Nonlinear Response

Mike Reppert

September 16, 2019

Previously on CHM676...

Material response can be expanded in a perturbative series

$$P_{\alpha}^{(n)}(t) = \sum_{n=0}^{\infty} P_{\alpha}^{(n)}(t).$$

Previously on CHM676...

Material response can be expanded in a perturbative series

$$P_\alpha^{(n)}(t) = \sum_{n=0}^{\infty} P_\alpha^{(n)}(t).$$

Linear response is the first-order term, characterized by the *susceptibility*

$$\chi^{(1)}(\omega) = \int d\tau R^{(1)}(\tau) e^{\mathrm{i}\omega\tau}.$$

Material response can be expanded in a perturbative series

$$P_{\alpha}^{(n)}(t) = \sum_{n=0}^{\infty} P_{\alpha}^{(n)}(t).$$

Linear response is the first-order term, characterized by the *susceptibility*

$$\chi^{(1)}(\omega) = \int d\tau R^{(1)}(\tau) e^{\mathrm{i}\omega\tau}.$$

Absorption spectroscopy probes the imaginary part:

$$A(\omega) = \frac{4\pi\omega\ell}{cn(\omega)\ln 10} \mathrm{Im}\chi(\omega).$$

Material response can be expanded in a perturbative series

$$P_\alpha^{(n)}(t) = \sum_{n=0}^{\infty} P_\alpha^{(n)}(t).$$

Linear response is the first-order term, characterized by the *susceptibility*

$$\chi^{(1)}(\omega) = \int d\tau R^{(1)}(\tau) e^{\mathrm{i}\omega\tau}.$$

Absorption spectroscopy probes the imaginary part:

$$A(\omega) = \frac{4\pi\omega\ell}{cn(\omega)\ln 10}\mathrm{Im}\chi(\omega).$$

Today: Nonlinear response

Outline for Today:

1. The Nonlinear Polarization
2. The Longitudinal and Transverse Fields
3. The Rare Medium Approximation

The Nonlinear Polarization

The Nonlinear Polarization

In **nonlinear materials**, Maxwell's equations are *complicated*:

$$
\begin{aligned}
\nabla \cdot \boldsymbol{E} &= -4\pi \nabla \cdot \boldsymbol{P}[\boldsymbol{E}] \\
\nabla \cdot \boldsymbol{B} &= 0 \\
\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} &= 0 \\
\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t} &= \frac{4\pi}{c}\frac{\partial \boldsymbol{P}[\boldsymbol{E}]}{\partial t}
\end{aligned}
$$

The Nonlinear Polarization

In **nonlinear materials**, Maxwell's equations are *complicated*:

$$\begin{aligned}
\nabla \cdot \boldsymbol{E} &= -4\pi \nabla \cdot \boldsymbol{P}[\boldsymbol{E}] \\
\nabla \cdot \boldsymbol{B} &= 0 \\
\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} &= 0 \\
\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t} &= \frac{4\pi}{c}\frac{\partial \boldsymbol{P}[\boldsymbol{E}]}{\partial t}
\end{aligned}$$

We need perturbative methods!

Is this a good idea?

Roughly speaking:

$$\text{Probability of } n\text{-th order processes} \propto \frac{1}{n!}\left(\frac{\text{Rate of excitation}}{\text{Rate of de-excitation}}\right)^n$$

Is this a good idea?

Roughly speaking:

$$\text{Probability of } n\text{-th order processes} \propto \frac{1}{n!}\left(\frac{\text{Rate of excitation}}{\text{Rate of de-excitation}}\right)^n$$

In direct sunlight:

- Chlorophyll *a* gets excited 10 times/second
- Chlorophyll excited states live for 1 ns.

Q: What's the probability of a nonlinear event?

Is this a good idea?

Roughly speaking:

$$\text{Probability of } n\text{-th order processes} \propto \frac{1}{n!}\left(\frac{\text{Rate of excitation}}{\text{Rate of de-excitation}}\right)^n$$

In direct sunlight:

- Chlorophyll *a* gets excited 10 times/second
- Chlorophyll excited states live for 1 ns.

Q: What's the probability of a nonlinear event?

A: Roughly 10^{-16}(!)

Is this a good idea?

Roughly speaking:

$$\text{Probability of } n\text{-th order processes} \propto \frac{1}{n!}\left(\frac{\text{Rate of excitation}}{\text{Rate of de-excitation}}\right)^n$$

In direct sunlight:

- Chlorophyll *a* gets excited 10 times/second
- Chlorophyll excited states live for 1 ns.

Q: What's the probability of a nonlinear event?

A: Roughly 10^{-16}(!)

For most materials, nonlinear processes happen only at very high intensities!

The Nonlinear Polarization

To build a perturbation theory, define the *nonlinear polarization*

$$\boldsymbol{P}^{(\mathsf{NL})}(\boldsymbol{x},t) = \boldsymbol{P}(\boldsymbol{x},t) - \boldsymbol{P}^{(1)}(\boldsymbol{x},t).$$

The Nonlinear Polarization

To build a perturbation theory, define the *nonlinear polarization*

$$\boldsymbol{P}^{(\mathsf{NL})}(\boldsymbol{x},t) = \boldsymbol{P}(\boldsymbol{x},t) - \boldsymbol{P}^{(1)}(\boldsymbol{x},t).$$

Key Point: We can solve the *linear* equations exactly. Exact knowledge of $\boldsymbol{P}^{(1)}(\boldsymbol{x},t)$ lets us study $\boldsymbol{P}^{(\mathsf{NL})}(\boldsymbol{x},t)$ perturbatively.

The Nonlinear Polarzation

Maxwell's Equations now become:

$$\nabla \cdot \left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)}\right) = -4\pi \boldsymbol{P}^{(\mathsf{NL})}$$

$$\nabla \cdot \boldsymbol{B} = 0$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0$$

$$\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial}{\partial t}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)}\right) = \frac{4\pi}{c}\frac{\partial \boldsymbol{P}^{(\mathsf{NL})}}{\partial t}$$

The Nonlinear Polarzation

Maxwell's Equations now become:

$$\nabla \cdot \left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)} \right) = -4\pi \boldsymbol{P}^{(\mathsf{NL})}$$

$$\nabla \cdot \boldsymbol{B} = 0$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0$$

$$\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial}{\partial t}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)} \right) = \frac{4\pi}{c}\frac{\partial \boldsymbol{P}^{(\mathsf{NL})}}{\partial t}$$

$$\Downarrow$$

$$\nabla \left(\nabla \cdot \boldsymbol{E} \right) - \nabla^2 \boldsymbol{E} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)} \right) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{P}^{(\mathsf{NL})}$$

The Nonlinear Polarzation

Maxwell's Equations now become:

$$\nabla \cdot \left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)} \right) = -4\pi \boldsymbol{P}^{(\mathsf{NL})}$$

$$\nabla \cdot \boldsymbol{B} = 0$$

$$\nabla \times \boldsymbol{E} + \frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t} = 0$$

$$\nabla \times \boldsymbol{B} - \frac{1}{c}\frac{\partial}{\partial t}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)} \right) = \frac{4\pi}{c}\frac{\partial \boldsymbol{P}^{(\mathsf{NL})}}{\partial t}$$

$$\Downarrow$$

$$\nabla \left(\nabla \cdot \boldsymbol{E} \right) - \nabla^2 \boldsymbol{E} + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\left(\boldsymbol{E} + 4\pi \boldsymbol{P}^{(1)} \right) = -\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{P}^{(\mathsf{NL})}$$

It looks (sort of) like the wave equation – but it's not!

Take-Home Point

In **nonlinear media** We can't solve Maxwell's equations exactly – so we use a perturbation expansion!

The **nonlinear polarization** $\boldsymbol{P}^{(\mathsf{NL})}$ is the part of the total polarization *not* captured by $\boldsymbol{P}^{(1)}$.

The equation governing **nonlinear processes** looks something like the wave equation, but with a nonlinear source on the right-hand side.

The Longitudinal and Transverse Fields

The Helmholtz Decomposition

As usual, solutions are easier in $\boldsymbol{k}$-space:

$$\boldsymbol{k}\left(\boldsymbol{k}\cdot\tilde{\boldsymbol{E}}\right)+k^2\tilde{\boldsymbol{E}}-\frac{\omega^2}{c^2}\left(\tilde{\boldsymbol{E}}+4\pi\tilde{\boldsymbol{P}}^{(1)}\right)=\frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}^{(\mathsf{NL})}.$$

The Helmholtz Decomposition

As usual, solutions are easier in $\boldsymbol{k}$-space:

$$\boldsymbol{k}\left(\boldsymbol{k}\cdot\tilde{\boldsymbol{E}}\right)+k^2\tilde{\boldsymbol{E}}-\frac{\omega^2}{c^2}\left(\tilde{\boldsymbol{E}}+4\pi\tilde{\boldsymbol{P}}^{(1)}\right)=\frac{4\pi\omega^2}{c^2}\tilde{\boldsymbol{P}}^{(\mathsf{NL})}.$$

Now decompose the field as the sum $\tilde{\boldsymbol{E}}=\tilde{\boldsymbol{E}}_{\parallel}+\tilde{\boldsymbol{E}}_{\perp}$ of two components

$$\tilde{\boldsymbol{E}}_{\parallel}(\boldsymbol{k},\omega)=\boldsymbol{k}\frac{\boldsymbol{k}\cdot\tilde{\boldsymbol{E}}(\boldsymbol{k},\omega)}{k^2}\qquad\leftarrow\qquad\text{Longitudinal Field}$$

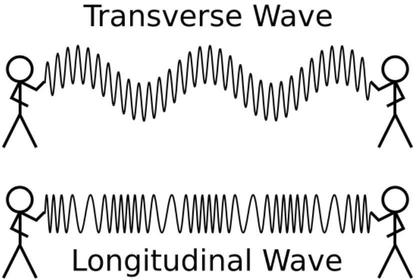
$$\tilde{\boldsymbol{E}}_{\perp}(\boldsymbol{k},\omega)=-\frac{\boldsymbol{k}\times\left(\boldsymbol{k}\times\tilde{\boldsymbol{E}}(\boldsymbol{k},\omega)\right)}{k^2}\qquad\leftarrow\qquad\text{Transverse Field.}$$

At any point in $\boldsymbol{k}$-space, $\tilde{\boldsymbol{E}}_{\parallel}$ is parallel to $\boldsymbol{k}$, and $\tilde{\boldsymbol{E}}_{\perp}$ is perpendicular!

Longitudinal vs. Transverse fields

Loosely speaking:

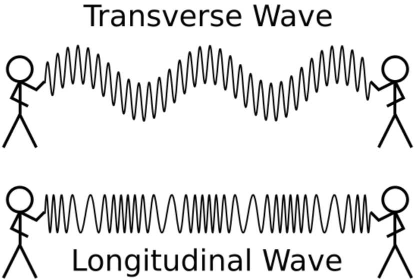
- Longitudinal fields are polarized along their propagation axis
- Transverse fields are polarized perpendicular to propagation axis



Longitudinal vs. Transverse fields

Loosely speaking:

- Longitudinal fields are polarized along their propagation axis
- Transverse fields are polarized perpendicular to propagation axis



Vacuum Waves: Longitudinal Or Transverse?

In vacuum MEs support only fields.

Vacuum Waves: Longitudinal Or Transverse?

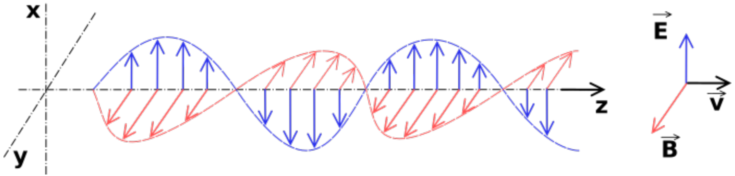
In vacuum MEs support only **transverse** fields.

Vacuum Waves: Longitudinal Or Transverse?

In vacuum MEs support only **transverse** fields.

$$\nabla \cdot \boldsymbol{E} = 0 \quad \Leftrightarrow \quad \boldsymbol{k} \cdot \tilde{\boldsymbol{E}} = 0$$

$$\nabla \cdot \boldsymbol{B} = 0 \quad \Leftrightarrow \quad \boldsymbol{k} \cdot \tilde{\boldsymbol{B}} = 0$$

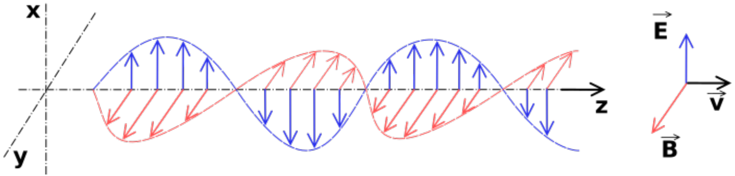


Vacuum Waves: Longitudinal Or Transverse?

In vacuum MEs support only **transverse** fields.

$$\nabla \cdot \boldsymbol{E} = 0 \quad \Leftrightarrow \quad \boldsymbol{k} \cdot \tilde{\boldsymbol{E}} = 0$$

$$\nabla \cdot \boldsymbol{B} = 0 \quad \Leftrightarrow \quad \boldsymbol{k} \cdot \tilde{\boldsymbol{B}} = 0$$



Longitudinal fields can exist only in matter!

$\Rightarrow$ not usually relevant to spectroscopy.

The Longitudinal and Transverse Fields

The HD splits one equation into two:

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

$$\Downarrow$$

$$-\tilde{\boldsymbol{E}}_{\parallel}+4\pi\tilde{\boldsymbol{P}}_{\parallel}^{(1)}=-4\pi\tilde{\boldsymbol{P}}_{\parallel}^{(\mathsf{NL})}$$

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

Looks like we could *almost* solve this. **But:** $\tilde{\boldsymbol{P}}_{\parallel}^{(\mathsf{NL})}$ and $\tilde{\boldsymbol{P}}_{\perp}^{(\mathsf{NL})}$ depend on the *total field*!

- Both equations are nonlinear.
- The equations are coupled.

Take-Home Points

The **Helmholz Decomposition** splits the EM field into *longitudinal* and *transverse* components.

The **longitudinal field** $E_{\|}$ is polarized *along* its propagation axis.

The **transverse field** $E_{\perp}$ is polarized *perpendicular* to its propagation axis.

In vacuum MEs support *only transverse fields*.

In matter ME $+$ HD gives a pair of coupled nonlinear equations that we cannot solve directly...

The Rare Medium Approximation

The Rare Medium Approximation

In **isotropic materials**, the problem is solved definitively by the *rare medium approximation*.

The Rare Medium Approximation

In **isotropic materials**, the problem is solved definitively by the *rare medium approximation*. Let

$$\boldsymbol{E} = \boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)} + \boldsymbol{E}^{(\text{NL})},$$

where

- $\boldsymbol{E}$ is the total field
- $\boldsymbol{E}_{\text{ext}}$ is the field *without the material*
- $\boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)}$ is the solution to Maxwell's equations *under linear response* .

The Rare Medium Approximation

Key Point: The linear field $\boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)}$ is *exactly solvable* and, for most systems, dominates the response.

The Rare Medium Approximation

Key Point: The linear field $\boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)}$ is *exactly solvable* and, for most systems, dominates the response.

This suggests an approximation:

$$\boldsymbol{P}^{(\mathrm{NL})}[\boldsymbol{E}] \approx \boldsymbol{P}^{(\mathrm{NL})}\left[\boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)}\right],$$

The Rare Medium Approximation

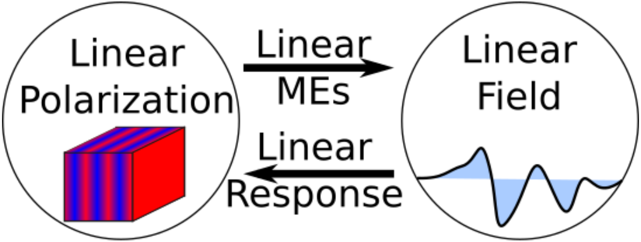
Key Point: The linear field $\boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)}$ is *exactly solvable* and, for most systems, dominates the response.

This suggests an approximation:

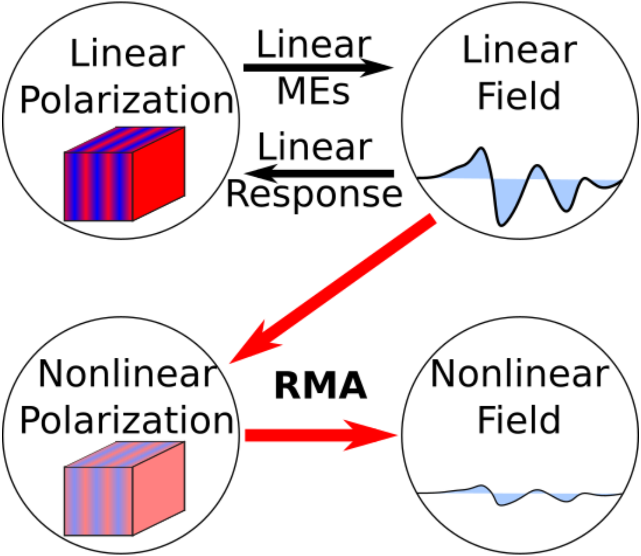
$$\boldsymbol{P}^{(\text{NL})}[\boldsymbol{E}] \approx \boldsymbol{P}^{(\text{NL})}\left[\boldsymbol{E}_{\text{ext}} + \boldsymbol{E}^{(1)}\right],$$

Now the nonlinear response is simply a *knowable* functional of a *known* quantity – this can be solved exactly!

The Rare Medium Approximation



The Rare Medium Approximation



The Longitudinal Field

This makes life much better.

Under the RMA, the equation for $\tilde{\boldsymbol{E}}_{\parallel}$ is *algebraic*:

$$\tilde{\boldsymbol{E}}_{\parallel}^{(\mathsf{NL})} = -4\pi \tilde{\boldsymbol{P}}_{\parallel}^{(\mathsf{NL})} \left[\tilde{\boldsymbol{E}}_{\mathsf{ext}} + \tilde{\boldsymbol{E}}^{(1)} \right].$$

The field is non-zero only where the polarization is non-zero.

The Longitudinal Field

This makes life much better.

Under the RMA, the equation for $\tilde{\boldsymbol{E}}_{\parallel}$ is *algebraic*:

$$\tilde{\boldsymbol{E}}_{\parallel}^{(\mathsf{NL})} = -4\pi\tilde{\boldsymbol{P}}_{\parallel}^{(\mathsf{NL})}\left[\tilde{\boldsymbol{E}}_{\mathsf{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right].$$

The field is non-zero only where the polarization is non-zero.

$\Rightarrow$ The longitudinal field vanishes outside the sample.

The Longitudinal Field

This makes life much better.

Under the RMA, the equation for $\tilde{\boldsymbol{E}}_{\parallel}$ is *algebraic*:

$$\tilde{\boldsymbol{E}}_{\parallel}^{(\mathsf{NL})} = -4\pi\tilde{\boldsymbol{P}}_{\parallel}^{(\mathsf{NL})}\left[\tilde{\boldsymbol{E}}_{\mathsf{ext}} + \tilde{\boldsymbol{E}}^{(1)}\right].$$

The field is non-zero only where the polarization is non-zero.

$\Rightarrow$ The longitudinal field vanishes outside the sample.
$\Rightarrow$ **The longitudinal polarization does not radiate!**

The Transverse Field

The **transverse field** follows the inhomogeneous wave equation, with the nonlinear polarization as a source:

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

The Transverse Field

The **transverse field** follows the inhomogeneous wave equation, with the nonlinear polarization as a source:

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

The transverse field radiates! In isotropic media, *the transverse field drives all nonlinear processes*!

Take-Home Points

In most materials, the **nonlinear response** is much weaker than the *linear response*.

Under the **rare medium approximation**:

- The linear equations are solved exactly

Take-Home Points

In most materials, the **nonlinear response** is much weaker than the *linear response*.

Under the **rare medium approximation**:

- The linear equations are solved exactly
- The *linear* field induces a *nonlinear* polarization

Take-Home Points

In most materials, the **nonlinear response** is much weaker than the *linear response*.

Under the **rare medium approximation**:

- The linear equations are solved exactly
- The *linear* field induces a *nonlinear* polarization
- The *transverse nonlinear polarization* acts as a source for the radiated *transverse nonlinear field*