue light) as the angle θ is swept through the critical angle θ_0. There is a much more modest variation with azimuthal angle ϕ. While the phase matching condition is in fact independent of ϕ in a uniaxial dielectric, factors such as the coefficient of transmission through the film surfaces and $\bar{\chi}^{(2)}$ depend on azimuth. The intensity of the second harmonic exhibits a dependence on ϕ as a consequence.

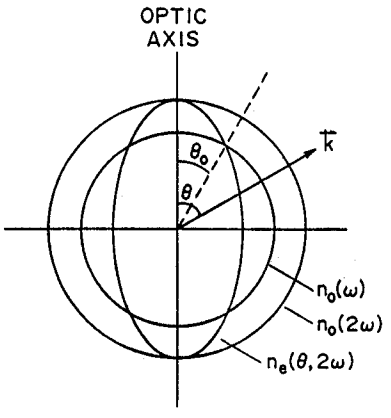

Fig. 4.2. An illustration of how one satisfies the phase matching condition in a uniaxial dielectric. We show the index of refraction $n_o(\omega)$ and $n_o(2\omega)$ for the ordinary ray, and $n_e(\theta,2\omega)$ as a function of propagation angle θ for the case $\varepsilon_{\parallel}(2\omega) < \varepsilon_{\perp}(\omega)$. One satisfies the phase matching condition at the particular angle θ_0

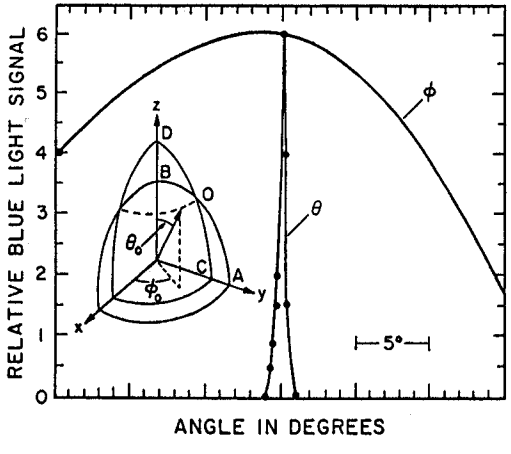

Fig. 4.3. The variation of second harmonic intensity (blue light) with polar angle θ and azimuthal angle ϕ, in KDP. The data is reproduced from [4.1]

While second harmonic generation is not possible in gasses or liquids, the generation of the third harmonic is allowed. The phase matching condition is now $n(\omega) = n(3\omega)$, which is in general not satisfied. It is, however, possible to "tune" the frequency variation of the dielectric constant of some gases, so that phase matching can be achieved at one desired frequency. Consider a gas of atoms, called species 1, where the constituents have an excited state that produces a resonance in the dielectric constant at a frequency ω_0 that lies between ω and 3ω. Then as we see from Fig. 2.3, $n_1(\omega) > n_1(3\omega)$. Now mix in atoms of type 2, whose first resonance lies above 3ω. For a gas of type 2 atoms, $n_2(\omega) < n_2(3\omega)$. For the mixture, the index of refraction is $(1 - f)n_1(\omega) + fn_2(\omega)$, where f is the fraction of type 2 atoms present. One may always choose f so that the phase matching condition is satisfied at selected frequencies. Generation of the third harmonic in the gas phase has been reported by *Bloom* et al. [4.2,3], under conditions where phase matching has been achieved.

4.3 Evolution of the Second-Harmonic Wave under Phase Matched Conditions

We have seen that when the process of second-harmonic generation is perfectly phased matched, the perturbation theory breaks down if the path length is sufficiently long, for arbitrarily small $\bar{\chi}^{(2)}$.

To proceed, we must realize that under these conditions, the pump beam at the frequency ω_1 is depleted, as the second harmonic is generated. The first step is thus to allow the amplitudes $E(\omega_1)$ and $E^*(\omega_1)$ in (4.3) to vary with distance of travel z. We thus begin by replacing $E(\omega_1)$ by $E(\omega_1, z)$ in (4.11), after setting $k_2 = 2k_1$. One then has

$$\frac{\partial E(\omega_2, z)}{\partial z} = \frac{4\pi i\omega_1^2}{c^2 k_1} \bar{\chi}^{(2)} E^2(\omega_1, z) \,. \tag{4.16}$$

We now require a second statement which describes the evolution with z of $E(\omega_1, z)$. There is, in fact, a contribution to the nonlinear polarization which exhibits the time variation $\exp(-i\omega_1 t)$. This arises, in our general expression (3.3), from the interaction of the Fourier component of the second harmonic with time variation $\exp(-i2\omega_1 t)$ with that of the pump beam with time variation $\exp(+i\omega_1 t)$. The former has amplitude proportional to $E(\omega_2, z)$, and the latter $E^*(\omega_1, z)$ [(4.3)]. We may write this contribution to the magnitude of the nonlinear polarization at frequency ω_1 in the form[1]

$$P^{(\mathrm{NL})}(\omega_1, z) = 2\bar{\chi}^{(2)} E(\omega_2, z) E^*(\omega_1, z) \,. \tag{4.17}$$

When this expression is inserted into the inhomogeneous wave equation for $E_{\perp}(\omega_1, z)$, and the slowly envelope approximation is invoked, one finds

$$\frac{\partial E(\omega_1, z)}{\partial z} = \frac{4\pi i\omega_1^2}{c^2 k_1} \bar{\chi}^{(2)} E(2\omega_1, z) E^*(\omega_1, z) \,. \tag{4.18}$$

These two differential equations are to be solved with the boundary conditions $E(2\omega_1, 0) = 0$, and $E(\omega_1, 0) = E(\omega_1)$, the amplitude of the pump beam at the surface. It is possible to solve this set in closed form. We next proceed with the solution.

[1] See remarks on the permutation symmetry of the second order susceptibility given in [4.4]. It is quite obvious from the structure of our (3.3) that $\chi^{(2)}_{\alpha\beta\gamma}(\boldsymbol{k}_1\omega_1, \boldsymbol{k}_2\omega_2)$ is invariant under simultaneous exchange of the combinations $(\alpha\boldsymbol{k}_1\omega_1)$ and $(\beta\boldsymbol{k}_2\omega_2)$ as we have remarked in Chap. 3.

We begin by writing

$$E(\omega_1, z) = E(\omega_1) f_1(z) \tag{4.19a}$$

and

$$E(\omega_2, z) = E(\omega_1) f_2(z), \tag{4.19b}$$

where $f_1(z)$ and $f_2(z)$ obey the boundary conditions

$$f_1(0) = 1 \tag{4.19c}$$

and

$$f_2(0) = 0\,. \tag{4.19d}$$

We also change to a dimensionless measure of length:

$$z = L_c \xi\,,$$

where $L_c = c^2 k_1 / 4\pi\omega_1^2 \tilde{\chi}^{(2)} E(\omega_1)$ is the critical length which entered our earlier discussion.

Our equations then become

$$\frac{\partial f_2}{\partial \xi} = \mathrm{i} f_1^2 \tag{4.20a}$$

and

$$\frac{\partial f_1}{\partial \xi} = \mathrm{i} f_2 f_1^*. \tag{4.20b}$$

One may proceed by breaking f_1 and f_2 into amplitudes and phases

$$f_{1,2}(\xi) = u_{1,2}(\xi) \mathrm{e}^{\mathrm{i}\phi_{1,2}(\xi)}\,, \tag{4.21}$$

then separating (4.20 a,b) into real and imaginary parts. This leads to a set of four coupled differential equations:

$$\frac{\partial u_2}{\partial \xi} = -u_1^2 \sin(2\phi_1 - \phi_2), \tag{4.22a}$$

$$u_2 \frac{\partial \phi_2}{\partial \xi} = u_1^2 \cos(2\phi_1 - \phi_2), \tag{4.22b}$$

$$\frac{\partial u_1}{\partial \xi} = u_1 u_2 \sin(2\phi_1 - \phi_2)\,, \tag{4.22c}$$

and

$$\frac{\partial \phi_1}{\partial \xi} = u_2 \cos(2\phi_1 - \phi_2)\,. \tag{4.22d}$$

These may be reduced to a set of three equations, by noting the phase angles enter only in the combination $\psi = 2\phi_1 - \phi_2$. Thus,

$$\frac{\partial u_2}{\partial \xi} = -u_1^2 \sin\psi\,, \tag{4.23a}$$

$$\frac{\partial u_1}{\partial \xi} = u_1 u_2 \sin\psi\,, \tag{4.23b}$$

and

$$\frac{\partial \psi}{\partial \xi} = \left(2u_2 - \frac{u_1^2}{u_2}\right) \cos\psi\,. \tag{4.23c}$$

Through use of (4.23 a,b), (4.23 c) may be arranged to read

$$\tan\psi \frac{\partial \psi}{\partial \xi} - \frac{2}{u_1}\frac{\partial u_1}{\partial \xi} - \frac{1}{u_2}\frac{\partial u_2}{\partial \xi} = 0 \tag{4.24}$$

which is in fact a statement of a conservation law:

$$\frac{\partial}{\partial \xi} \ln[u_2 u_1^2 \cos\psi] = 0 \tag{4.25}$$

or

$$u_2(\xi) u_1^2(\xi) \cos[\psi(\xi)] = \text{const}\,. \tag{4.26}$$

Now as $\xi \to 0$, $u_2(\xi) \to 0$. Hence the constant of integration on the right-hand side of (4.26) vanishes and we must have $\psi(\xi) = +\pi/2$ or $-\pi/2$, independent of ξ everywhere. We choose the minus sign so that $\partial u_2/\partial \xi > 0$ in (4.23 a) and the second harmonic grows with increasing ξ.

We are then left with the pair of equations

$$\frac{\partial u_2}{\partial \xi} = +u_1^2\,, \tag{4.27a}$$

$$\frac{\partial u_1}{\partial \xi} = -u_1 u_2\,, \tag{4.27b}$$

which require

$$u_2 \frac{\partial u_2}{\partial \xi} + u_1 \frac{\partial u_1}{\partial \xi} = 0 \tag{4.28}$$

or

$$u_1^2(\xi) + u_2^2(\xi) = 1\,. \tag{4.29}$$

The result in (4.29) is a statement of energy conservation. From the time average of the Poynting vector, the energy per unit area per unit time carried by the pump beam is (in our slowly varying envelope approximation)

$$S_1(\xi) = \frac{ck_1}{2\pi\omega_1}|E(\omega_1)|^2 u_1^2(\xi) \tag{4.30a}$$

while that carried by the second harmonic is

$$S_2(\xi) = \frac{ck_2}{2\pi\omega_2}|E(\omega_1)|^2 u_2^2(\xi)\,. \tag{4.30b}$$

Under the conditions of perfect matching, $k_1/\omega_1 = k_2/\omega_2$, so (4.29) is equivalent to the statement $S_1(\xi) + S_2(\xi) = S_1(0)$.

It is now a straightforward matter to integrate (4.27 a), eliminating u_1^2 from (4.27 a) by use of (4.29). One finds

$$u_2(\xi) = \tanh\xi \tag{4.31a}$$

and

$$u_1(\xi) = \frac{1}{\cosh\xi}\,, \tag{4.31b}$$

or returning to our original variables,

$$E(\omega_2, z) = iE(\omega_1)\tanh(z/L_c) \tag{4.32a}$$

and

$$E(\omega_2, z) = \frac{E(\omega_1)}{\cosh(z/L_c)}\,, \tag{4.32b}$$

where we note that the choice $\phi_1 = 0$ leads to $\phi_2 = \pi/2$.

For small values of z, $z \ll L_c$, the result in (4.32 a) agrees with the perturbation theoretic expression in (4.13).

We see that as z increases, all of the intensity of the pump beam is converted to the second harmonic. We have seen that even for the most intense electric fields to which matter may be exposed without breakdown, the nonlinear polarization $P^{(NL)}$ is in fact very small compared to the linear contribution to the dipole moment per unit volume (we assume one is not operating very close to a resonance in $\chi^{(2)}_{\alpha\beta\gamma}$ with this remark). A weak perturbation acting over a very long distance, or over a very long time may have dramatic effects, under suitable conditions. Although we are operating in the regime of weak nonlinearity, in a sense defined earlier, the end effect of the perturbation is very large.

We saw that second harmonic generation, when phase matched, can be viewed in quantum theory as the consequence of photon-photon interactions, with origin in the nonlinear response of the medium to light. Once again, the photons in the pump beam interact to form the second harmonic until the supply is exhausted.

We direct the reader's attention to a most dramatic photograph, the cover of the July 1963 issue of the jounal *Scientific American*. One sees a transparent KDP crystal, struck from the left by a red laser beam. A blue beam emerges from the right![2] This is a dramatic illustration of the behavior described by the equation of (4.32).

This discussion serves to illustrate a general principle of nonlinear optics, and in fact of nonlinear wave interactions in matter quite generally. The key to generating intense output from any particular nonlinear interaction, possibly controlled by a modest or small nonlinear coupling constant, is to achieve phase matching. This in combination with a sufficiently long path length or interaction volume, will allow an appreciable fraction of the pump beam or beams to be converted to output. In our remarks in Chap. 3, we have seen that the mixing of two laser beams, one of frequency ω_1 and one of frequency ω_2, produces radiation at the frequencies $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$, and $\omega_1 - \omega_2$ through action of $\chi^{(2)}_{\alpha\beta\gamma}$. An additional "zoo" of frequencies arises from the presence of the third order susceptibility $\chi^{(3)}_{\alpha\beta\gamma\delta}$. All of these radiations will be very weak, but one or more will become very intense if phase matching is achieved.

4.4 Other Examples of Nonlinear Wave Interactions

4.4.1 Four Wave Mixing Spectroscopy

There are a variety of other nonlinear interactions one may explore, as the remarks of the previous paragraph suggest. In this section, we comment on two that prove particularly interesting, in the view of the present author. Both of these are referred to as four wave interactions, and are mediated by the third order susceptibility $\chi^{(3)}_{\alpha\beta\gamma\delta}$.

The first is the process diagrammed in Fig. 3.1. We have the interaction between two laser beams, one with frequency ω_1 and wave vector $\boldsymbol{k}_1$, and one with frequency ω_2 and wave vector $\boldsymbol{k}_2$. The output is at frequency $2\omega_1 - \omega_2$, and with wave vector $2\boldsymbol{k}_1 - \boldsymbol{k}_2$.

A description of this process must recognize that the output can be generated in various steps, similar in character to the processes diagrammed in Fig. 3.1. Three waves may mix directly through $\chi^{(3)}_{\alpha\beta\gamma\delta}$, to produce a nonlinear dipole moment $P^{(NL)}_\alpha$ with the desired character. The input electric field is

$$E_\alpha(\boldsymbol{r}, t) = E_\alpha(\boldsymbol{k}_1\omega_1)e^{i(k_1\cdot r - \omega_1 t)} + E_\alpha(\boldsymbol{k}_2\omega_2)e^{i(k_2\cdot r - \omega_2 t)} + \text{c.c.}\,, \tag{4.33}$$

[2] The red light, when doubled in frequency, produces radiation which lies in the near ultra violet and which is thus invisible as a consequence. Such radiation, however, leaves a blue image on the film used to take the photograph shown on the cover of the journal Scientific American.

Chapter 4

4.1 P.D. Maker, R.W. Terhune, M. Niesenoff, C.M. Savage: Phys. Rev. **8**, 21 (1962)
4.2 D.M. Bloom, G.W. Bekkers, J.F. Young, S.E. Harris: Appl. Phys. Lett. **26**, 687 (1975)
4.3 D.M. Bloom, J.F. Young, S.E. Harris: Appl. Phys. Lett. **27**, 390 (1975)
4.4 N. Bloembergen: *Nonlinear Optics* (Benjamin, New York 1965) p. 11
4.5 M.D. Levenson: Phys. Today **30**, 44 (1977)
4.6 W.E. Bron, J. Kuhl, B.K. Rhee: Phys. Rev. B **34**, 6961 (1986)
4.7 C.R. Guiliano: Phys. Today **34**, 27 (April 1980)

Chapter 5

5.1 H. Goldstein: *Classical Mechanics* (Addison Wesley, Reading, MA 1950) Chap. 10
5.2 K. Huang, M. Born: *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford 1954) p. 57
5.3 A.D. Boardman, D.E. O'Connor, A.P.Young: *Symmetry and Its Applications in Science* (Wile New York 1973) Chap. 7
5.4 J.D. Jackson: *Classical Electrodynamics* 1st edn. (Wiley, New York 1973) p. 272
5.5 R.W. Woods: Philos. Mag. **6**, 729 (1928)
5.6 G. Baym: *Lectures on Quantum Mechanics* (Benjamin, New York 1969) p. 271
5.7 [Ref. 5.4, p. 123ff.]
5.8 [Ref. 5.6, p. 276ff.]
5.9 Y.R. Shen: *The Principles of Nonlinear Optics* (Wiley, New York 1984) Chap. 10
5.10 M.D. Levenson, N. Bloembergen: J. Chem. Phys. **60**, 1323 (1974)
5.11 L.D. Landau, E.M. Lifshitz: *Theory of Elasticity* (Pergamon, Oxford 1959) Chap. 1
5.12 D.F. Nelson, M. Lax: Phys. Res. Lett. **34**, 379 (1970)
5.13 [Ref. 5.11, Chap. 3]
5.14 C. Kittel: *Quantum Theory of Solids* (Wiley, New York 1963)
5.15 G.B. Wright (ed.): *Light Scattering Spectra of Solids* (Springer, Berlin, Heidelberg 1969)

Chapter 6

6.1 G. Baym: *Lectures on Quantum Mechanics* (Benjamin, New York 1969)
6.2 A.A. Abragam: *Principles of Nuclear Magnetic Resonance* (Clarendon, Oxford 1962)
6.3 R. Loudon: *Quantum Theory of Light* (Oxford Univ. Press, London 1973)
6.4 S.L. McCall, E.L.Hahn: Phys. Rev.Lett. **18**, 908 (1967); Phys. Rev.Lett. **183**, 457 (1969)
6.5 J.D. Jackson: *Classical Electrodynamics*, 2nd edn. (Wiley, New York 1975) p. 299
6.6 K. Leung, D. Hone, P. Riseborough, S.E. Trullinger, D.L. Mills: Phys. Rev. B **21**, 4017 (19
6.7 [Ref. 6.1, Chap. 22]
6.8 G.L.Lamb: *Elements of Soliton Theory* (Wiley, New York 1980)

Chapter 7

7.1 A. Yariv: *Quantum Electronics*, 2nd edn. (Wiley, New York 1975) p. 498ff.
7.2 M. Abramowitz, I.A. Stegun: *Handbook of Mathematical Functions*, NBS, Applied Mathen Series No. 55 (National Bureau of Standards, U.S. Government Printing Office, Washingtor 1965) p. 374
7.3 [Ref. 7.2, p. 355ff.]
7.4 J.D. Jackson: *Classical Electrodynamics*, 2nd edn. (Wiley, New York 1975) p. 232
7.5 L.F. Mollenauer: Philos. Trans. R. Soc. London A **315**, 437 (1985)
7.6 V.E. Zakharov, A.V. Mikailov: Soc. Phys.–JETP **47**, 1017 (1978)
7.7 J. Satsuma, N. Yajima: Prog. Theor. Phys., Suppl. **55**, 284 (1974)
7.8 L.F. Mollenauer, R.H. Stolen, J.P. Gordon: Phys. Rev. Lett. **45**, 1095 (1988)