Module 2 Review: Response Theory and Spectroscopy
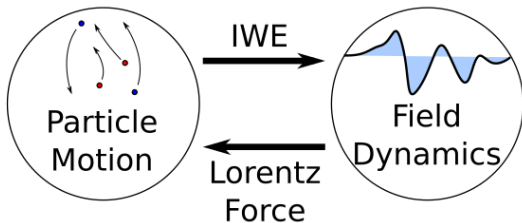
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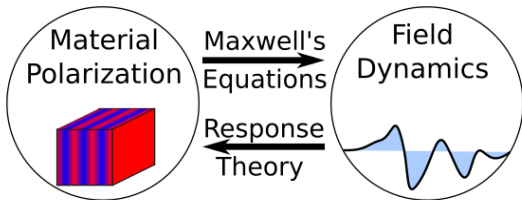
October 26, 2020

Microscopic electrodynamics:

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Take-home: Response Theory

In *response theory*, we study how the material *polarization responds to the electric field*.

Physical constraints:
- locality
- causality
- stability
- time-translation invariance

strongly limit the possible forms for the **mathematical** dependence of $\boldsymbol{P}$ on $\boldsymbol{E}$:

$$
P_\alpha^{(n)}(t) = \sum_{\alpha_1,...,\alpha_n} \int_{-\infty}^{\infty} d\tau_n ... \int_{-\infty}^{\infty} d\tau_1 R_{\alpha_1...\alpha_n\alpha}^{(n)}(\tau_1,...,\tau_n)
$$
$$
\times E_{\alpha_1}(t - \tau_1 - ... - \tau_n) E_{\alpha_2}(t - \tau_2 - ... - \tau_n) ... E_{\alpha_n}(t - \tau_n).
$$

Neumann's principle: Spatial symmetries in the material must be reflected in the response tensors $R_{\alpha_1 \dots \alpha_n \alpha}(\tau_1, \dots, \tau_n)$.

In **isotropic media**:

- Response elements with unpaired axes vanish
- Surviving elements are symmetry-related
- Even-order spectroscopies are forbidden – hence useful for detecting defects

Take-Home: Linear Response
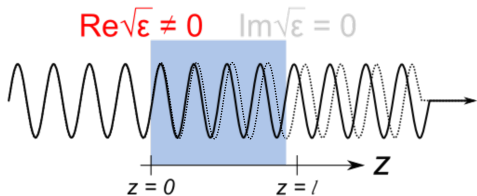
Linear Response: $R^{(1)}$ dominates when

- Field intensity is low
- Material response is weak
- Field is **not** resonant with material frequencies

In **isotropic media** linear response is governed by *scalar* quantities:
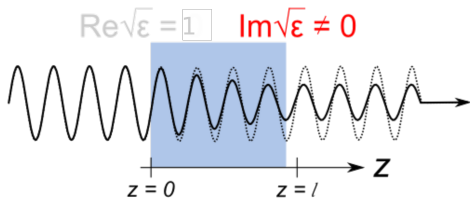
- The response function $R^{(1)}(\tau)$ **or**
- the *susceptibility* $\chi(\omega) = \int d\tau R^{(1)}(\tau)e^{i\omega\tau}$ **or**
- the *permittivity* $\varepsilon(\omega) \equiv 1 + 4\pi\chi(\omega)$

Under linear response, solutions to MEs resemble propagating waves with **attenuated amplitude** and **shifting phase** due to $\varepsilon(\omega)$.

Linear Processes

$$\boldsymbol{E}(\boldsymbol{x}, t) \propto \mathrm{e}^{\mathrm{i}\omega\left(\frac{z}{c}\sqrt{\varepsilon(\omega)}-t\right)}$$

Re$\sqrt{\varepsilon} \neq 0$ Im$\sqrt{\varepsilon} = 0$

$z = 0$ $z = l$

The *refractive index* $n(\omega) \equiv \mathrm{Re}\sqrt{\varepsilon(\omega)}$ decreases the wavelength: dispersion.

Re$\sqrt{\varepsilon} = 1$ Im$\sqrt{\varepsilon} \neq 0$

$z = 0$ $z = l$

The *extinction coefficient* $\kappa(\omega) \equiv \mathrm{Im}\sqrt{\varepsilon(\omega)}$ decreases the amplitude.

In isotropic media linear response is characterized by *scalar quantities*:

- Response function $R^{(1)}(\tau)$
- *Susceptibility* $\chi^{(1)}(\omega) = \int d\tau R^{(1)}(\tau) e^{i\omega\tau}$
- *Permittivity* $\varepsilon(\omega) \equiv 1 + 4\pi\chi(\omega)$
- *Extinction coefficient:* $\kappa(\omega) \equiv \mathsf{Im}\sqrt{\varepsilon(\omega)}$
- *Refractive index:* $n(\omega) \equiv \mathsf{Re}\sqrt{\varepsilon(\omega)}$

Absorption spectroscopy monitors $\kappa(\omega) \approx \mathsf{Im}\chi^{(1)}$.

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

The **nonlinear polarization** $\boldsymbol{P}^{(\text{NL})}$ 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.

Take-Home: Nonlinear Response

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

The **longitudinal field** $E_\parallel$ is polarized *along* its propagation axis.

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

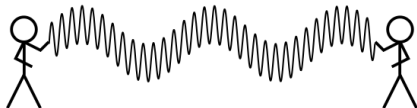*In vacuum* MEs support *only transverse fields*.

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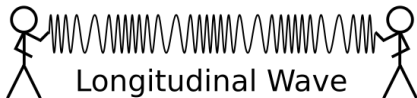
Loosely speaking:

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


Transverse Wave

Longitudinal Wave

Take-Home: Nonlinear Response

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*
- The emitted *nonlinear field* has (roughly) the same frequency and propagation axis as the *nonlinear polarization* that drives it.
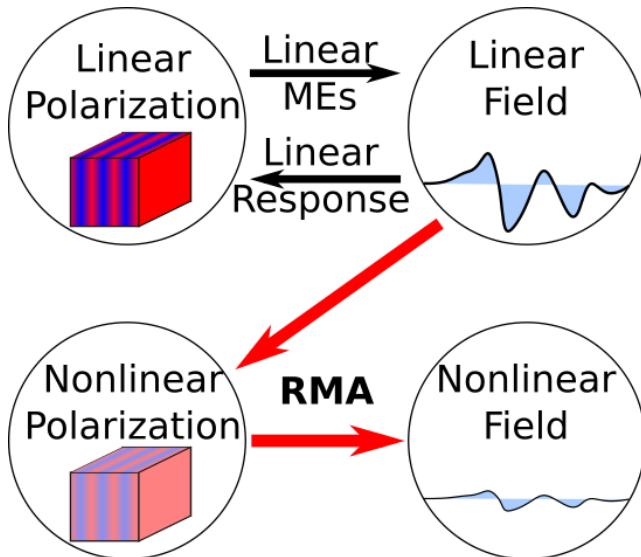
The nonlinear polarization *must* satisfy:

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

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.

A nonlinear *polarization* can only emit a *nonlinear 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: $k \approx \frac{n(\omega)}{c}\omega$.

Fluorescence corresponds to radiation of light from a completely *dephased* sample – the phase of each microscopic emitter is random!

This process falls **outside** the scope of *our development* of response theory since the average field is zero. (Though it can be related!)

Even though the mean *field* vanishes, the mean *intensity* – and hence the radiant energy – is nonzero.

The **Stokes shift** between absorption and emission spectra results from the quantum population weighting of vibrational energy states.

Take-Home: Broadening

Two types of **broadening** in disordered systems:

- **Homogeneous broadening** affects all sites the same $\Rightarrow$ Single-site spectrum
- **Inhomogeneous broadening** affects each pigment differently $\Rightarrow$ Site-energy distribution

Low-temperature spectra are a **convolution** of the single-site spectrum and the site-energy distribution.

The **convolution** $f * g$ is an f-weighted average of all possible *shifted* copies of g.

Fourier transforms convert convolutions to products:

$$\widetilde{f * g} = \tilde{f} \cdot \tilde{g}$$

Take-Home: Hole Burning

Hole Burning monitors changes to low-temperature absorption due to narrow-band excitation.

The narrow-band laser **selectively excites** resonant pigments and "burns a hole" in the spectrum.

Hole burning can

- Separate homogeneous and inhomogeneous broadening effects
- Provide single-site spectra and site-energy distributions
- Give details on electronic/vibrational interactions
- Uncover excitonic interactions

Take-Home: Pump-probe

- Pump-probe setup:
  - Two pulsed lasers cross in a sample
  - $\Delta OD =$ "pump on" $-$ "pump off"
- Third-order process
  - Two interactions with "pump" pulse
  - One interaction with "probe" pulse
- Two pathways:
  - **Rephasing:** $-\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3$
  - **Nonrephasing:** $\boldsymbol{k}_1 - \boldsymbol{k}_2 + \boldsymbol{k}_3$
- As a function of time delay:
  - Does **not** oscillate at high frequencies
  - Monitors **dissipation**
  - **Not** sensitive to dephasing
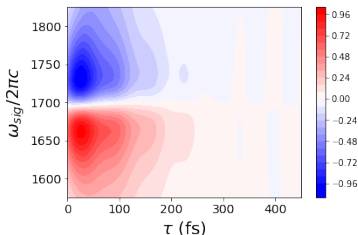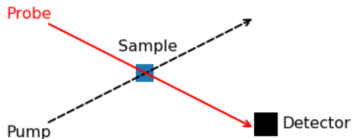
2D Spectroscopy is a generalization of pump-probe spectroscopy, where both **excitation** and **detection** frequencies are resolved.

Four basic types of 2D spectrum:
- Double-Quantum Coherence
- Nonrephasing
- Rephasing
- Correlation = R + NR

Diagonal vs. **Antidiagonal** linewidths distinguish homogeneous and inhomogeneous broadening

Cross-peaks indicate coupling and energy transfer