

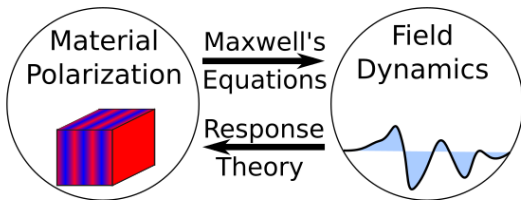
Response Theory

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Previously on CHM676...

In homogeneous dielectric materials, the dynamics of \mathbf{E} and \mathbf{B} are determined by the polarization density \mathbf{P} .



Today: How does \mathbf{P} respond to the field?

Outline for Today:

- 1 Physical Guidelines
- 2 Mathematical Framework
- 3 Symmetry and Invariance of Response Tensors

Physical Guidelines

Physical Guidelines

We study P as a *functional* of E and B :

$$P(\mathbf{x}, t) = P[E(\mathbf{x}', t'), B(\mathbf{x}', t')].$$

Physically, we expect:

- Response to B is negligible
- Response is *local*: $P(\mathbf{x})$ depends only on $E(\mathbf{x})$.
- Response is *causal*: $P(t)$ depends only on $E(t' \leq t)$.
- Response is *stable*:
 - Must exist a time scale δt *below* which P no longer cares about variations in $E(t + \delta t)$
 - Must exist a time scale T *beyond* which P doesn't remember $E(t - T)$.

Take-Home Point

Physical constraints:

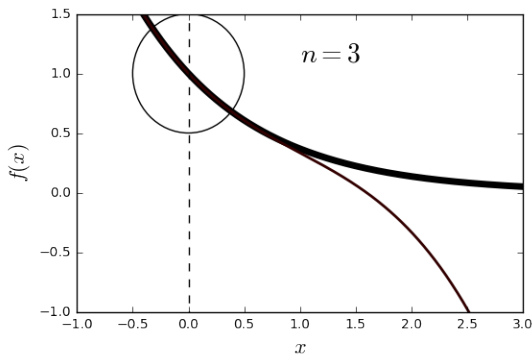
- locality
- causality
- stability

strongly limit the possible forms for the **mathematical** dependence of P on E .

Mathematical Framework

Mathematical Framework

The *response theory* framework is essentially a Taylor series expansion for functionals.



$$f(x) \approx f(0) + \left. \frac{df}{dx} \right|_{x=0} x + \frac{1}{2} \left. \frac{d^2 f}{dx^2} \right|_{x=0} x^2 + \frac{1}{6} \left. \frac{d^3 f}{dx^3} \right|_{x=0} x^3 \dots$$

Mathematical Framework

The Taylor series of a multi-variable function $g(x_1, \dots, x_N)$ looks like:

$$\begin{aligned}
 g(x_1, \dots, x_N) = & g(0, \dots, 0) \\
 & + \frac{\partial g}{\partial x_1} \Big|_{\mathbf{x}=\mathbf{0}} x_1 + \frac{\partial g}{\partial x_2} \Big|_{\mathbf{x}=\mathbf{0}} x_2 + \dots + \frac{\partial g}{\partial x_N} \Big|_{\mathbf{x}=\mathbf{0}} x_N \\
 & + \frac{1}{2!} \frac{\partial^2 g}{\partial x_1^2} \Big|_{\mathbf{x}=\mathbf{0}} x_1^2 + \frac{\partial g}{\partial x_1 \partial x_2} \Big|_{\mathbf{v}=\mathbf{0}} x_1 x_2 + \dots + \frac{1}{2!} \frac{\partial^2 g}{\partial x_N^2} \Big|_{\mathbf{x}=\mathbf{0}} x_N^2 \\
 & + \dots
 \end{aligned}$$

What is the corresponding expansion for a functional like $P[\mathbf{E}]$?

Mathematical Framework

Since the response is stable, we can sample \mathbf{E} at a finite number of time points:

$$P_I(t) \approx f_I(E_x(t_0), E_y(t_0), E_z(t_0), E_x(t_1), \dots, E_z(t_N); t, \delta t, T).$$

Expanding in a Taylor series:

$$\begin{aligned} P_I(t) \approx & f_I(0, \dots, 0; t, \delta t, T) \\ & + \frac{\partial f_I}{\partial E_x(t_0)} \Big|_{\mathbf{E}=\mathbf{0}} E_x(t_0) + \dots + \frac{\partial f_I}{\partial E_z(t_N)} \Big|_{\mathbf{E}=\mathbf{0}} E_z(t_N) \\ & + \frac{1}{2!} \frac{\partial^2 f_I}{\partial [E_x(t_0)]^2} \Big|_{\mathbf{E}=\mathbf{0}} [E_x(t_0)]^2 + \frac{\partial^2 f_I}{\partial E_x(t_0) \partial E_y(t_0)} \Big|_{\mathbf{E}=\mathbf{0}} E_x(t_0) E_y(t_0) + \dots \end{aligned}$$

Mathematical Framework

As our sampling points get closer together, the sums converge to integrals:

$$\begin{aligned}
 P(t) = & \sum_{n=0}^{\infty} \sum_{\alpha_1, \dots, \alpha_n} \int_{-\infty}^t dt_n \int_{-\infty}^{t_n} dt_{n-1} \dots \int_{-\infty}^{t_2} dt_1 \\
 & \times E_{\alpha_1}(t_1) E_{\alpha_2}(t_2) \dots E_{\alpha_n}(t_n) \\
 & \times R_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(t, t_n, t_{n-1}, \dots, t_1)
 \end{aligned}$$

where $R_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(t, t_n, t_{n-1}, \dots, t_1)$ is the n^{th} -order *response function** – the target of n^{th} -order spectroscopies.

*Almost. Actually $R^{(n)}$ depends only on time *differences*. Stay tuned!

Symmetry and Invariance of Response Tensors

Time-translation Invariance

All systems we study will satisfy **time-translation invariance**: Only time *differences* matter!

$$R_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(t, t_n, t_{n-1}, \dots, t_1) \Rightarrow R_{\alpha_1 \dots \alpha_n \alpha}^{(n)}(t - t_n, t_n - t_{n-1}, \dots, t_2 - t_1)$$

Rearranging:

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

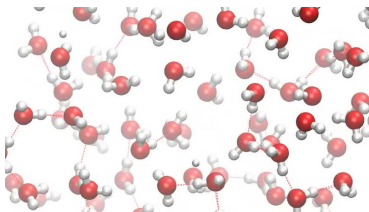
Causality dictates that $R_{\alpha_1, \dots, \alpha_n, \alpha}^{(n)}$ is non-zero only for *positive time delays*.

Spatial Symmetries

Neumann's Principle: Spatial symmetries of the material *must* be reflected in the response tensor.

This **dramatically** simplifies the analysis of nonlinear experiments!

NB: Only *macroscopic* symmetry is relevant!

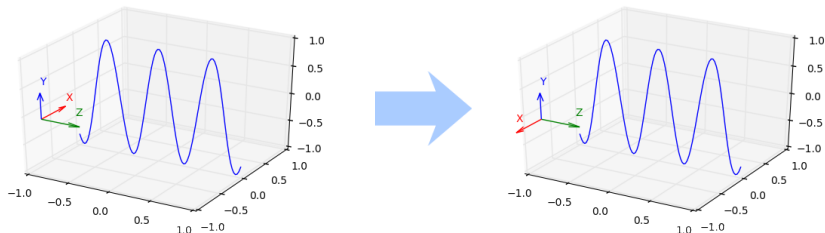


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Spatial Symmetries

Example: $R_{xy}^{(1)}$ in an isotropic sample

Suppose \mathbf{E} is polarized along the y -axis. What happens to $P_x^{(1)}$ when we invert the y -axis?



Nothing!

Spatial Symmetries

Under y -axis inversion:

- $y \rightarrow -y$
- $P_x^{(1)} \rightarrow P_x^{(1)}$
- $E_y \rightarrow -E_y$
- $R_{xy} \rightarrow R_{xy} \Leftarrow$ **Neumann's Principle**

But response theory says:

$$P_x^{(1)}(t) = \int_{-\infty}^{\infty} d\tau_1 R_{xy}^{(1)}(\tau_1) E_y(t - \tau_1) = -P_x^{(1)}(t).$$

The only possible conclusion is that $R_{xy}^{(1)} = 0$!

Spatial Symmetries

More generally: In isotropic media

- All tensor elements with an odd number *of any index* vanish (e.g., $R_{xxxy}^{(3)} = 0$)
- Corollary: all even-order response functions vanish(!)
- Response tensor elements are symmetry-related (e.g., $R_{xxyy}^{(3)} = R_{yyxx}^{(1)}$)

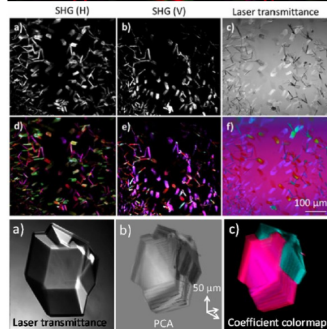
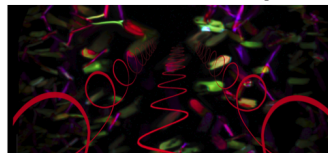
Even-Order Spectroscopies

But remember: Not all materials are isotropic

Even-order spectroscopies are *specifically sensitive* to material boundaries
 \Rightarrow Imaging!



Garth Simpson



Take-Home Points

Time-translation invariance and **causality** dictate that response functions depend only on *positive time delays* between interactions.

Spatial symmetries in the material must be reflected in the response tensors.

In **isotropic media**:

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