

# Nonlinear Spectroscopy

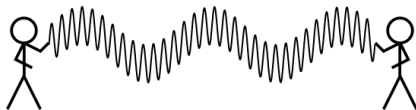
Mike Reppert

September 18, 2019

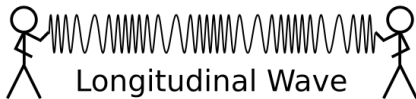
## Previously on CHM676...

We showed that in *rare, isotropic media*, nonlinear spectroscopy is driven by the *transverse field*  $\tilde{\mathbf{E}}_{\perp}$ .

Transverse Wave

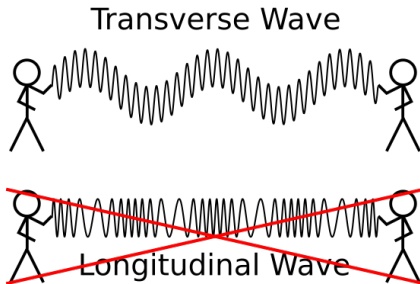


Longitudinal Wave



## Previously on CHM676...

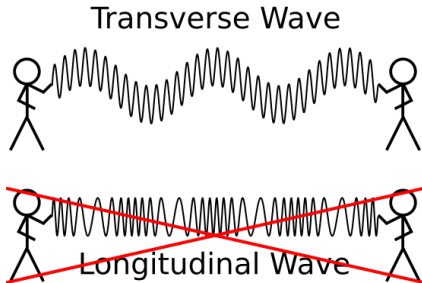
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$$\left( k^2 - \frac{\omega^2}{c^2} \varepsilon(\omega) \right) \tilde{\mathbf{E}}_{\perp}^{(\text{NL})} = \frac{4\pi\omega^2}{c^2} \tilde{\mathbf{P}}_{\perp}^{(\text{NL})} \left[ \tilde{\mathbf{E}}_{\text{ext}} + \tilde{\mathbf{E}}^{(1)} \right].$$

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**Today:** What do nonlinear signals look like?

# Outline

- 1 Resonance
- 2 Phase Matching
- 3 Nonlinear Fields

# Resonance

# Getting Nonlinear Signals

How do you make a ratio big?

$$\tilde{\mathbf{E}}^{(\text{NL})} = 4\pi \frac{\tilde{\mathbf{P}}^{(\text{NL})} \left[ \tilde{\mathbf{E}}_{\text{ext}} + \tilde{\mathbf{E}}^{(1)} \right]}{\frac{c^2 k^2}{\omega^2} - \varepsilon(\omega)}$$

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Two options:

- ① Make the numerator big  $\Rightarrow$  **Intensity + Resonance**
- ② Make the denominator small  $\Rightarrow$  **Phase matching**



# The Numerator – Nonlinear Polarization

“Recall”

$$\begin{aligned} \tilde{P}_{\alpha}^{(n)} \left[ \tilde{\mathbf{E}}^{(\text{exc})} \right] &= \sum_{\alpha_1, \dots, \alpha_n} \int d\tau_n \dots \int d\tau_1 R_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(\tau_1, \dots, \tau_n) \\ &\times \int_V d\mathbf{x} \int dt e^{i(\omega t - \mathbf{k} \cdot \mathbf{x})} E_{\alpha_1}^{(\text{exc})}(\mathbf{x}, t - \tau_1 - \dots - \tau_n) \dots E_{\alpha_n}^{(\text{exc})}(\mathbf{x}, t - \tau_n) \end{aligned}$$

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 &\quad \Downarrow \\
 \tilde{P}_{\alpha}^{(n)}(\mathbf{k}, \omega) &\approx \frac{1}{(2\pi)^{4(n-1)}} \sum_{\alpha_1, \dots, \alpha_n} \int d\omega_1 \dots \int d\omega_n \int d\mathbf{k}_1 \dots \int d\mathbf{k}_n \\
 &\times \delta(\omega_1 + \dots + \omega_n - \omega) \delta(\mathbf{k}_1 + \dots + \mathbf{k}_n - \mathbf{k}) \\
 &\times \tilde{R}_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(\omega_1, \dots, \omega_1 + \dots + \omega_n) \\
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 \end{aligned}$$

# Sum Conditions

This leads to two strict sum conditions:

$$\omega = \omega_1 + \dots + \omega_n$$

$$\mathbf{k} = \mathbf{k}_1 + \dots + \mathbf{k}_n.$$

The **signal frequency** is a sum of *field frequencies*.

The **signal wavevector** is a sum of *field wavevectors*.

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**Two important points:**

- The signs on  $\omega_n$  and  $\mathbf{k}_n$  can be positive or negative – but must match:  $E(\mathbf{k}, t) \sim e^{i(\omega_n t - \mathbf{k}_n \cdot \mathbf{x})} + e^{-i(\omega_n t - \mathbf{k}_n \cdot \mathbf{x})}$ .

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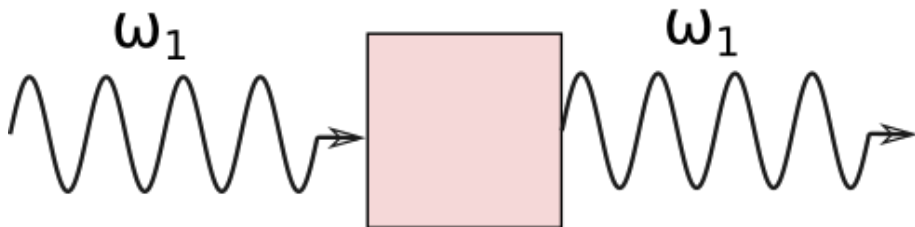
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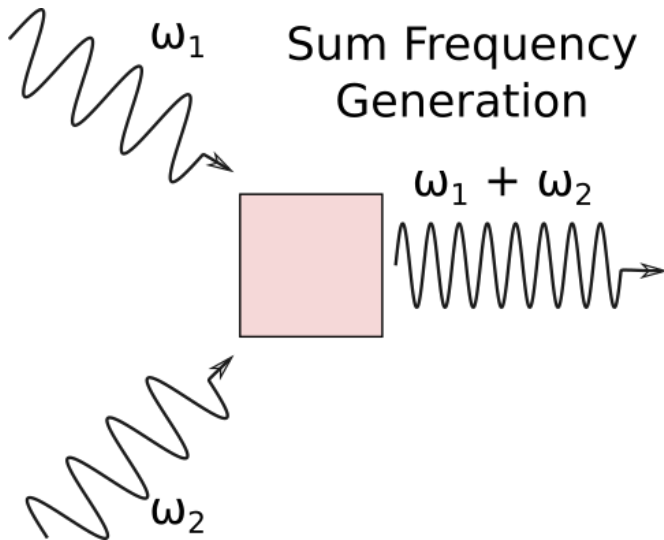
- The signs on  $\omega_n$  and  $\mathbf{k}_n$  can be positive or negative – but must match:  $\mathbf{E}(\mathbf{k}, t) \sim e^{i(\omega_n t - \mathbf{k}_n \cdot \mathbf{x})} + e^{-i(\omega_n t - \mathbf{k}_n \cdot \mathbf{x})}$ .
- The absolute signs on  $\omega$  and  $\mathbf{k}$  are irrelevant! The *relative sign* determines the propagation direction.

# Linear Response

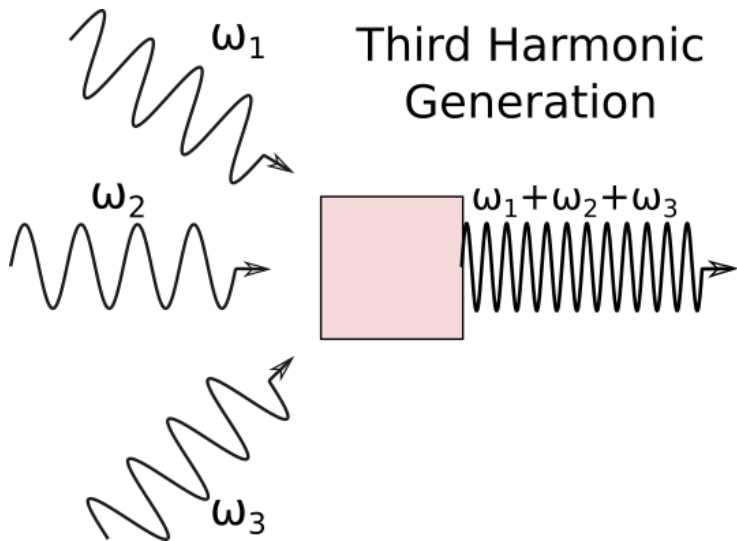
## Linear Response



# Sum Frequency Generation



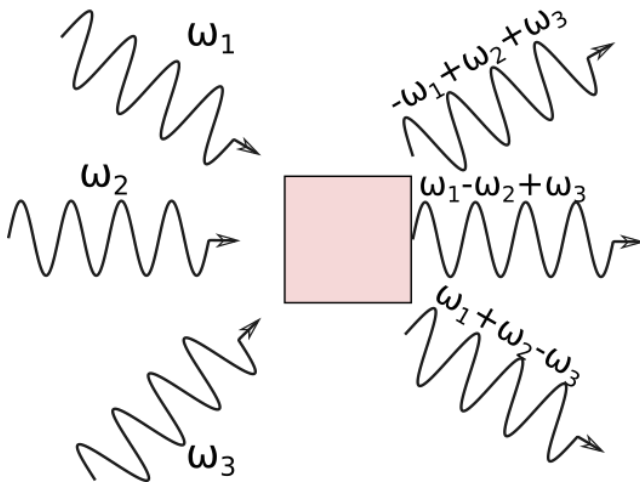
# Third Harmonic Generation





# Four-Wave Mixing

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# Resonance

But wait, there's more!

$$\tilde{\mathbf{E}}^{(\text{NL})} = 4\pi \frac{\tilde{\mathbf{P}}^{(\text{NL})} [\tilde{\mathbf{E}}_{\text{ext}} + \tilde{\mathbf{E}}^{(1)}]}{\frac{c^2 k^2}{\omega^2} - \varepsilon(\omega)}$$

Large polarization can be induced only if the field frequencies are **resonant** with peaks of

$$\tilde{R}_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(\omega_1, \dots, \omega_1 + \dots + \omega_n).$$

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**NB:** Nonlinear signals tell us about material properties  $\Leftarrow$

Why we care about nonlinear spectroscopy

# Take-Home Points

The nonlinear polarization *must* satisfy:

$$\omega_S = \omega_1 + \dots + \omega_n$$

$$\mathbf{k}_S = \mathbf{k}_1 + \dots + \mathbf{k}_n.$$

The nonlinear polarization is maximized when the electric field is **resonant** with characteristic response function frequencies.

**Response function resonances** (and hence nonlinear spectroscopy) tell us about the characteristic *microscopic dynamics* of materials.

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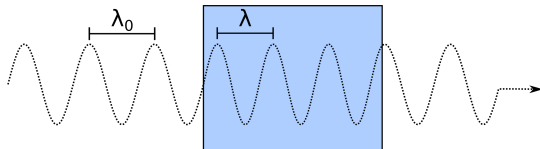
# Phase Matching

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Propagating waves must satisfy the material *dispersion relation*

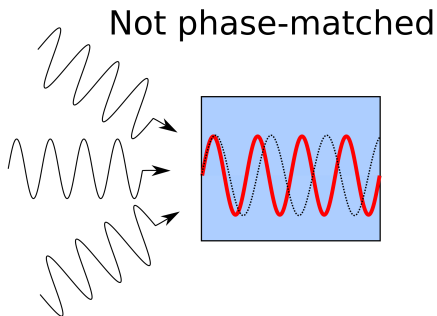


$$\lambda = \frac{c}{n\omega}$$

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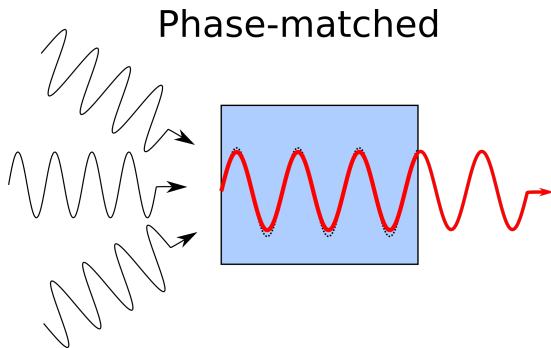
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The nonlinear polarization *radiates* only if its *phase matches* that of the induced field over the entire sample!

# Phase Matching Examples

Suppose all incoming field vectors point in the same direction  $\hat{\mathbf{s}}_o$ . Neglecting  $\text{Im } \varepsilon(\omega)$ :

$$\mathbf{k}_i \approx n(\omega_i) \frac{\omega_i}{c} \hat{\mathbf{s}}_o$$

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$$\mathbf{k}_i \approx n(\omega_i) \frac{\omega_i}{c} \hat{\mathbf{s}}_o$$

so that

$$\frac{c^2 \|\mathbf{k}_1 + \dots + \mathbf{k}_n\|^2}{(\omega_1 + \dots \omega_n)^2} \approx n^2(\omega_1 + \dots \omega_n)$$

$$\Downarrow$$

$$n(\omega_1)\omega_1 + \dots + n(\omega_n)\omega_n \approx n(\omega_1 + \dots \omega_n)(\omega_1 + \dots \omega_n)$$



# Phase-Matching Examples

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**Rephasing:** 
$$-n(\omega_1)\omega_1 + n(\omega_2)\omega_2 + n(\omega_3)\omega_3$$
$$\approx n(-\omega_1 + \omega_2 + \omega_3)(-\omega_1 + \omega_2 + \omega_3)$$

**Nonrephasing:** 
$$-n(\omega_1)\omega_1 - n(\omega_2)\omega_2 + n(\omega_3)\omega_3$$
$$\approx n(+\omega_1 - \omega_2 + \omega_3)(\omega_1 - \omega_2 + \omega_3)$$

**Double Quantum Coherence:** 
$$n(\omega_1)\omega_1 + n(\omega_2)\omega_2 - n(\omega_3)\omega_3$$
$$\approx n(+\omega_1 + \omega_2 - \omega_3)(\omega_1 + \omega_2 - \omega_3)$$

# Take-Home Points

A nonlinear *polarization* can only emit a *non-linear field* if it satisfies **phase matching**.

**Phase matching** means that  $P(\mathbf{x}, t)$  must be capable of oscillating *in phase* with a propagating EM field with the same frequency and  $\mathbf{k}$ -vector.

For a given frequency and  $\mathbf{k}$ -vector, the *refractive index* of the medium determines whether phase-matching is satisfied:  $k \approx \frac{n(\omega)}{c}\omega$ .

# Nonlinear Fields

# The Emitted Field

## What does the signal *field* look like?

To make life easier:

- Neglect  $\text{Im } \varepsilon(\omega)$
- Take  $\text{Re } \varepsilon(\omega) = n^2 = \text{constant}$

Then the nonlinear field satisfies the IWE with solution:

$$\mathbf{E}^{(\text{NL})}(\mathbf{x}, t) = -\frac{4\pi}{c^2} \int d\mathbf{x}' \frac{\frac{\partial^2}{\partial t^2} \mathbf{P}^{(\text{NL})}(\mathbf{x}', t - |\mathbf{x} - \mathbf{x}'|n/c)}{|\mathbf{x} - \mathbf{x}'|}$$

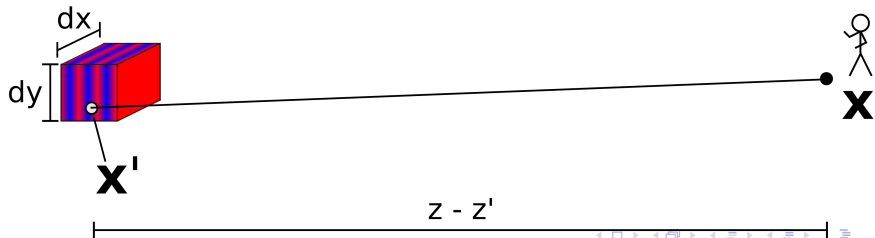
# Plane Wave Polarization

Now assume a **plane wave polarization** propagating along the  $z$  axis:

$$\mathbf{P}^{(\text{NL})}(t) \propto e^{i\omega(t - \frac{n}{c}z)} + c.c.$$

Let's look at the field at an observation point  $\mathbf{x}$  *near the  $z$ -axis in the far-field limit* so that

$$|\mathbf{x} - \mathbf{x}'| \approx z - z'$$





# Far-Field Limit

In this limit:

$$\begin{aligned}
 \mathbf{E}^{(\text{NL})}(\mathbf{x}, t) &\approx -\frac{4\pi}{c^2} \int_V d\mathbf{x}' \frac{\frac{\partial^2}{\partial t^2} e^{i\omega(t - \frac{n}{c}(z-z') - \frac{n}{c}z')}}{z - z'} + c.c. \\
 &\approx -\frac{4\pi}{c^2} \int_V d\mathbf{x}' \frac{\frac{\partial^2}{\partial t^2} e^{i\omega(t - \frac{n}{c}z)}}{z - z'} + c.c. \\
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**A plane-wave polarization induces a plane-wave field!**

**NB:** Factor of  $\omega$  difference in comparison to [*Phys. Rev. A*, 62, 033820]

# Take-Home Point

Plane waves beget plane waves! – A plane-wave polarization induces a propagating electromagnetic field with the same wavevector.