Designing *ab initio* calculations

Francesco Sottile

École Polytechnique, Palaiseau - France
European Theoretical Spectroscopy Facility (ETSF)

22 October 2010

Outline

Engineering problem $\rightarrow$ atomistic model

Computation of the physical properties

Validation

Connection with measurable quantities

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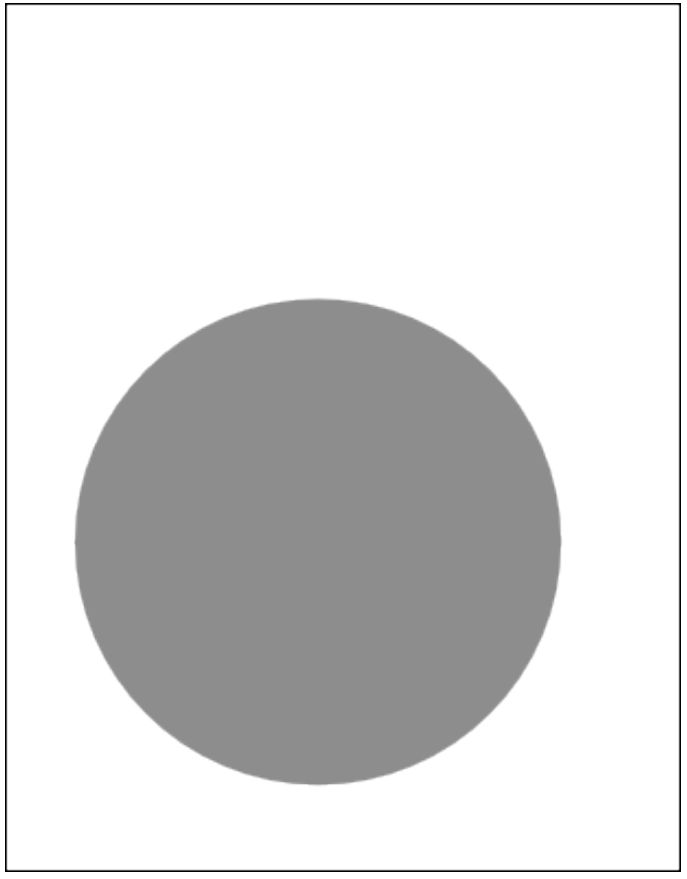
- Catalytic system
- Construction of surface adsorption site
- Water adsorbtion
- Photon absorption $\{e^- \; h^+\}$
- Charge separation
- Suppression of recombination
- Migration to surface reaction sites
- Construction of surface reaction site for H_2 and O_2



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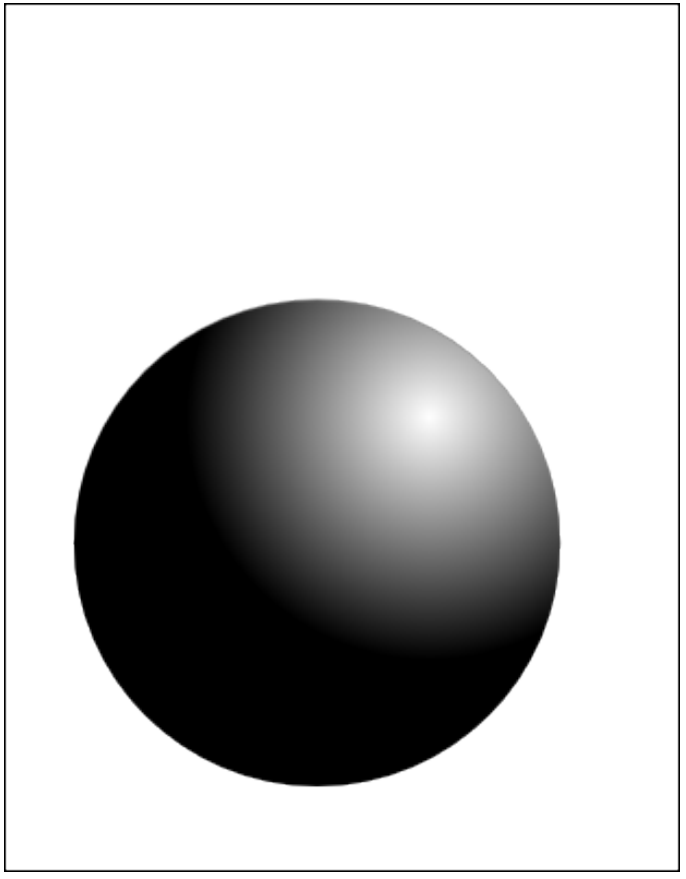

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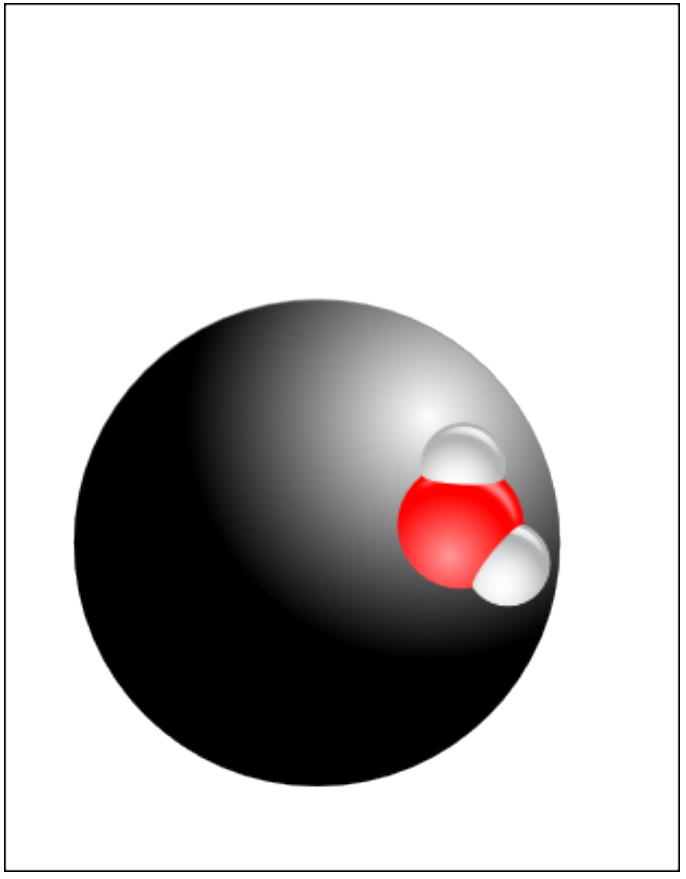

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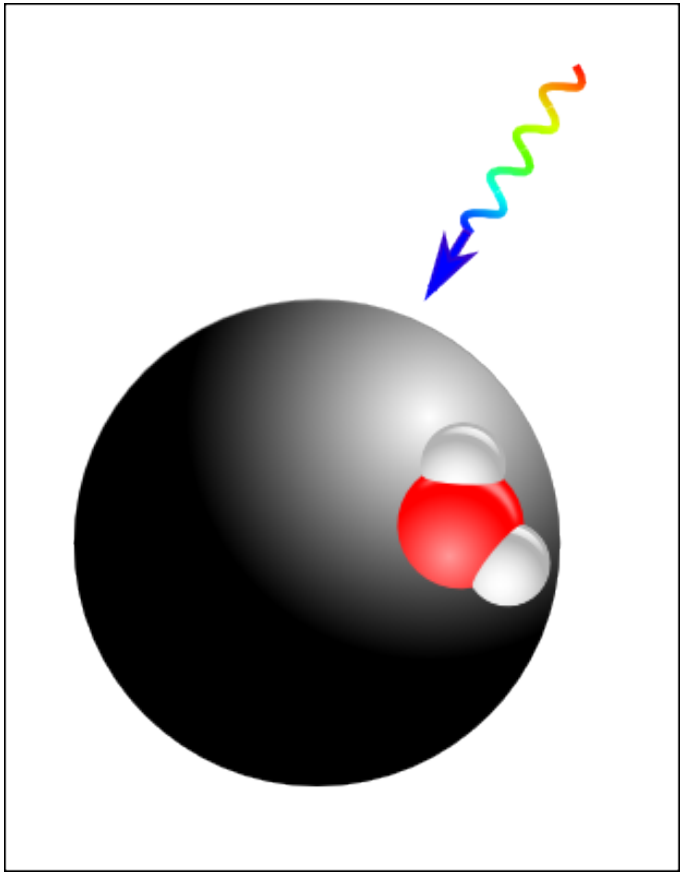

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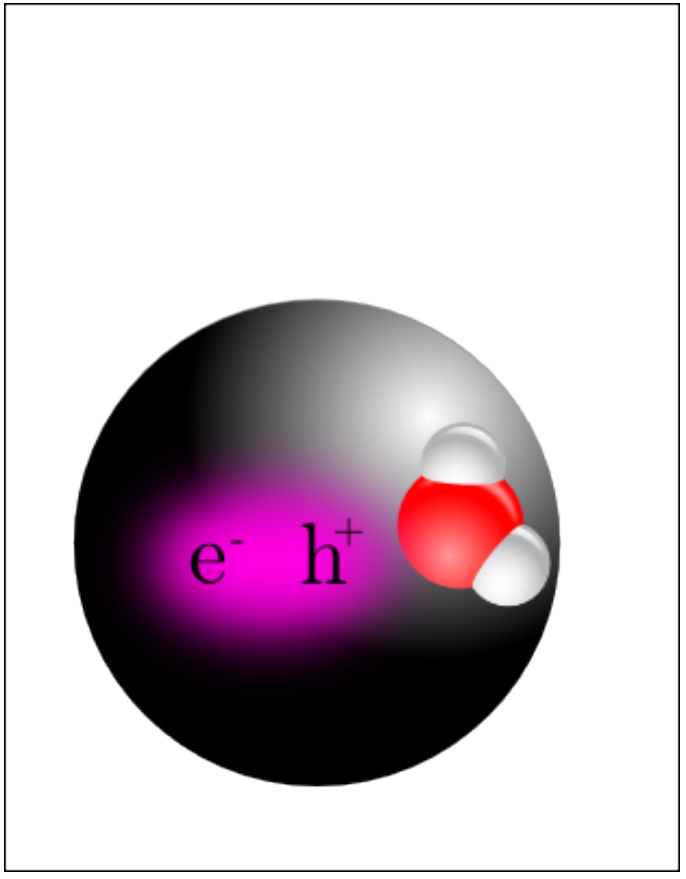

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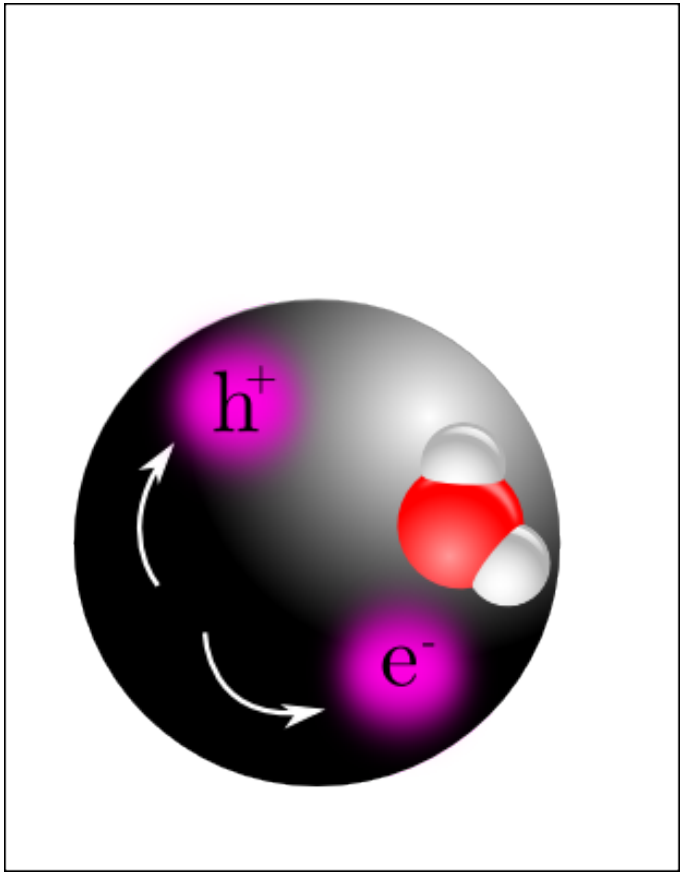

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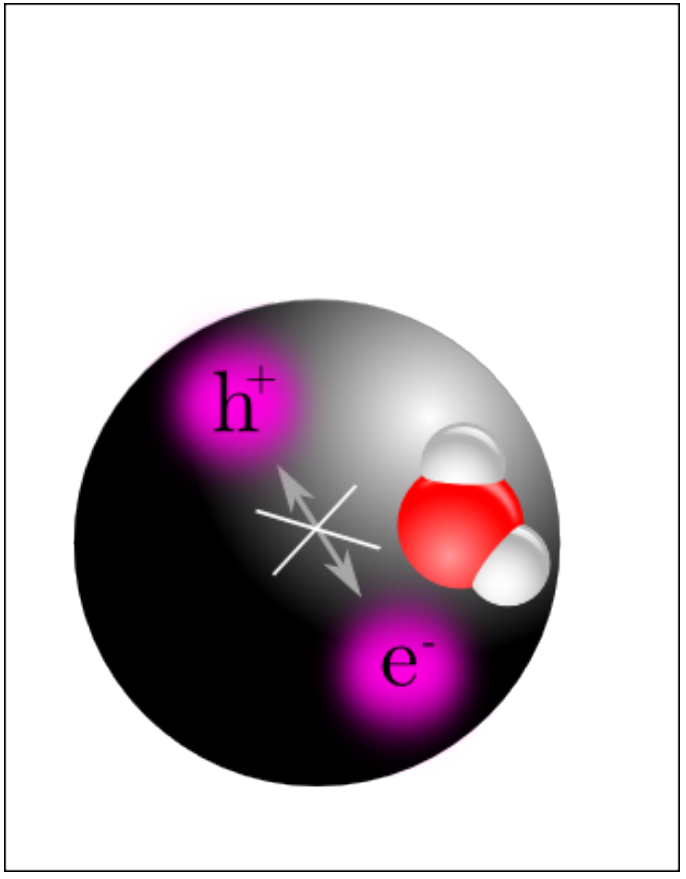

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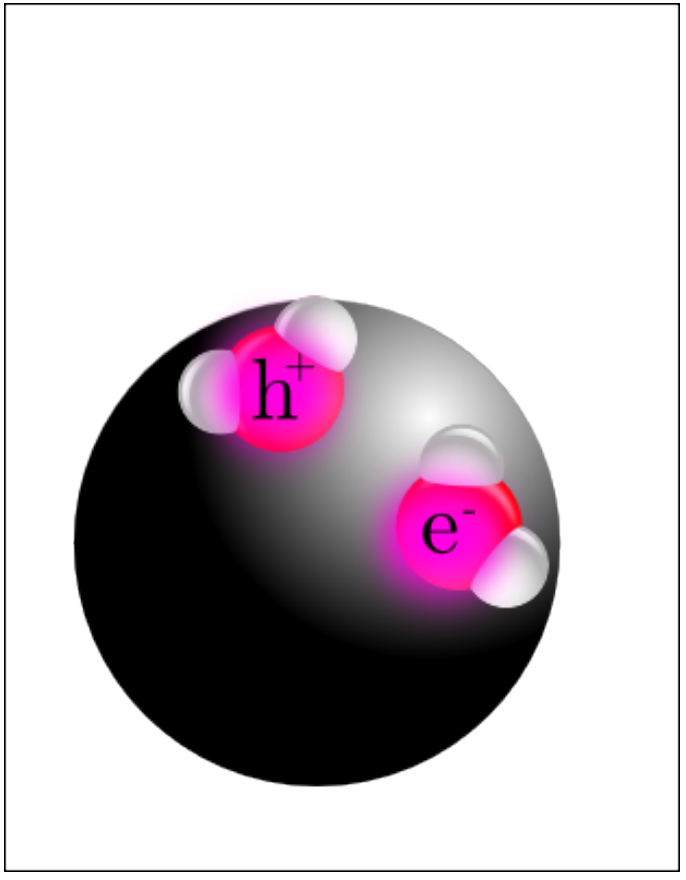

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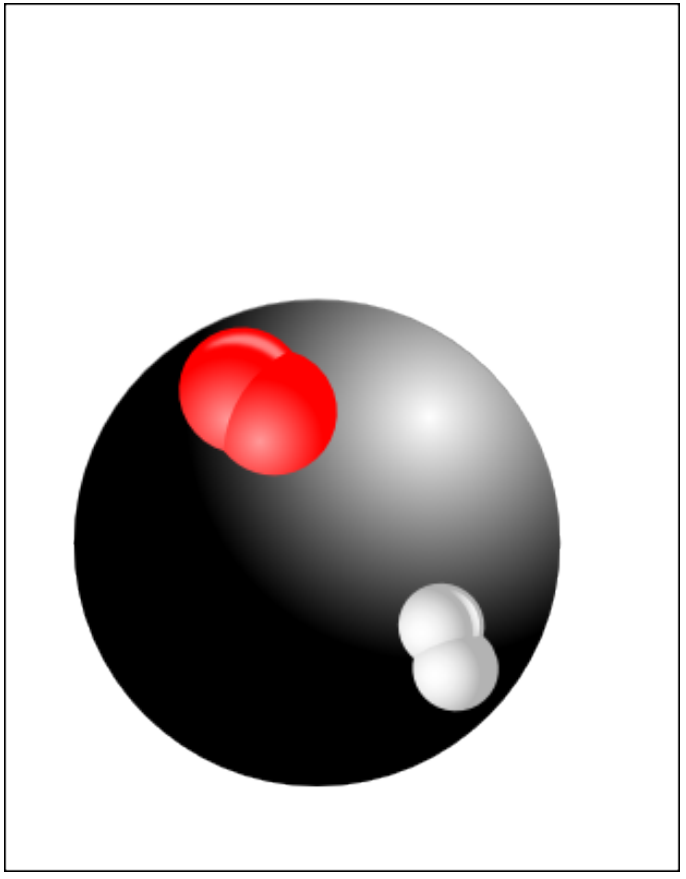

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Basic Steps for Predictive Materials Simulations

- select appropriate theory for given phenomenon and material
- master approximations and their effects (error estimates)
- obtain right answer for right reason (correct physics, correct phenomenon)

No universal method works
for all materials and all phenomena

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- Properties of interest
- Materials of interest
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- Properties of interest valence excitations properties
- Materials of interest bulk, nanostructures
- Scale of the features nanoscale

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Ab initio

The term *ab initio* indicates that the calculation is from first principles and that no empirical data is used.

$$V(\{\mathbf{r}\}) = \sum_{i \neq j} \frac{4\pi}{|\mathbf{r}_i - \mathbf{r}_j|}$$

R.G.Parr *et al.* Journal of Chemical Physics **18**, 1561 (1950)

Schrödinger equation

$$H\Big(\{\mathbf{r}\},t\Big)\Psi\Big(\{\mathbf{r}\},t\Big) = \imath\frac{\partial}{\partial t}\Psi\Big(\{\mathbf{r}\},t\Big)$$

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Ab initio approaches

$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_N, t)$ $\longrightarrow$ $G(\mathbf{r}_1, t_1, \mathbf{r}_2, t_2)$ $\longrightarrow$ $\rho(\mathbf{r}, t)$

CI, QMC

Ab initio approaches

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CI, QMC GF methods (GW, BSE)

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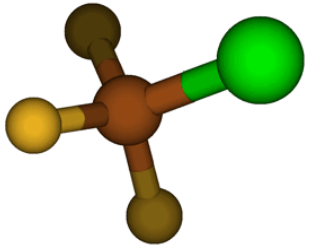

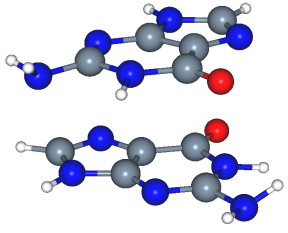

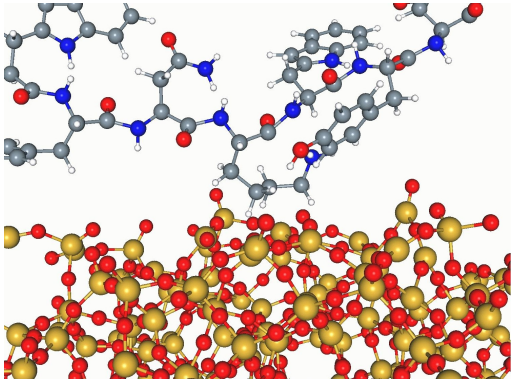

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- inaccuracy of the computational approach
- between experimental and theoretical situation

but always keep in mind that ...

computational model (also) provides information that is not accessible (or accessible with great difficulty) by laboratory experiments

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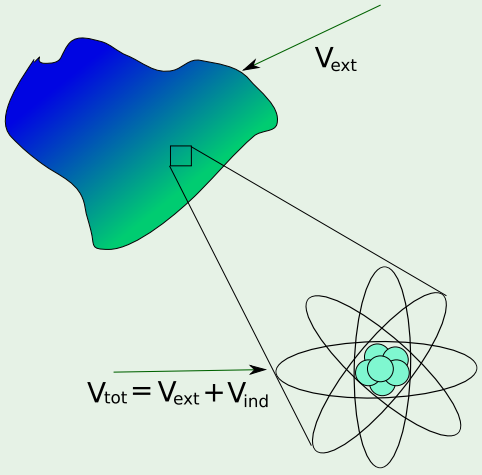
System submitted to an external perturbation



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Dielectric function ε

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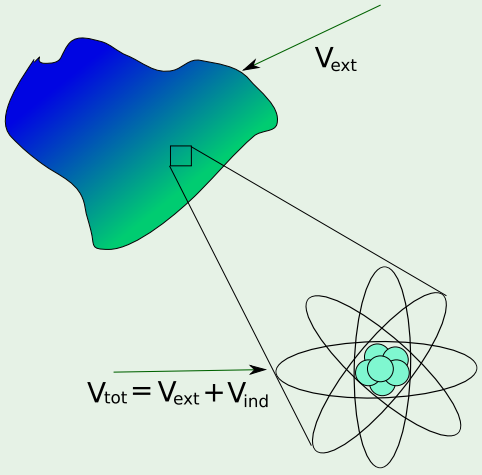

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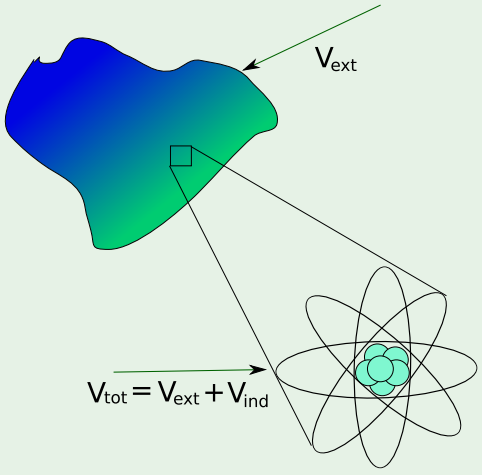

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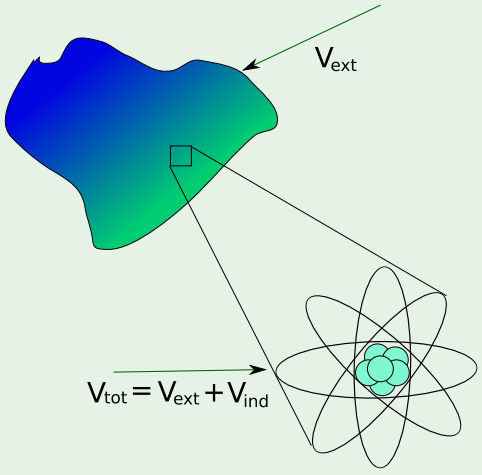

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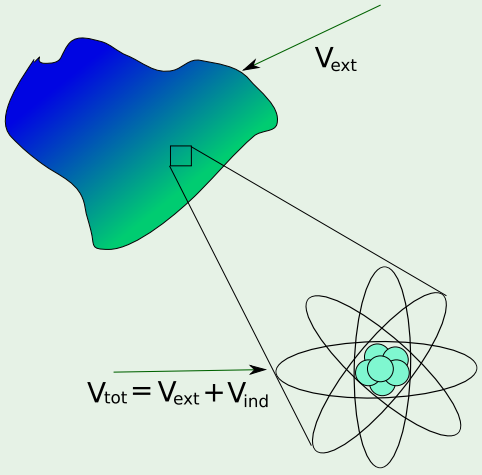

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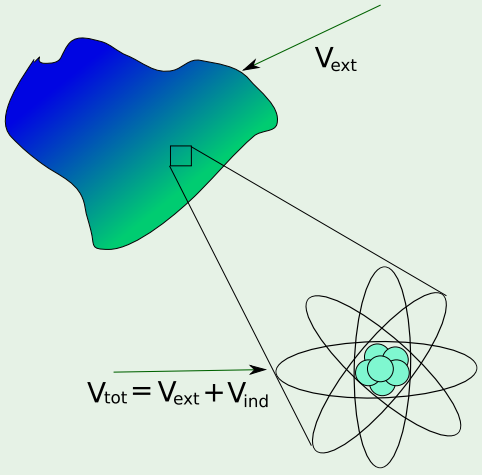

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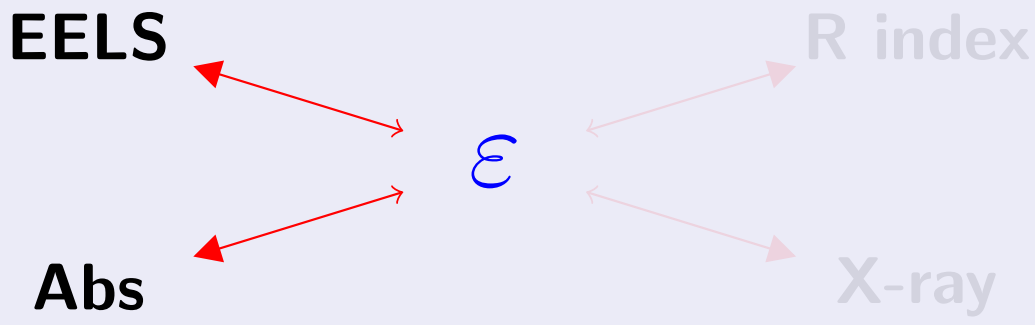

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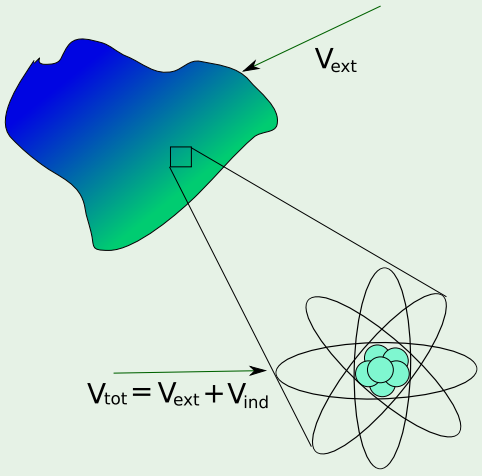

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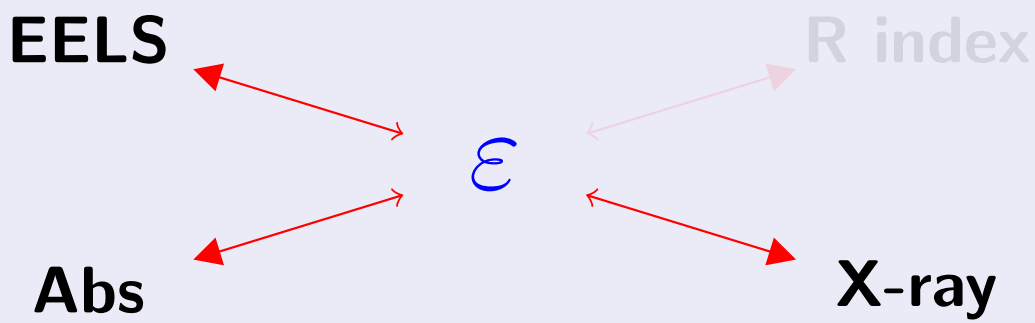

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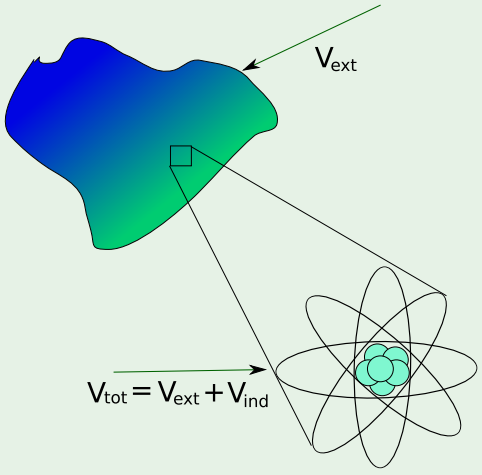

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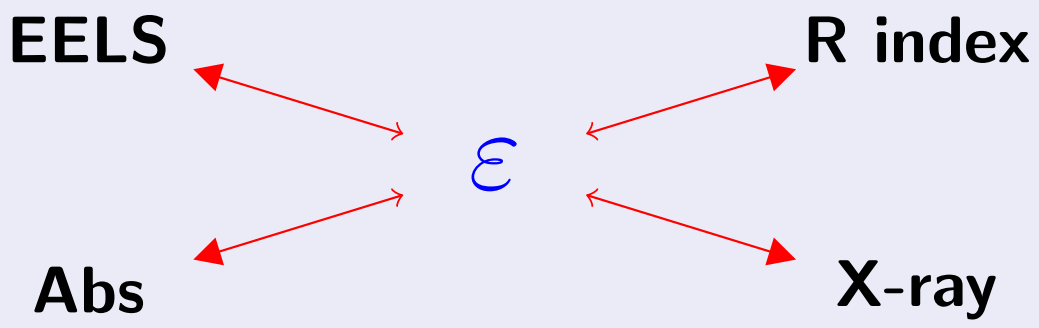

Linear Response Approach

Definition of polarizability

not polarizable $\Rightarrow$ $V_{tot} = V_{ext}$ $\Rightarrow$ $\varepsilon^{-1} = 1$

polarizable

$\varepsilon^{-1} = 1 + v\chi$

χ is the polarizability of the system

Linear Response Approach

Definition of polarizability

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Absorption coefficient

General solution of Maxwell's equation

$$\text{in vacuum} \quad \mathbf{E}(x,t) = \mathbf{E}_0 e^{i\omega(x/c-t)}$$

$$\text{in a medium} \quad \mathbf{E}(x,t) = \mathbf{E}_0 e^{i\omega(Nx/c-t)}$$

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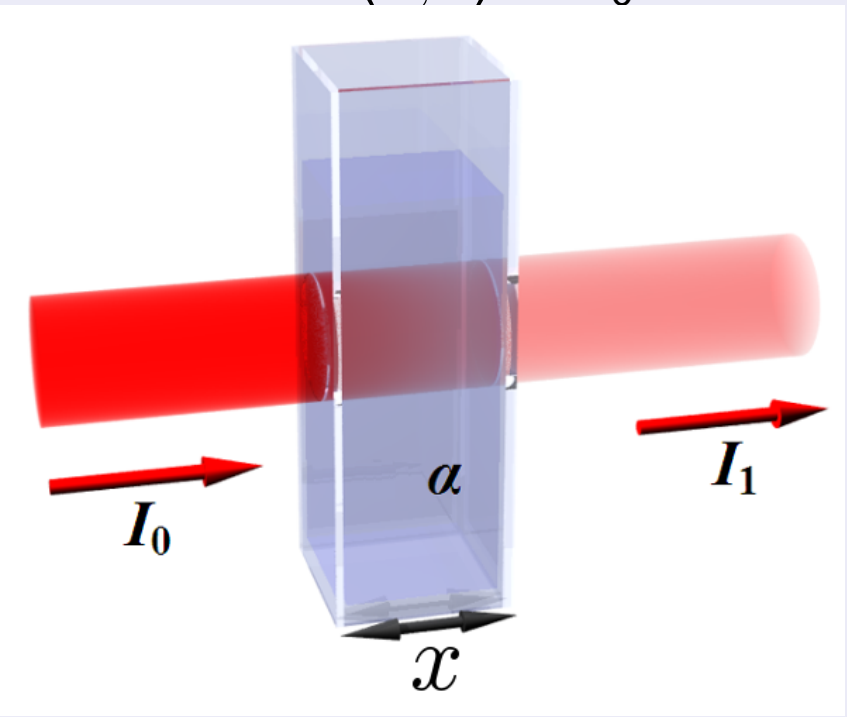

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complex (macroscopic) refractive index N

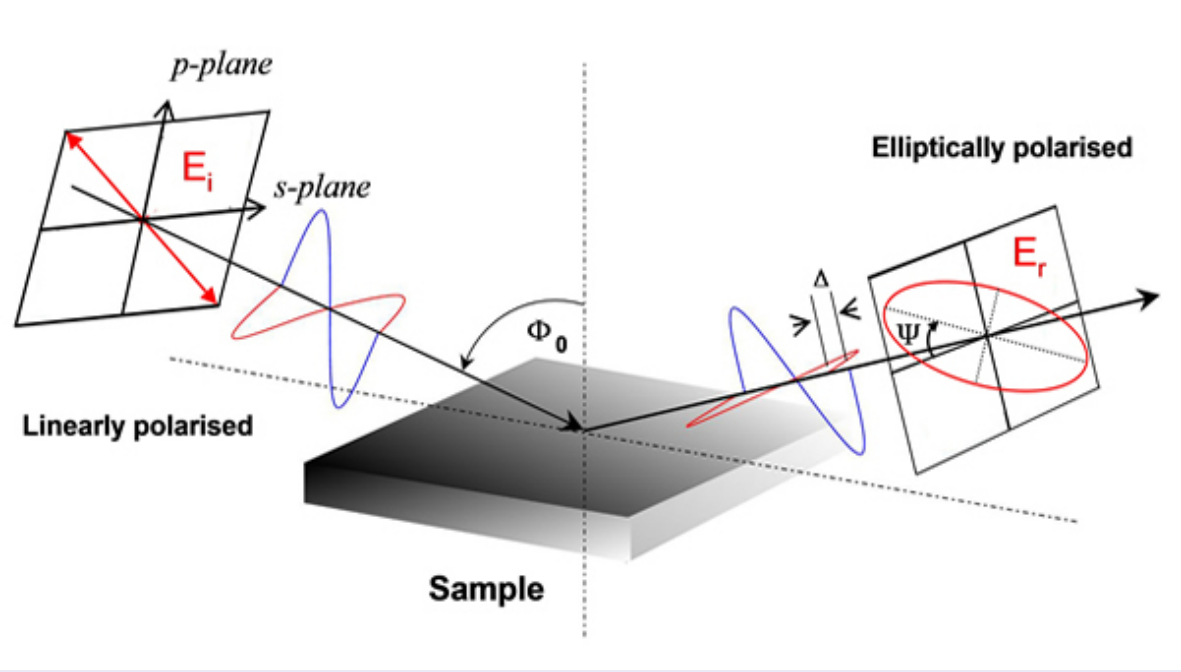
$$N = \sqrt{\varepsilon_M} = \nu + i\kappa \quad ; \quad \mathbf{D} = \varepsilon_M \mathbf{E}$$

absorption coefficient α (inverse distance $\left| \frac{|\mathbf{E}(x)|^2}{|\mathbf{E}_0|^2} = \frac{1}{e} \right.$)

$$\alpha = \frac{\omega \mathrm{Im}\varepsilon_\mathrm{M}}{\nu c}$$

Absorption coefficient

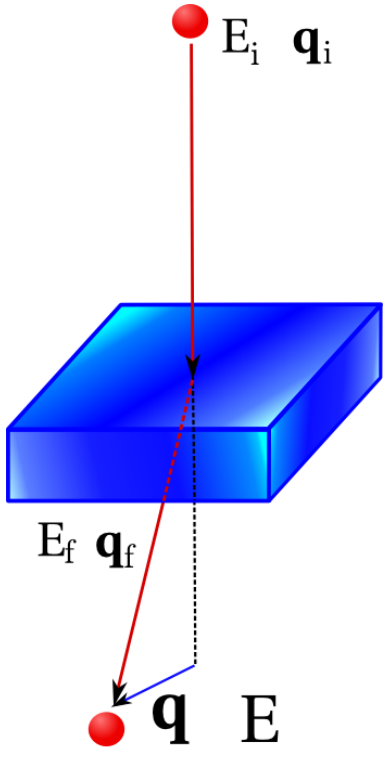
Ellipsometry Experiment



$$\varepsilon_M = sin^2\Phi + sin^2\Phi tan^2\Phi \left(\frac{1 - \frac{E_r}{E_i}}{1 + \frac{E_r}{E_i}} \right)$$

Dynamical Structure Factor

$$S(\mathbf{q},\omega) \propto \frac{1}{\varepsilon_M(\mathbf{q},\omega)}$$



Microscopic-Macroscopic Connection

Theoretical definition

$$\mathbf{E}(\mathbf{r},\omega) = \int d\mathbf{r}\, \varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)\mathbf{D}(\mathbf{r}',\omega)$$

constitutive closure to Maxwell equations

The connection ?

$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) \Longrightarrow \varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega) \propto \int d\mathbf{r}d\mathbf{r}' e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)$$

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Theoretical definition in G space

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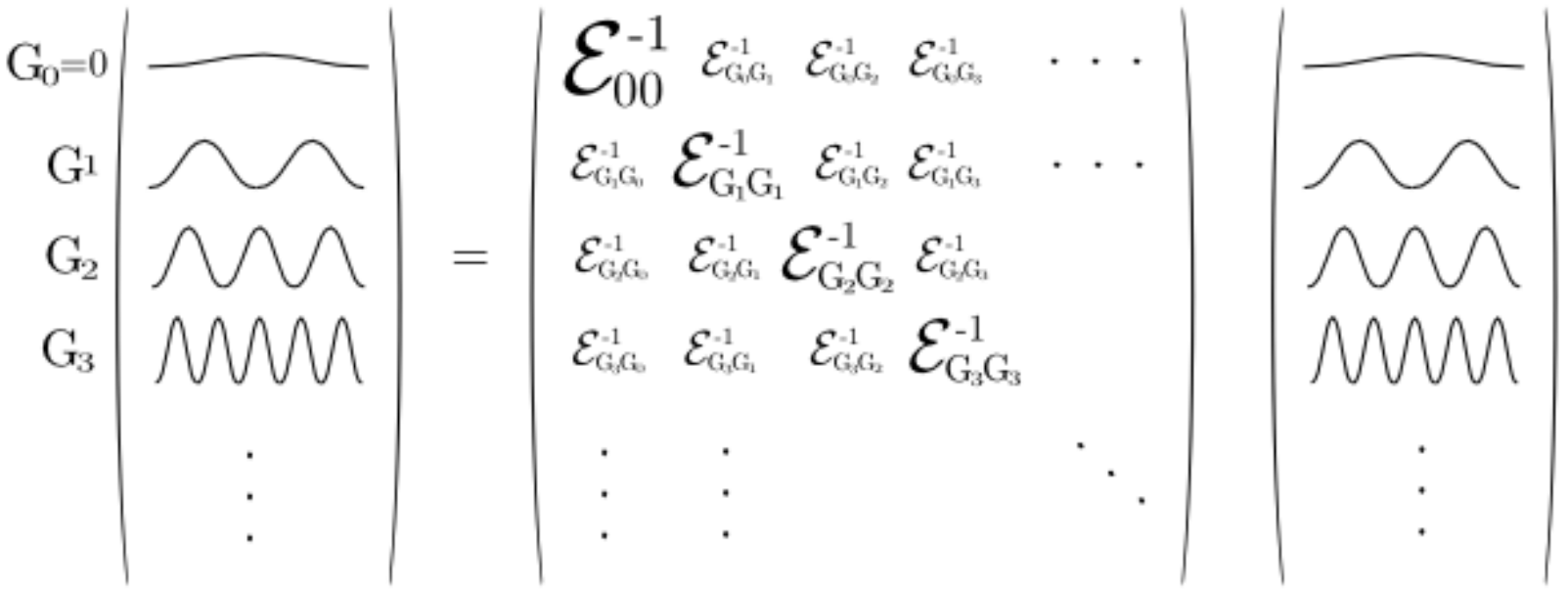
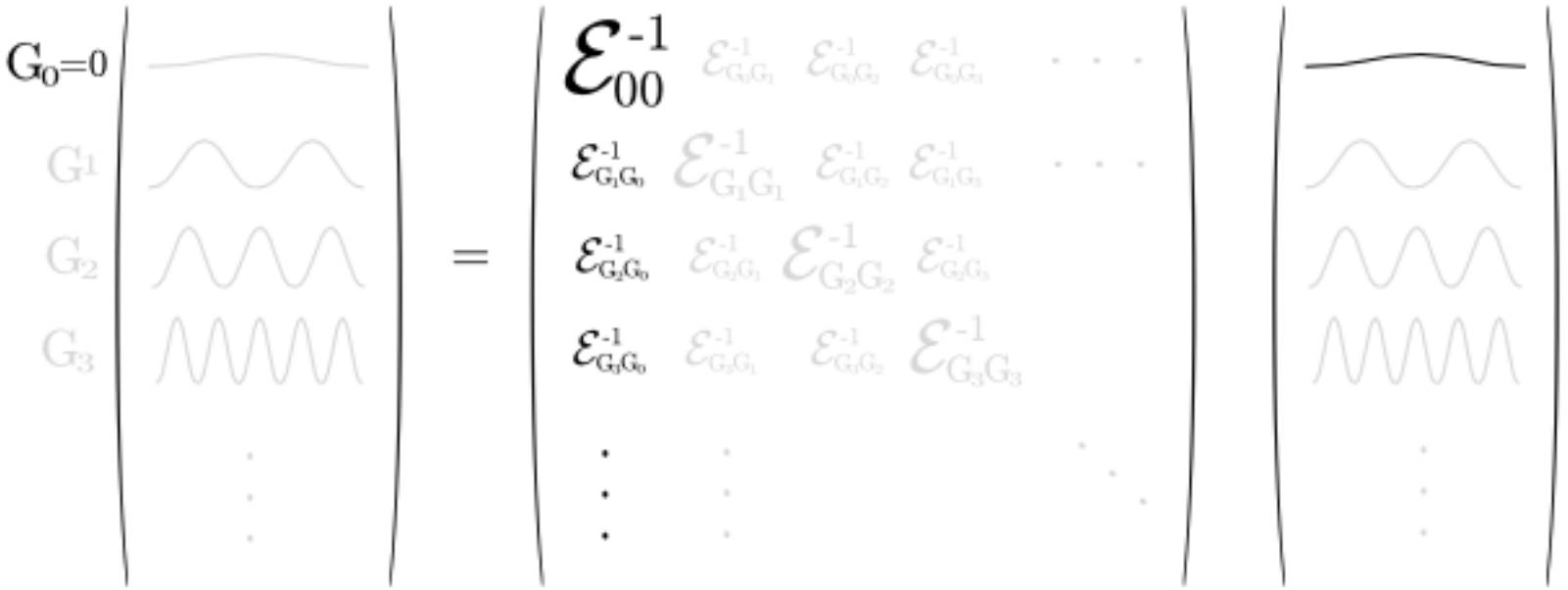


Theoretical definition in G space

$$\mathbf{E}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon^{-1}_{\mathbf{G},0}(\mathbf{q},\omega)\mathbf{D}(\mathbf{q}+0,\omega)$$



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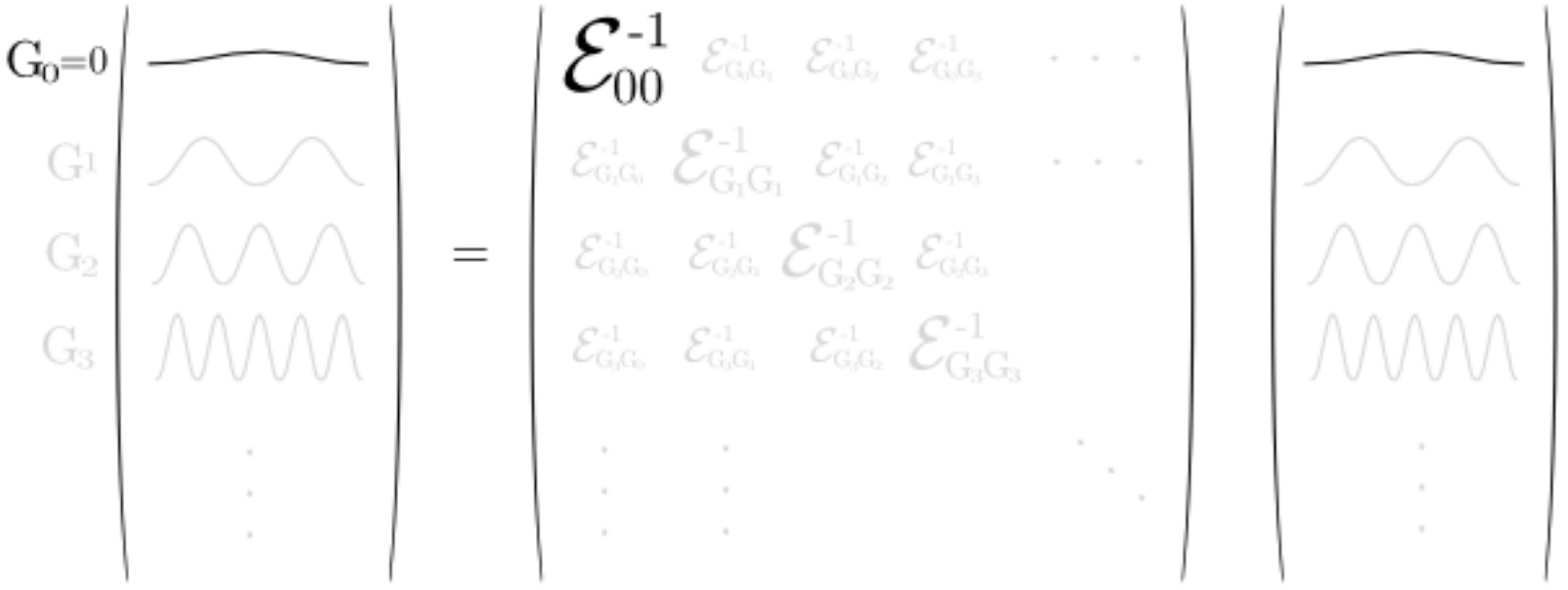
$$\mathbf{E}(\mathbf{q}+0,\omega) = \varepsilon^{-1}_{0,0}(\mathbf{q},\omega)\mathbf{D}(\mathbf{q}+0,\omega)$$



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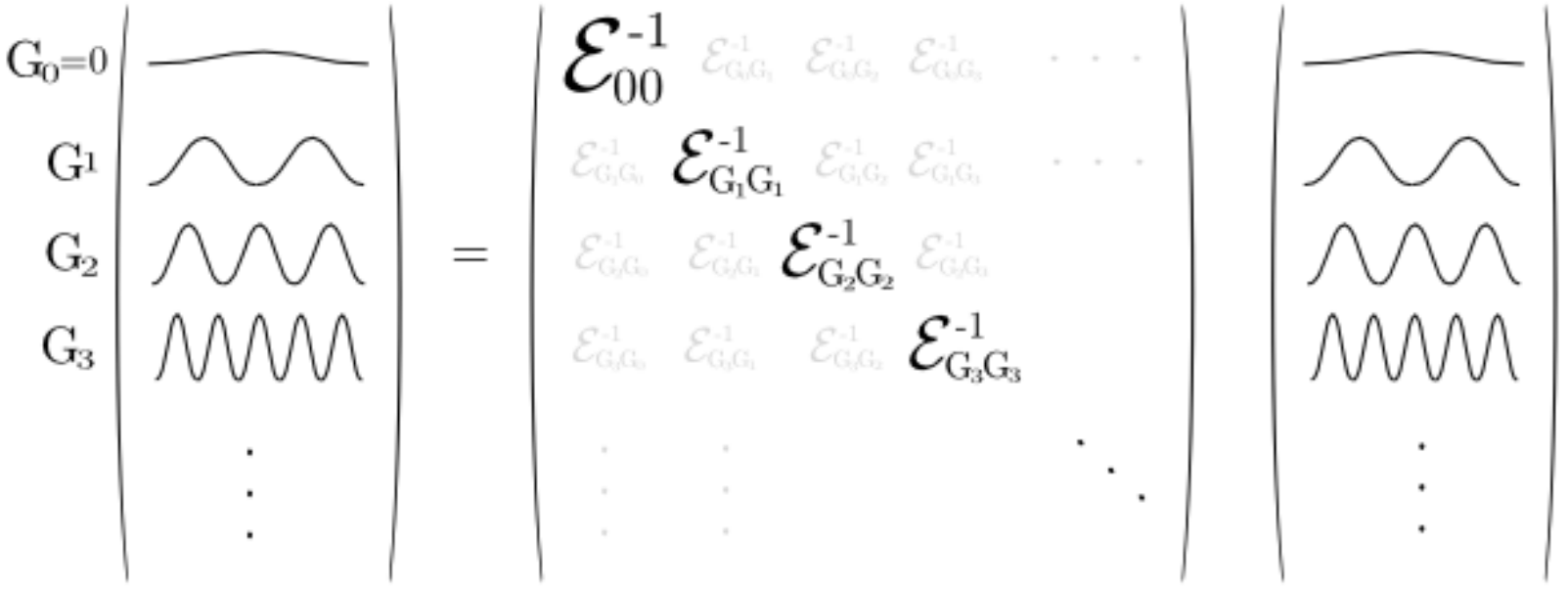

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