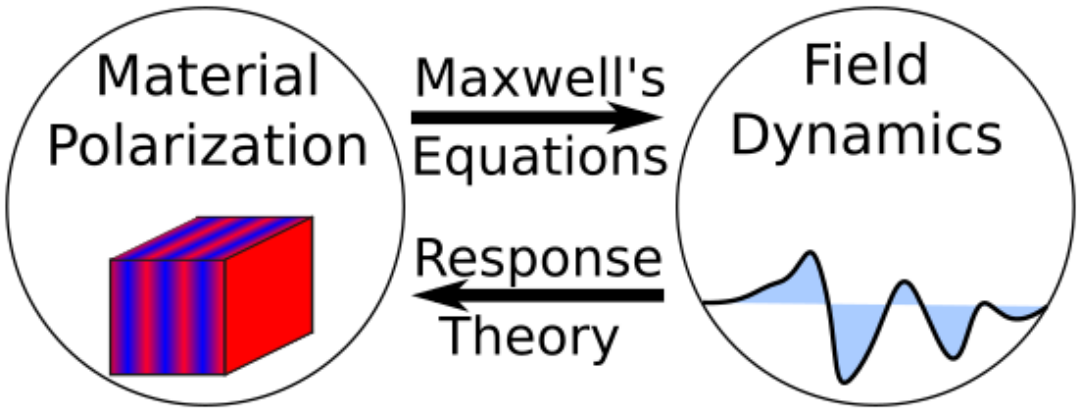
Response Theory

Mike Reppert

September 28, 2020

Previously on CHM676...

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



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

Outline for Today:

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

Physical Guidelines

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We study $\boldsymbol{P}$ as a *functional* of $\boldsymbol{E}$ and $\boldsymbol{B}$:

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  - Must exist a time scale T *beyond* which $\boldsymbol{P}$ doesn't remember $\boldsymbol{E}(t - T)$.

Take-Home Point

Physical constraints:

- locality
- causality
- stability

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

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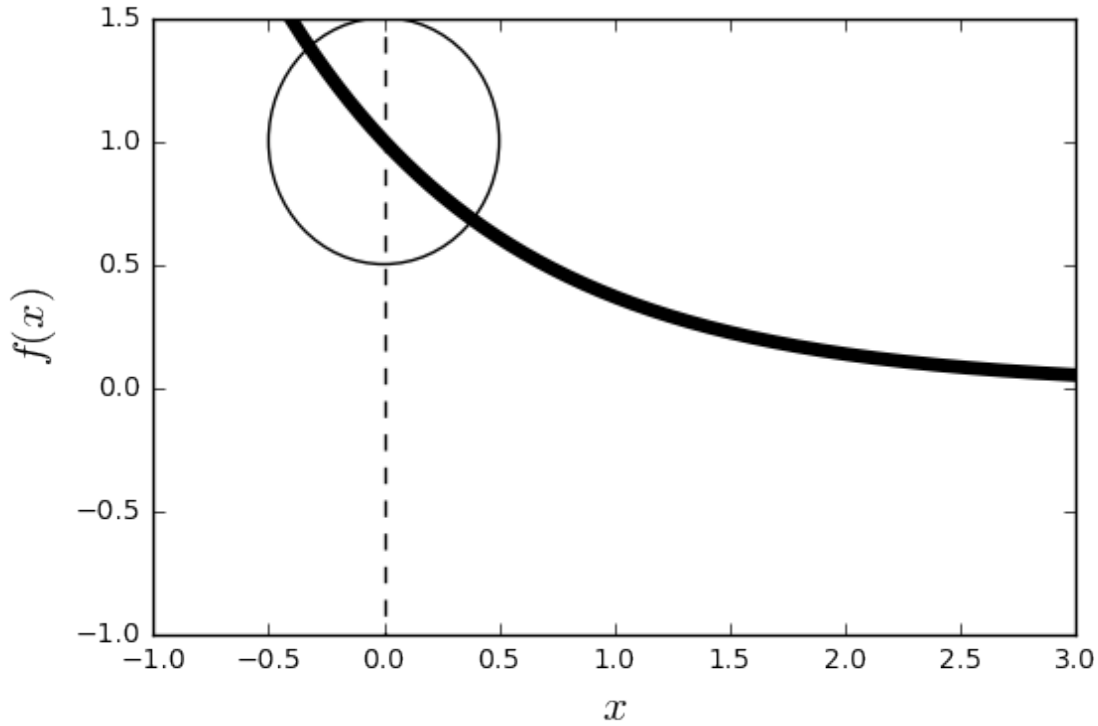

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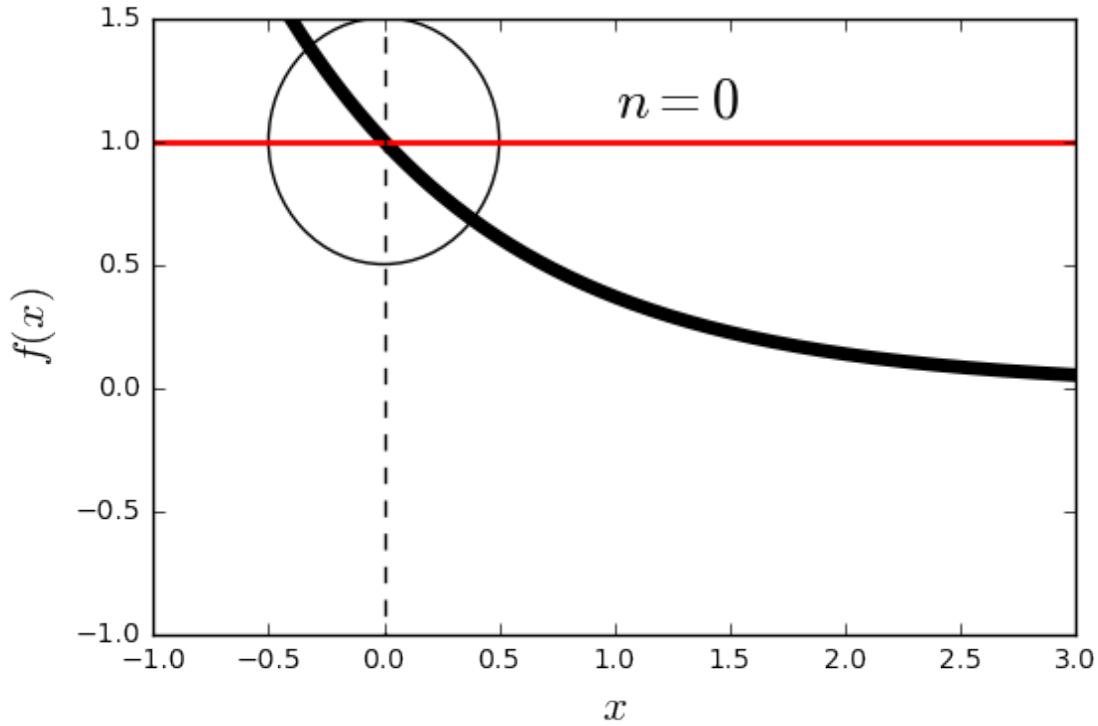

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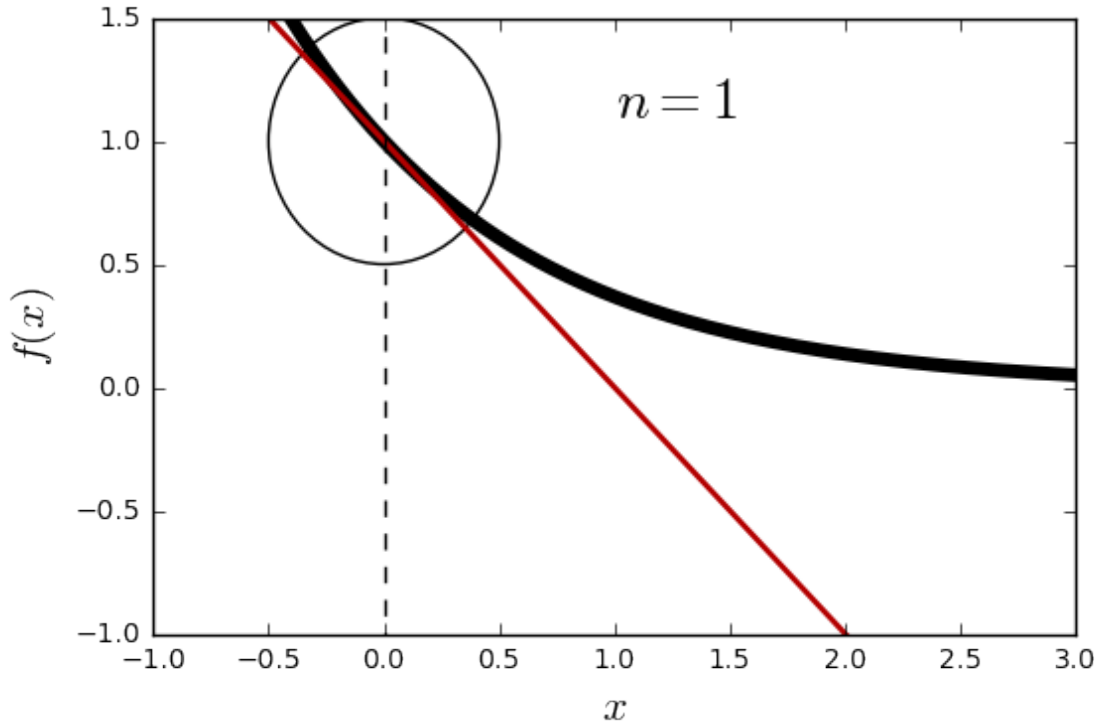

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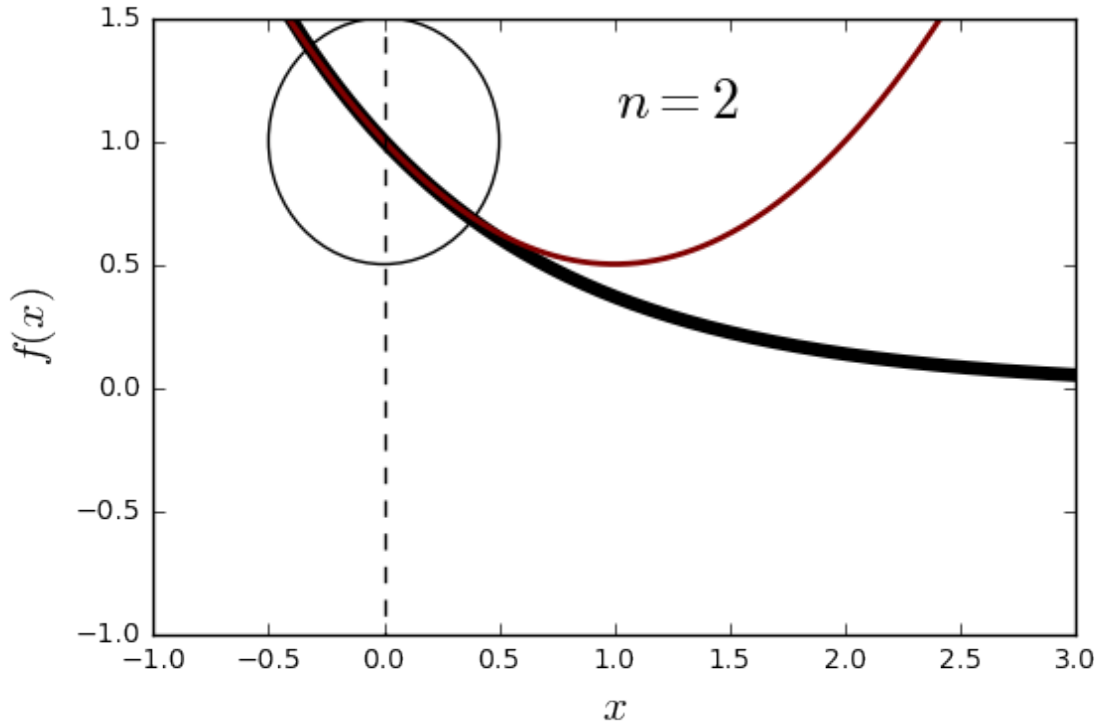

$$f(x) \approx f(0) + \left.\frac{df}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2 f}{dx^2}\right|_{x=0} x^2$$

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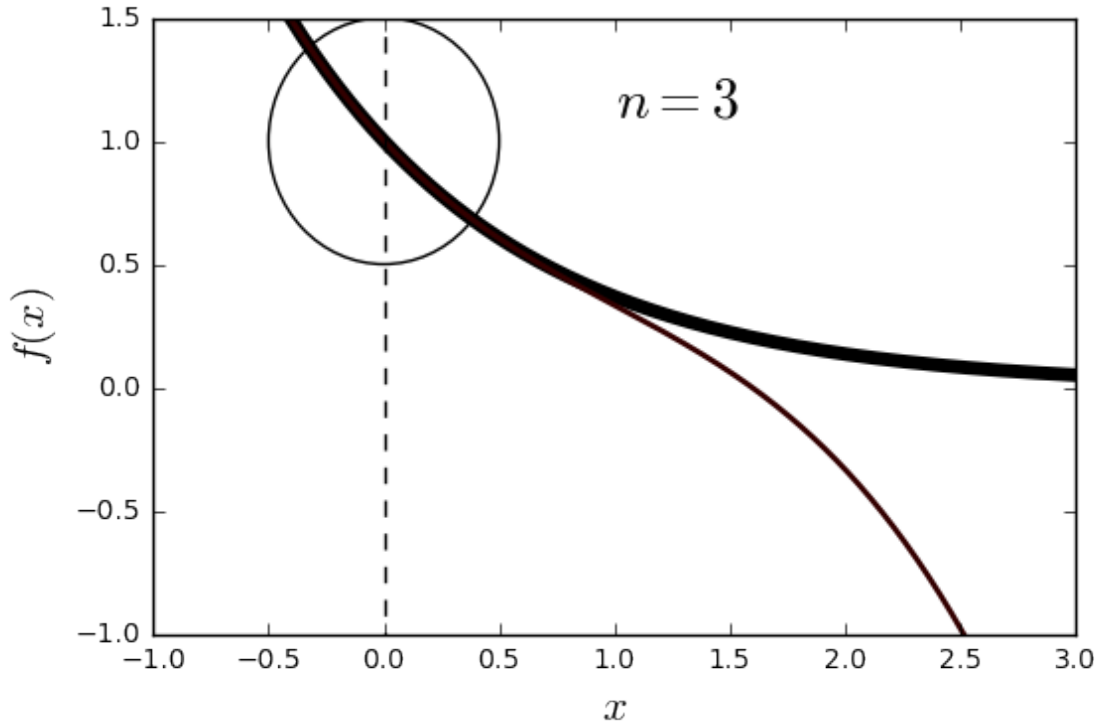

$$f(x) \approx f(0) + \left.\frac{df}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2 f}{dx^2}\right|_{x=0} x^2 + \frac{1}{6}\left.\frac{d^3 f}{dx^3}\right|_{x=0} x^3 \ldots$$

Mathematical Framework

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

$$g(x_1, ..., x_N) = g(0, ..., 0) + \left.\frac{\partial g}{\partial x_1}\right|_{\boldsymbol{x}=\mathbf{0}} x_1 + \left.\frac{\partial g}{\partial x_2}\right|_{\boldsymbol{x}=\mathbf{0}} x_2 + ... + \left.\frac{\partial g}{\partial x_N}\right|_{\boldsymbol{x}=\mathbf{0}} x_N + \left.\frac{1}{2!}\frac{\partial^2 g}{\partial x_1^2}\right|_{\boldsymbol{x}=\mathbf{0}} x_1^2 + \left.\frac{\partial g}{\partial x_1 \partial x_2}\right|_{\boldsymbol{v}=\mathbf{0}} x_1 x_2 + ... + \left.\frac{1}{2!}\frac{\partial^2 g}{\partial x_N^2}\right|_{\boldsymbol{x}=\mathbf{0}} x_N^2 + ...$$

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

Mathematical Framework

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

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

Expanding in a Taylor series:

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

Mathematical Framework

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

$$\boldsymbol{P}(t) = \sum_{n=0}^{\infty} \sum_{\alpha_1,\ldots,\alpha_n} \int_{-\infty}^{t} dt_n \int_{-\infty}^{t_n} dt_{n-1} \ldots \int_{-\infty}^{t_2} dt_1 \times E_{\alpha_1}(t_1) E_{\alpha_2}(t_2) \ldots E_{\alpha_n}(t_n) \times R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t, t_n, t_{n-1}, \ldots, t_1)$$

where $R^{(n)}_{\alpha_1 \ldots \alpha_n \alpha}(t, t_n, t_{n-1}, \ldots, t_1)$ 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!

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

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Rearranging:

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

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

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

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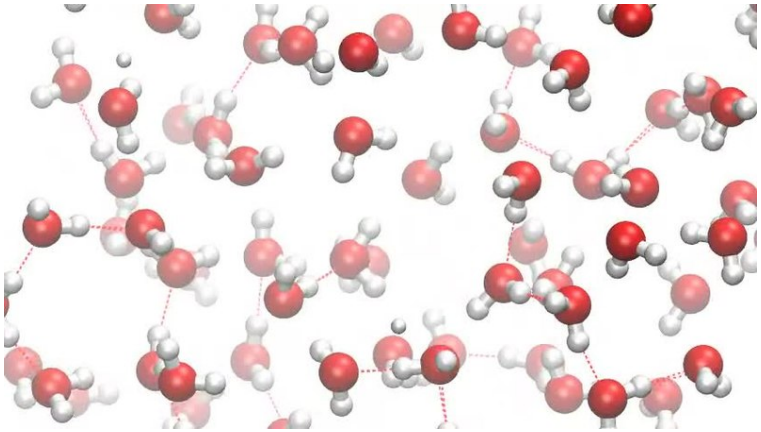
NB: Only *macroscopic* symmetry is relevant!

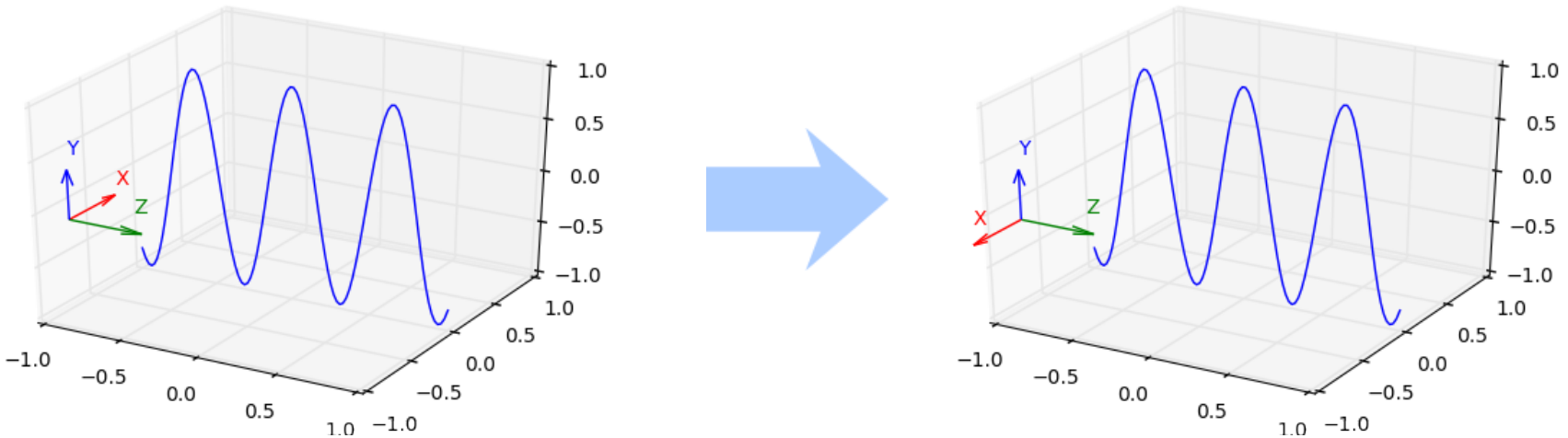


https://commons.wikimedia.org/wiki/File:A_Molecular_Dynamics_Simulation_of_Liquid_Water_at_298_K.webm

Spatial Symmetries

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

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



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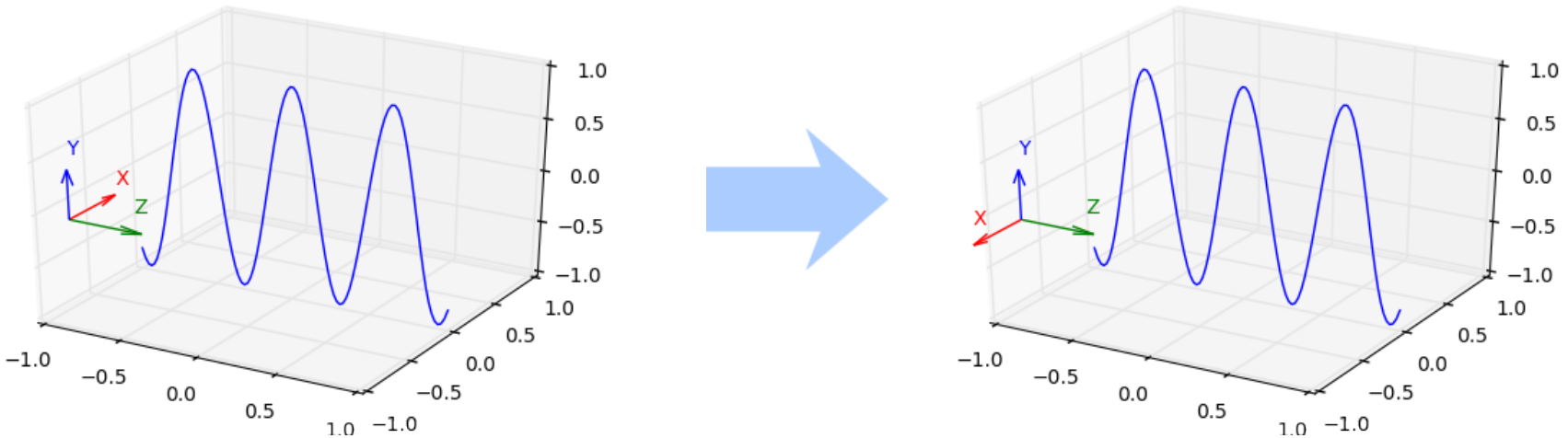

Nothing!

Spatial Symmetries

Under y-axis inversion:

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

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- Corollary: all even-order response functions vanish(!)
- Response tensor elements are symmetry-related (e.g., $R^{(3)}_{xxyy} = R^{(1)}_{yyxx}$)

Even-Order Spectroscopies

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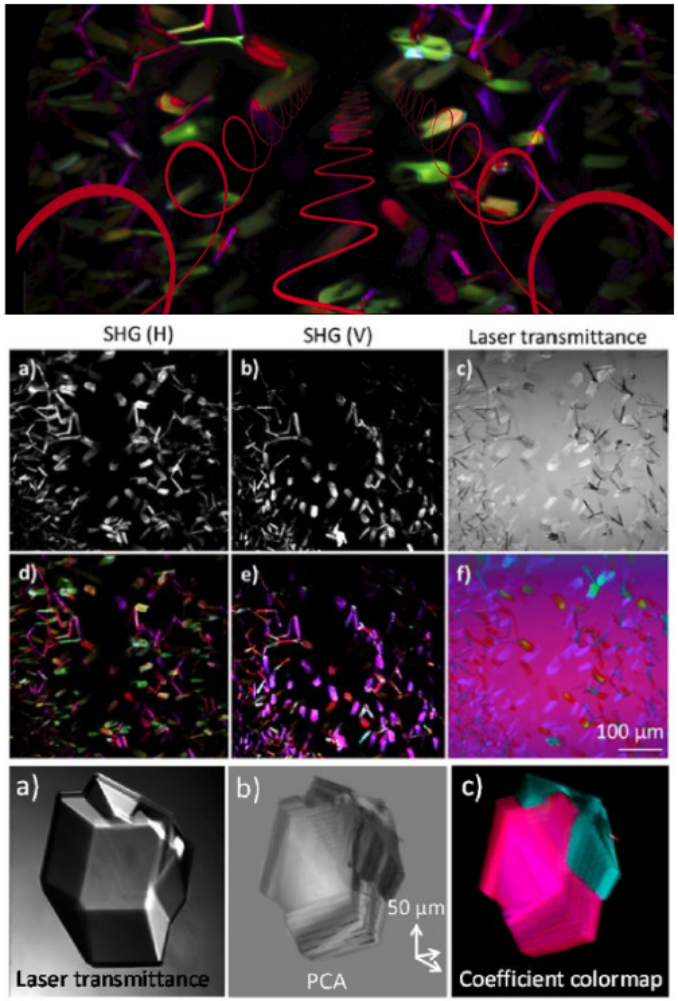
Garth Simpson



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