Nonlinear Spectroscopy

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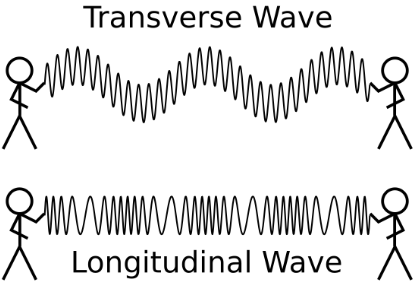
October 7, 2020

Previously on CHM676...

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



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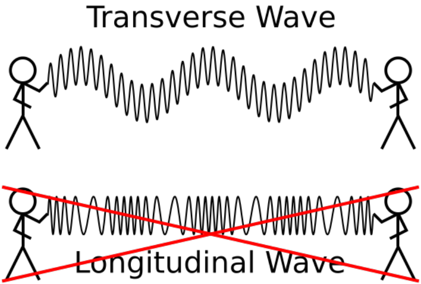

$$\left(k^2 - \frac{\omega^2}{c^2}\varepsilon(\omega)\right)\tilde{\boldsymbol{E}}_{\perp}^{(\mathrm{NL})} = \frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}_{\perp}^{(\mathrm{NL})}\left[\tilde{\boldsymbol{E}}_{\mathrm{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right].$$

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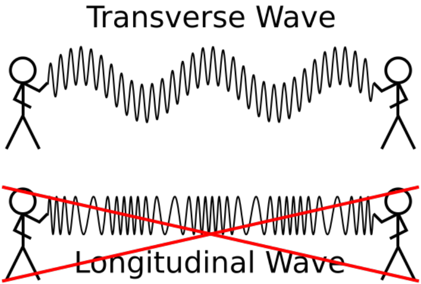

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Today: What do nonlinear signals look like?

Outline

Resonance

Getting Nonlinear Signals

How do you make a ratio big?

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

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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"

$$\tilde{P}_{\alpha}^{(n)}\left[\tilde{\boldsymbol{E}}^{(\mathsf{exc})}\right] = \sum_{\alpha_1,\ldots,\alpha_n} \int d\tau_n \ldots \int d\tau_1 R^{(n)}_{\alpha_1\ldots\alpha_n\alpha}(\tau_1, \ldots, \tau_n)$$

$$\times \int_V d\boldsymbol{x} \int dt\, \mathrm{e}^{\mathrm{i}(\omega t - \boldsymbol{k}\cdot\boldsymbol{x})} E^{(\mathsf{exc})}_{\alpha_1}(\boldsymbol{x}, t - \tau_1 - \ldots - \tau_n) \ldots E^{(\mathsf{exc})}_{\alpha_n}(\boldsymbol{x}, t - \tau_n)$$

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$$\Downarrow$$

$$\tilde{P}_\alpha^{(n)}(\boldsymbol{k},\omega) \approx \frac{1}{(2\pi)^{4(n-1)}} \sum_{\alpha_1,\dots,\alpha_n} \int d\omega_1 \dots \int d\omega_n \int d\boldsymbol{k}_1 \dots \int d\boldsymbol{k}_n$$

$$\times\, \delta\left(\omega_1+\dots+\omega_n-\omega\right)\delta\left(\boldsymbol{k}_1+\dots+\boldsymbol{k}_n-\boldsymbol{k}\right)$$

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

$$\times\, \tilde{E}^{(\text{exc})}_{\alpha_1}(\boldsymbol{k}_1,\omega_1)\dots\tilde{E}^{(\text{exc})}_{\alpha_n}(\boldsymbol{k}_n,\omega_n)$$

Sum Conditions

This leads to two strict sum conditions:

$$\omega = \omega_1 + ... + \omega_n$$
$$\boldsymbol{k} = \boldsymbol{k}_1 + ... + \boldsymbol{k}_n.$$

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

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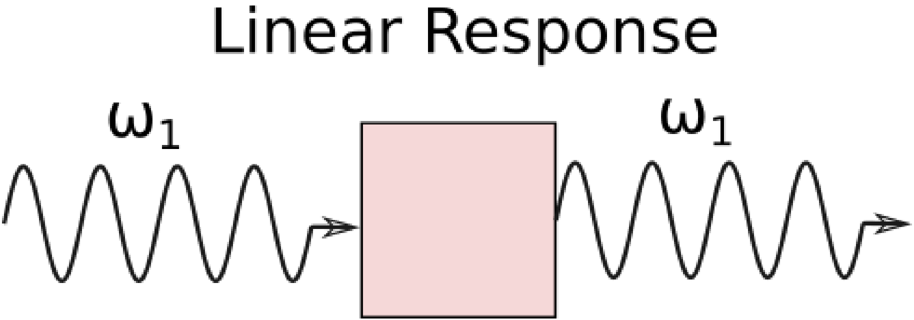
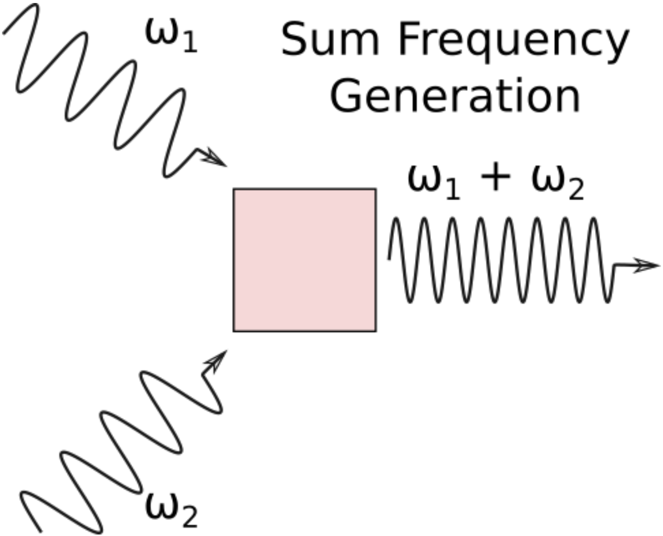
- The absolute signs on ω and $\boldsymbol{k}$ are irrelevant! The *relative sign* determines the propagation direction.

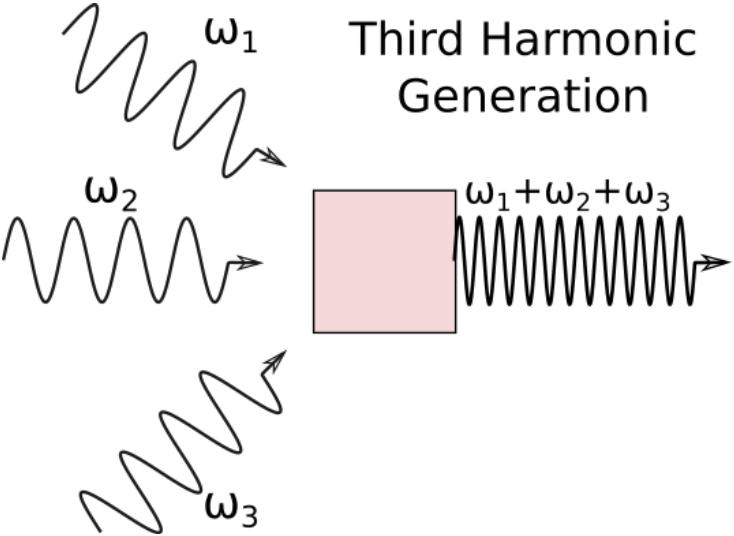
Linear Response



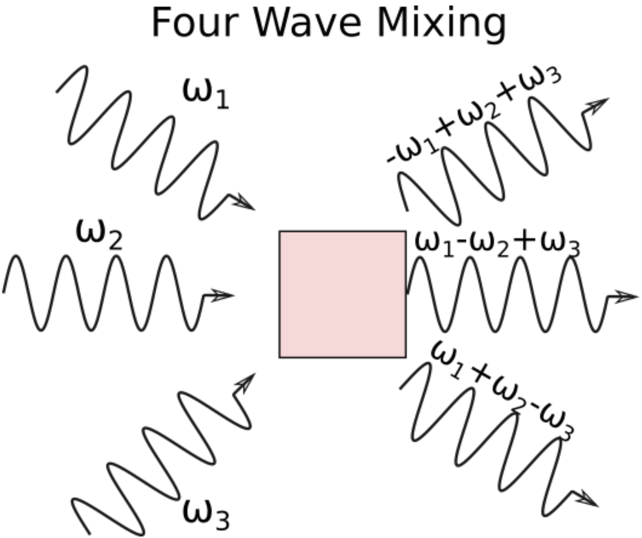
Sum Frequency Generation



Third Harmonic Generation



Four-Wave Mixing



Resonance

But wait, there's more!

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

Large polarization can be induced only if the field frequencies are **resonant** with peaks of $\tilde{R}^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(\omega_1, \ldots, \omega_1 + \ldots + \omega_n)$.

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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:

$$\omega_S = \omega_1 + \ldots + \omega_n$$
$$\boldsymbol{k}_S = \boldsymbol{k}_1 + \ldots + \boldsymbol{k}_n.$$

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.

Phase Matching

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$$\times\, \delta\left(\omega_1 + \ldots + \omega_n - \omega\right) \delta\left(\boldsymbol{k}_1 + \ldots + \boldsymbol{k}_n - \boldsymbol{k}\right)$$

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Need $\frac{c^2\|\boldsymbol{k}_1 + \dots + \boldsymbol{k}_n\|^2}{(\omega_1 + \dots \omega_n)^2} \approx \varepsilon(\omega_1 + \dots \omega_n)$

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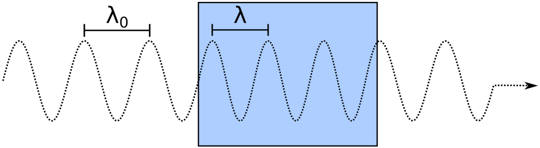
Propagating waves must satisfy the material *dispersion relation*



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

Phase Matching

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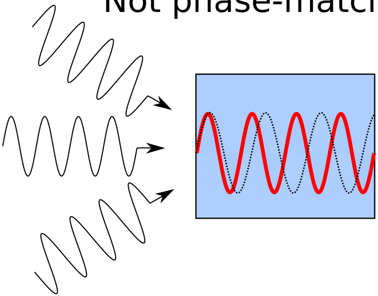
Propagating waves must satisfy the material *dispersion relation* – the **induced polarization** doesn't have to!

Not phase-matched



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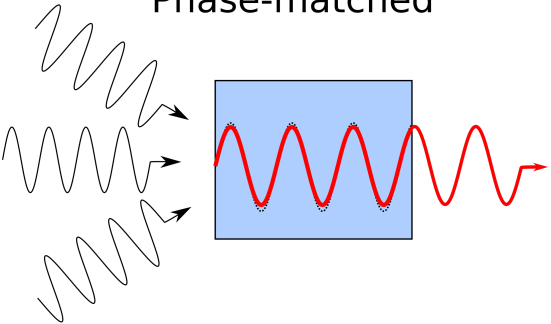

The nonlinear polarization *radiates* only if its *phase matches* that of the induced field over the entire sample!

Phase Matching Examples

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

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

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so that

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

$$\Downarrow$$

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

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

For a given frequency and $\boldsymbol{k}$-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 Im $\varepsilon(\omega)$
- Take Re $\varepsilon(\omega) = n^2 =$ constant

Then the nonlinear field satisfies the IWE with solution:

$$\boldsymbol{E}^{(\mathsf{NL})}(\boldsymbol{x}, t) = -\frac{4\pi}{c^2} \int \mathrm{d}\boldsymbol{x}' \frac{\frac{\partial^2}{\partial t^2} \boldsymbol{P}^{(\mathsf{NL})}\left(\boldsymbol{x}', t - |\boldsymbol{x} - \boldsymbol{x}'|n/c\right)}{|\boldsymbol{x} - \boldsymbol{x}'|}$$

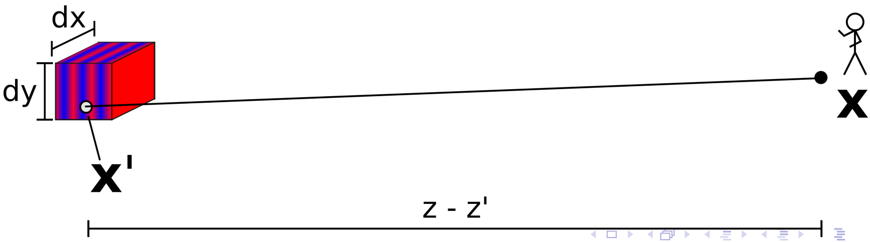
Plane Wave Polarization

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

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

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

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



Far-Field Limit

In this limit:

$$\begin{aligned} \boldsymbol{E}^{(\mathsf{NL})}(\boldsymbol{x},t) &\approx -\frac{4\pi}{c^2}\int_V \mathrm{d}\boldsymbol{x}' \, \frac{\frac{\partial^2}{\partial t^2} e^{i\omega(t-\frac{n}{c}(z-z')-\frac{n}{c}z')}}{z-z'} + c.c. \\ &\approx -\frac{4\pi}{c^2}\int_V \mathrm{d}\boldsymbol{x}' \, \frac{\frac{\partial^2}{\partial t^2} e^{i\omega(t-\frac{n}{c}z)}}{z-z'} + c.c. \\ &\approx \frac{4\pi\omega^2\ell^3}{rc^2} e^{i\omega(t-\frac{n}{c}z)} + c.c. \end{aligned}$$

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$$\approx \frac{4\pi\omega^2\ell^3}{rc^2}e^{i\omega(t-\frac{n}{c}z)} + c.c.$$

A plane-wave polarization induces a plane-wave field!

NB: Factor of ω 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.