Nonlinear optics I

What are nonlinear-optical effects and why do they occur?

Maxwell's equations in a medium

Nonlinear-optical media

Second-harmonic generation

Conservation laws for photons ("Phasematching")

Quasi-phase-matching

Frequency Doubling Inside a Nonlinear Crystal Warning: Science Happening Inside





Reminder: linear optics

Recall that, in "ordinary" linear optics, a light wave acts on a molecule, which vibrates and then emits its own light wave that interferes with the original light wave.



In linear optical processes, the output E-field is always proportional to the input E-field: $E_{out} \propto E_{in}$

Why do nonlinear-optical effects occur?

Now, suppose the irradiance is high enough that many molecules are excited to the higher-energy state. This state can then act as the lower level for additional excitation. This yields vibrations at all frequencies corresponding to all energy differences between populated states.



Beware: This picture can be misleading, because it implies that there need to be real energy levels resonant with the photon's energy. This is not necessary!

Emitted wave

New color!!!

Reminder: Maxwell's Equations in a Medium

The induced polarization, *P*, contains the effect of the medium. The inhomogeneous wave equation (in one dimension):

$$\frac{\partial^2 E}{\partial x^2} - \frac{1}{c_0^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2}$$

The polarization is usually proportional to the electric field:

$$\vec{P} = \varepsilon_0 \chi \vec{E}$$
 χ = unitless proportionality constant

Recall, for example, in the forced oscillator model, we found:

$$P(t) = \frac{Ne^2}{m} \frac{E(t)}{\omega_0^2 - \omega^2 + i\gamma\omega}$$

Then, the wave equation becomes:

$$\frac{\partial^{2} E}{\partial x^{2}} - \frac{1}{c_{0}^{2}} \frac{\partial^{2} E}{\partial t^{2}} = \varepsilon_{0} \mu_{0} \chi \frac{\partial^{2} E}{\partial t^{2}}$$

or
$$\frac{\partial^{2} E}{\partial x^{2}} - \frac{(1+\chi)}{c_{0}^{2}} \frac{\partial^{2} E}{\partial t^{2}} = 0 \qquad \text{since } \frac{1}{c_{0}^{2}} = \varepsilon_{0} \mu_{0}$$

Reminder: Maxwell's Equations in a Medium

$$\frac{\partial^2 E}{\partial x^2} - \frac{\left(1 + \chi\right)}{c_0^2} \frac{\partial^2 E}{\partial t^2} = 0$$

But this is the same equation as the usual homogeneous equation, if we define a new constant *c* such that: $\frac{1}{c^2} = \frac{(1+\chi)}{c^2}$

And, we call the quantity $\sqrt{1+\chi}$ the "refractive index".

So, we can describe light in a medium just like light in vacuum, as long as we take into account the refractive index correction.

But this only worked because P was proportional to E...

What if it isn't? Then P is a *non-linear* function of E!

Maxwell's Equations in a Nonlinear Medium

Nonlinear optics is what happens when the polarization is the result of higher-order terms in the field:

$$P = \varepsilon_0 \left[\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots \right]$$
$$= \frac{P_{Linear}}{P_{Linear}} + \frac{P_{non-linear}}{P_{linear}}$$

Then the wave equation must look like this:

$$\frac{\partial^2 E}{\partial x^2} - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P_{non-linear}}{dt^2}$$

The linear term can be treated in the same way as before, giving rise to the refractive index. But the non-linear term is different...

$$\frac{\partial^2 E}{\partial x^2} - \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \varepsilon_0 \mu_0 \chi^{(2)} \frac{\partial^2}{\partial t^2} \left(E^2 \right) + \varepsilon_0 \mu_0 \chi^{(3)} \frac{\partial^2}{\partial t^2} \left(E^3 \right) + \dots$$

Usually, $\chi^{(2)}$, $\chi^{(3)}$, etc., are very small and can be ignored. But not if E is big...

The effects of the non-linear terms

What sort of effect does the non-linear term have? Consider $\chi^{(2)}$.

If we write the field as: $E(t) \propto E_0 \exp(i\omega t) + E_0^* \exp(-i\omega t)$ then $E(t)^2 \propto E_0^2 \exp(2i\omega t) + 2|E_0|^2 + E_0^{*2} \exp(-2i\omega t)$ f terms that vary at a new frequency, the 2nd harmonic, $2\omega!$

Nonlinearity can lead to the generation of new frequency components.

This can be extremely useful:



Mechanisms for nonlinear interactions

The $\chi^{(n)}$ formalism can describe (nearly) all nonlinear optical interactions.

But this formalism doesn't tell us anything about the physical mechanism that is the origin of the nonlinearity. There are many sources of nonlinearity.

Here's one key example: Real springs do not obey Hooke's Law perfectly. Use Newton's Law, F = ma, to write down an equation of motion, including a nonlinear spring force:



Hooke's Law nonlinear spring: e.g.,
$$F_{NL} \sim x_e^2$$

 $m_e \frac{d^2 x_e(t)}{dt^2} = -k_s x_e(t) + \beta F_{NL}(x_e) + eE_0 e^{-i\omega t} - 2m_e \Gamma \frac{dx_e(t)}{dt}$

Nonlinearity of the electron motion

Hooke's Law nonlinear spring

$$m_{e} \frac{d^{2} x_{e}(t)}{dt^{2}} = -k_{s} x_{e}(t) + \beta F_{NL}(x_{e}) + eE_{0} e^{-i\omega t} - 2m_{e} \Gamma \frac{dx_{e}(t)}{dt}$$

If the electron is driven sinusoidally at frequency ω , the motion must include frequencies other than ω .

$$x_e(t) = C_0 + C_\omega \exp(-i\omega t) + C_{2\omega} \exp(-i2\omega t) + \dots$$



This animation shows a decomposition of the motion into the fundamental (blue) as well as a DC term (red) and the 2nd harmonic term (green).

This is one common physical origin of the nonlinear response of many materials.

It is sometimes known as the "hyperpolarizability".

Electronic hyperpolarizability

The characteristic response time of this process is the time required for the electron cloud to become distorted.

This can be estimated: it must be on the order of the orbital period of an electron about its nucleus:

 $\tau = \frac{2\pi a_0}{v}$ $a_0 = \text{Bohr radius (0.5 x 10^{-8} \text{ cm})}$ v = typical electron velocity (0.01c)

 $\tau = 10^{-16}$ sec

→ faster than any laser pulse (almost)

There are many other sources of nonlinearity, but most of them are much slower, and therefore less relevant to ultrafast optics.

Sum and difference frequency generation

Suppose there are two different-color beams present in a $\chi^{(2)}$ medium, not just one:

$$E(t) = E_1 \exp(i\omega_1 t) + E_1^* \exp(-i\omega_1 t) + E_2 \exp(i\omega_2 t) + E_2^* \exp(-i\omega_2 t)$$

Then $E(t)^2$ has 16 terms:

$$\begin{split} E(t)^2 \propto E_1^2 \exp(2i\omega_1 t) + E_1^{*2} \exp(-2i\omega_1 t) & \text{2nd harmonic of } \omega_1 \\ + E_2^2 \exp(2i\omega_2 t) + E_2^{*2} \exp(-2i\omega_2 t) & \text{2nd harmonic of } \omega_2 \\ + 2E_1E_2 \exp(i\left[\omega_1 + \omega_2\right]t) + 2E_1^*E_2^* \exp(-i\left[\omega_1 + \omega_2\right]t) & \text{sum frequency} \\ + 2E_1E_2 \exp(i\left[\omega_1 - \omega_2\right]t) + 2E_1^*E_2^* \exp(-i\left[\omega_1 - \omega_2\right]t) & \text{difference frequency} \\ + 2\left|E_1\right|^2 + 2\left|E_2\right|^2 & \text{zero frequency - known as "optical rectification"} \end{split}$$

This is an awful lot of processes - do they all occur simultaneously? Which one dominates (if any)? What determines the efficiency?

Complicated nonlinear-optical effects can occur.



This cartoon illustrates a 6-wave mixing process. It would involve the $\chi^{(5)}$ term in the wave equation.

The more photons (i.e., the higher the order) the weaker the effect, however. Very-high-order effects can be seen, but they require very high irradiance, since usually $\chi^{(2)} > \chi^{(3)} > \chi^{(4)} > \chi^{(5)} \dots$

Conservation laws for photons in nonlinear optics



Energy must be conserved. Recall that the energy of a photon is $\hbar\omega$. Thus:

$$\omega_1 + \omega_2 + \omega_3 - \omega_4 + \omega_5 = \omega_0$$

Photon momentum must also be conserved. The momentum of a photon is $\hbar \vec{k}$, so:

$$\vec{k}_1 + \vec{k}_2 + \vec{k}_3 + \vec{k}_4 + \vec{k}_5 = \vec{k}_0$$

But \vec{k}_0 is related to ω_0 : $\left|\vec{k}_0\right| = 2\pi n/\lambda = n\omega_0/c_0$

The \vec{k}_0 determined from this second condition may not correspond to the frequency ω_0 determined from the first one.

Satisfying these two relations simultaneously is called "phase-matching."

Usually, only one (or zero) of the many possible N-wave mixing processes can be phase-matched at a time.

Phase-matching: an example

Consider the 2nd harmonic generation process:



The solution: birefringence

The molecular "spring constant" can be different for different directions.





The x- and y-polarizations can see different refractive index curves.

Hence, the refractive index of a material can depend on the orientation of the material relative to the polarization axis!

Uniaxial crystals have an optic axis



Uniaxial crystals have one refractive index for light polarized along the optic axis (n_e) and another for light polarized in either of the two directions perpendicular to it (n_o).

Light polarized along the optic axis is called the extraordinary ray, and light polarized perpendicular to it is called the ordinary ray. These polarization directions are the crystal "principal axes."

Birefringent Materials

The phenomenon of 'double refraction' is easily visible to the eye, if the birefringence is large enough.

Calcite, CaCO₃



Refractive Indices of Uniaxial Crystals

(20°C; λ = 589.3nm)

n _o	n _e
1.669	1.638
1.6584	1.4864
1.5443	1.5534
1.5854	1.3369
1.309	1.313
2.616	2.903
	<i>n</i> _o 1.669 1.6584 1.5443 1.5854 1.309 2.616

Calcite is one of the most birefringent materials known. It is particularly useful because it's also transparent over the entire visible spectrum and even into the UV (~300nm).

Birefringence for polarization control

If both polarizations are present, this has the effect of changing the relative phase of the x and y fields, and hence altering the polarization.

Suppose we illuminate a slab of birefringent material with a wave that is not polarized along either of the principal axes.

This wave must be broken down into its ordinary and extraordinary components, considered individually, and added back together afterward.





Birefringent media: the index ellipsoid

Things are more complicated if the k vector is at an angle θ to the extraordinary axis, as shown here:

Then one component of the field (the orange arrow) is parallel to the ordinary axis and propagates with refractive index n_o .

But the other component (**red**) is not parallel to any of the principal axes. It propagates with an index that lies between n_o and n_e , as:

$$\frac{1}{n^2(\theta)} = \frac{\cos^2(\theta)}{n_o^2} + \frac{\sin^2(\theta)}{n_e^2}$$



This equation describes the index ellipsoid. -

The propagation speed of the extraordinary component depends on angle.

Phase-matching Second-Harmonic Generation using birefringence

Using birefringence, we can satisfy the phase-matching condition.

For example:
Use the extraordinary polarization
for
$$\omega$$
 and the ordinary for 2ω :
$$n_o(2\omega) = n_e(\omega)$$

 n_e depends on propagation angle, so by rotating the birefringent crystal, we can tune the condition precisely by moving the red curve up and down relative to the blue curve.

Light created in real crystals



Note that SH beam is brighter as phase-matching is achieved.

Second-Harmonic Generation

SHG KDP crystals at Lawrence Livermore National Laboratory

These crystals convert as much as 80% of the input light to its second harmonic. Then additional crystals produce the third harmonic with similar efficiency!

They do it that way because the cascading of two second-order processes is usually much more efficient than a single-step third-order process.



Difference-Frequency Generation: Optical Parametric Generation, Amplification, Oscillation

Difference-frequency generation takes many useful forms.



The wave equation with nonlinearity

We have derived the wave equation in a medium, for the situation where the polarization is non-linear in E:

$$\frac{\partial^2 E}{\partial x^2} \frac{n^2}{c^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P^{NL}}{\partial t^2}$$

linear optics

where
$$P^{NL} = \varepsilon_0 \left[\chi^{(2)} E^2 + \chi^{(3)} E^3 + ... \right]$$

Usually,
$$\chi^{(2)} >> \chi^{(3)}$$

In these cases, we neglect the third (and higher) orders.

A good example: second harmonic generation

Second Harmonic Generation: SHG



In this process, we imagine that one laser (at frequency ω) is used to illuminate a nonlinear medium.

As this field propagates through the medium, its intensity will be depleted and the intensity of the 2nd harmonic wave (initially zero) will grow.



Describing the 2nd harmonic wave

We are interested in the behavior of the field that oscillates at 2ω ; that is, the 2nd harmonic. We can assume that this field is of the form:

$$E_{2\omega}(z,t) = A_{2\omega}(z)e^{ik_{2\omega}z-i2\omega t} + c.c.$$

where we require that the amplitude $A_{2\omega}(z)$ is slowly varying, and also that it vanishes at the input facet of the nonlinear medium:

$$A_{2\omega}\left(z=0\right)=0$$

Furthermore, the wave vector of this wave depends on the refractive index of the nonlinear medium at frequency 2ω :

$$k_{2\omega} = n\left(2\omega\right)\frac{2\omega}{c}$$

Our goal is to determine its intensity: $I_{2\omega}(z) \propto |A_{2\omega}(z)|^2$

What equation must the 2nd harmonic obey?

The 2nd harmonic wave must obey the wave equation, of course.

$$\frac{\partial^2 E_{2\omega}}{\partial z^2} - \left(\frac{n(2\omega)}{c}\right)^2 \frac{\partial^2 E_{2\omega}}{\partial t^2} = \mu_0 \frac{\partial^2 P^{(2)}}{dt^2}$$

As we have seen, the 2nd-order polarization results from the field at frequency ω - the fundamental. Putting in the spatial dependence explicitly:

$$P^{(2)}(t) = 2\varepsilon_{0}\chi^{(2)}E_{0}e^{-i\omega t + ik_{\omega}z})^{2}$$

this is the *k* of the incident field incident field:
(the one at frequency ω)
$$k_{\omega} = n(\omega)\frac{\omega}{c}$$
$$P^{(2)}(t) = 2\varepsilon_{0}\chi^{(2)}E_{0}^{2}e^{i[2k_{\omega}z - 2\omega t]}$$

Plugging in to the wave equation...

Plug our assumed forms for $E_{2\omega}(z,t)$ and $P^{(2)}$, to find:



Slowly Varying Envelope Approximation (SVEA):

$$\frac{\partial^2 A_{2\omega}}{\partial z^2} < |k_{2\omega} \frac{\partial A_{2\omega}}{\partial z}|$$

So we neglect the second derivative of $A_{2\omega}$.

Solving the wave equation in second order

The nonlinear wave equation becomes:

$$2ik_{2\omega}\frac{\partial A_{2\omega}}{\partial z} = -\frac{8\chi^{(2)}\omega^2}{c^2}E_0(z)^2e^{i2k_{\omega}z}e^{-ik_{2\omega}z}$$

Now, we *could* find a similar first-order differential equation for E_0 , and then solve the two coupled equations.

But, instead of doing that, let's see if we can gain some physical insight by making another simplifying assumption:

Assume: The incident field is not significantly depleted by the conversion process. That is, E_0 does not decrease very much with increasing z.

 \longrightarrow E_0 is independent of z.

In this case, we can easily integrate both sides of this equation.

Integrate both sides

$$\left(\int_{0}^{z} \frac{\partial A_{2\omega}}{\partial z'} dz'\right) = \frac{4i\chi^{(2)}\omega^{2}}{k_{2\omega}c^{2}} E_{0}^{2} \int_{0}^{z} e^{i[2k_{\omega}z'-k_{2\omega}z']} dz'$$

This is just $A_{2\omega}(z)$.

Define the 'phase mismatch' $\Delta k = 2k_{\omega} - k_{2\omega}$

We can do the integral on the right side:

$$\int_{0}^{z} e^{i\Delta k \cdot z'} dz' = \frac{1}{i\Delta k} \left[e^{i\Delta k \cdot z} - 1 \right]$$

Thus we've arrived at a result!

$$A_{2\omega}(z) \propto E_0^2 \cdot \frac{\exp[i\Delta kz] - 1}{\Delta k}$$

Note, this is just the difference in the two refractive indices:

$$\Delta k = 2 \frac{2\pi}{\lambda_{in}} n_{\omega} - \frac{2\pi}{\lambda_{in}/2} n_{2\omega}$$
$$= \frac{4\pi}{\lambda_{in}} (n_{\omega} - n_{2\omega})$$

The solution

The intensity of the second harmonic radiation is proportional to $|A_{2\omega}|^2$.

$$I_{2\omega}(z) \propto |A_{2\omega}(z)|^2 \propto {I_0}^2 \frac{\sin^2(\Delta k \cdot z/2)}{(\Delta k)^2} \qquad \delta = \text{dimensionless}$$
$$= I_0^2 z^2 \frac{\sin^2(\delta)}{\delta^2} \qquad \text{where } \delta = \Delta k \cdot z/2$$

The intensity of the 2nd harmonic is proportional to the square of the intensity of the fundamental.

It also depends sensitively on the product of Δk and z.



Phase matching for a $\chi^{(2)}$ process

$$I_{2\omega}(z) \propto I_0^2 z^2 \frac{\sin^2(\Delta k \cdot z/2)}{(\Delta k \cdot z/2)^2}$$

To summarize:

- SVEA and zero-depletion approximations give lowest order solution.
- Intensity of SHG radiation is proportional to the square of the input intensity.
- Intensity of SHG radiation grows quadratically with propagation distance.
- Intensity of SHG is very sensitive to phase mismatch maximum when $\Delta k = 0$



SHG intensity is most efficient for $|\delta| < 1$

f
$$\delta$$
 = 1, then sin² δ/δ^2 = 0.71.

$$\delta | < 1$$
 corresponds to $|\Delta k| < \frac{2}{L}$

→ If the SHG medium is too thick for a given ∆k, conversion efficiency suffers.

What does phase matching mean?

When $\Delta k = 0$, $\gamma = 0$, this means that $n(\omega) = n(2\omega)$. The phase velocity of the input and the 2nd harmonic are equal. $\lambda_{\omega} = 2 \lambda_{2\omega}$.



The two waves maintain the same relative phase as they propagate.

phase-matched:

propagation distance z

When Δk is not zero, the phase velocity of the fundamental and 2nd harmonic are different, and $\lambda_{\omega} \neq 2 \lambda_{2\omega}$. As *z* increases, the 2nd harmonic wave walks out of phase with the input wave.

not phase-matched:



propagation distance z

The condition $\Delta k L << 1$ ensures that the two waves don't walk too far out of phase with each other before reaching the end of the SHG crystal.

Materials for $\chi^{(2)}$ non-linear optics

There are a number of materials commonly used for SHG or other frequency conversion effects based on $\chi^{(2)}$.

- KDP (KH₂PO₄): potassium di-hydrogen phosphate
- BBO (β -BaB₂O₄): beta-barium borate
- LiNbO₃: lithium niobite
- AgGaSe₂: silver gallium selenide
- ZnTe: zinc telluride
- and *many* others

Each material has advantages and disadvantages:

- size of the nonlinear coefficient $\chi^{(2)}$
- ease of phase-matching
- wavelength range of transparency
- optical damage threshold
- price / ease of fabrication



LiNbO₃ crystals





What if the phase matching is not perfect?



The SHG intensity oscillates as a function of propagation distance:





Another way to boost the SHG efficiency



Why does the signal oscillate?

If phase matching condition is not perfect, then after a certain length (called the 'coherence length' L_{coh}), the fundamental and 2nd harmonic walk out of phase with each other.

At that point, the process reverses itself, and the fundamental grows while the 2ω beam diminishes. This process then oscillates.

What if, at $z = L_{coh}$, we could flip the sign of $\chi^{(2)}$? This would change the phase of $E_{2\omega}$ by π . Instead of cancelling out as it propagates beyond L_{coh} , $E_{2\omega}$ would be further enhanced.

In some cases, we can control the sign of $\chi^{(2)}$ by changing the crystal structure.



Quasi-phase matching

Flipping the sign of $\chi^{(2)}$ once each coherence length is known as "quasi-phase matching." It has recently become a critically important method for efficient second harmonic generation.

