

# Natural optical activity from DFPT

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# Natural optical activity

Natural optical activity refers to the first-order spatial dispersion effect of the macroscopic dielectric tensor

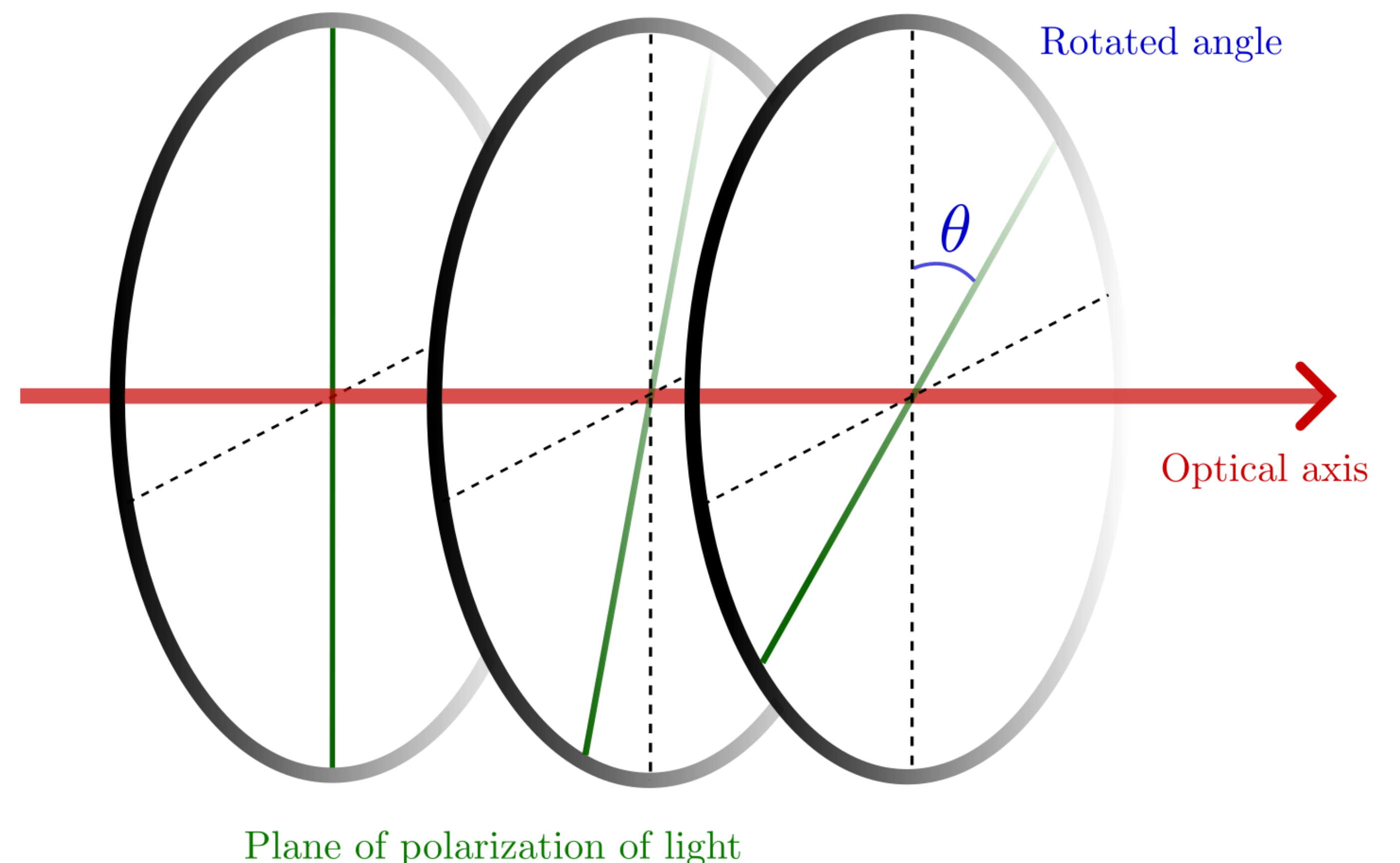
$$\epsilon_{\alpha\beta}(\omega, \mathbf{q}) = \epsilon_{\alpha\beta}(\omega, \mathbf{q} = \mathbf{0}) + iq_{\gamma}\eta_{\alpha\beta\gamma}(\omega) + \dots$$

Dielectric tensor

Frequency

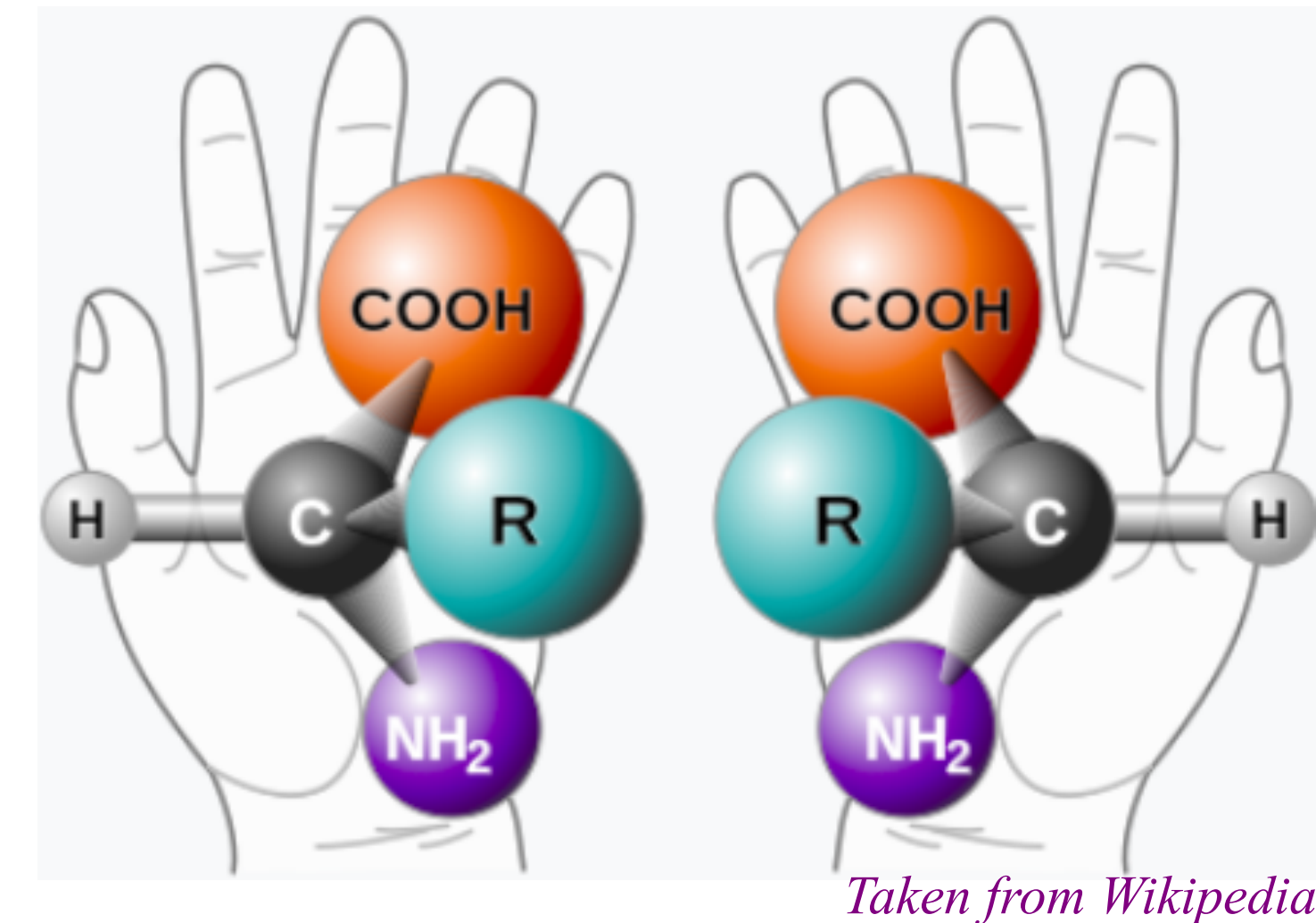
Natural optical activity (NOA)

- Important for pharmaceutical industry, material science, and fundamental research in physics, chemistry or biology.
- It describes one of the fundamental aspects of the interaction between light and matter.
- Unlike other optical effects, it does not require magnetism to be present.
- Empirically, NOA is manifested as optical rotation (OR), which is a property of certain structures to rotate the plane of the polarization of light that travels through them.



# Natural optical activity

- NOA was first measured in quartz crystals back in 1811.
- Historically, most of the studied optically active materials turned out to be *chiral*.
- Reliable experimental measurements exist for many materials, both in molecular and crystalline form.



Chirality is a *sufficient but not necessary condition* for NOA to be present, as optically active achiral systems also exist.

## Molecules

Electric dipole operator

$$\eta \longrightarrow -2\omega \sum_{n \neq 0} \frac{\langle \psi_0 | \hat{\mu}_\alpha | \psi_n \rangle \langle \psi_n | \hat{m}_\beta | \psi_0 \rangle}{\omega_{n0}^2 - \omega^2}$$

$$\hat{\mu}_\alpha = -r_\alpha$$

$$\hat{m}_\beta = -\frac{1}{2}(\mathbf{r} \times \mathbf{p})_\beta$$

Magnetic dipole operator

## Solids

- Numerical long-wavelength expansion of the electromagnetic vector potential response (Zhong, Levine, Allan, and Wilkins).
- Analytical expressions (Malashevic, Pozo and Souza).
- Semiclassical and tight-binding models.
- *Ab initio* implementations.



# Limitations of the existing implementations

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- Correct treatment of self consistent field (SCF) terms.
- Cumbersome sums over empty states.
- Numerical differentiation with respect to the wave vector  $\mathbf{q}$ .
- Appropriate treatment of the current-density response in the presence of nonlocal pseudopotentials.

Solution?



Natural optical activity is a *spatial dispersion* property

$$\epsilon_{\alpha\beta}(\omega, \mathbf{q}) = \epsilon_{\alpha\beta}(\omega, \mathbf{q} = \mathbf{0}) + iq_{\gamma}\eta_{\alpha\beta\gamma}(\omega) + \dots$$

Spatial dispersion properties (e.g., flexoelectric tensor or dynamical quadrupoles) can be computed with the *longwave module of Abinit*

# Long-wave density-functional perturbation theory

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## DFPT

Perturbation expansion

$$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \frac{1}{2} \lambda^2 \hat{H}^{(2)} + \dots$$

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \frac{1}{2} \lambda^2 E^{(2)} + \dots$$

$$\psi_m(\lambda) = \psi_m^{(0)} + \lambda \psi_m^{(1)} + \dots$$

Monochromatic perturbations

$$\hat{H}^{(1)} = e^{i\mathbf{q}\cdot\mathbf{r}} \hat{H}_{\mathbf{q}}^{(1)} \quad \text{cell-periodic part}$$

$$\psi_{m\mathbf{k}}^{(0)} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{m\mathbf{k}}^{(0)}$$



$$E_{\mathbf{q}}^{\lambda_1 \lambda_2} = \frac{dE}{d\lambda_1 d\lambda_2}$$

The linear response problem reduces to finding the variational minimum of a **constrained** second-order energy functional

$$\min_{u_{m\mathbf{k}}^{(1)}} E_{\mathbf{q}}^{\lambda_1 \lambda_2} [u_{m\mathbf{k}}^{(1)}] \quad \text{with} \quad \langle u_{m\mathbf{k}+\mathbf{q}}^{(0)} | u_{n\mathbf{k}}^{(1)} \rangle = 0, \quad \forall m, n \in \mathcal{V}$$

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## Long-wave DFPT

Reformulate the problem as finding the variational minimum of an **unconstrained** second-order energy functional

$$\min_{u_{m\mathbf{k}}^{(1)}} E_{\mathbf{q}}^{\lambda_1 \lambda_2} [u_{m\mathbf{k}}^{(1)}] \quad \text{without constraints}$$

Only the operators depend explicitly on  $\mathbf{q}$ , and these are well-defined objects independent of the phase indeterminacy inherent to the ground-state Bloch functions.

*Analytical expansion* in  $\mathbf{q}$ , via the 2n+1 theorem

$$E_{\gamma}^{\lambda_1 \lambda_2} = \left. \frac{dE_{\mathbf{q}}^{\lambda_1 \lambda_2}}{dq_{\gamma}} \right|_{\mathbf{q}=0} = \left. \frac{\partial E_{\mathbf{q}}^{\lambda_1 \lambda_2}}{\partial q_{\gamma}} \right|_{\mathbf{q}=0}$$

Implemented in Abinit to compute the flexoelectric tensor and the dynamical quadrupoles.

# Computational strategy

$$\epsilon_{\alpha\beta}(\mathbf{q}) = \delta_{\alpha\beta} - \frac{4\pi}{\Omega} E_{\mathbf{q}}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} \longrightarrow \boxed{\eta_{\alpha\beta\gamma} = -\frac{4\pi}{\Omega} \text{Im } E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}}}$$

Electric fields  
Unit cell volume

$$E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = 2s \int_{\text{BZ}} [d^3k] E_{\mathbf{k},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} + \int_{\Omega} \int n^{\mathcal{E}_{\alpha}}(\mathbf{r}) K_{\gamma}(\mathbf{r}, \mathbf{r}') n^{\mathcal{E}_{\beta}}(\mathbf{r}') d^3r d^3r'$$

Spin multiplicity
↓
First  $\mathbf{q}$  derivative of the Hxc kernel
↓ ↓
First-order electronic densities

$\frac{\Omega}{(2\pi)^3} d^3k$

$$\boxed{E_{\mathbf{k},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = \chi_{\mathbf{k}}^{\mathcal{E}_{\alpha}k_{\gamma}\mathcal{E}_{\beta}} + \mathcal{Y}_{\mathbf{k}}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}k_{\gamma}} + \mathcal{Y}_{\mathbf{k}}^{k_{\gamma}\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} + \mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} + \left(\mathcal{W}_{\mathbf{k}}^{\beta,\alpha\gamma}\right)^*}$$

$$\left. \begin{aligned} \chi_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3} &= \sum_m \langle u_{m\mathbf{k}}^{\lambda_1} | \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{\lambda_3} \rangle \\ \mathcal{Y}_{\mathbf{k}}^{\lambda_1\lambda_2\lambda_3} &= - \sum_{mn} \langle u_{m\mathbf{k}}^{\lambda_1} | u_{n\mathbf{k}}^{\lambda_3} \rangle \langle u_{n\mathbf{k}}^{(0)} | \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda_2} | u_{m\mathbf{k}}^{(0)} \rangle \end{aligned} \right\} \begin{array}{l} \text{Well-known objects in} \\ \text{the context of DFPT} \end{array} \longrightarrow \hat{\mathcal{H}}_{\mathbf{k}}^{\lambda} = \hat{H}_{\mathbf{k}}^{\lambda} + \hat{V}^{\lambda}$$

SCF potential response

$$\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \sum_m i \langle u_{m\mathbf{k}}^{\mathcal{E}_{\alpha}} | u_{m\mathbf{k},\gamma}^{A_{\beta}} \rangle \longrightarrow \text{Wave-function response to an electromagnetic vector potential at first order in } \mathbf{q}$$

# Computational strategy

$$\mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \sum_m i \langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha} | u_{m\mathbf{k},\gamma}^{A_\beta} \rangle \longrightarrow \mathcal{W}_{\mathbf{k}}^{\alpha,\beta\gamma} = \underbrace{\mathcal{S}_{\mathbf{k}}^{\alpha,\beta\gamma}}_{\substack{\text{symmetric} \\ \beta \leftrightarrow \gamma}} + \underbrace{\mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma}}_{\substack{\text{antisymmetric} \\ \beta \leftrightarrow \gamma}}$$

$$\mathcal{S}_{\mathbf{k}} = \sum_m \frac{i}{2} \langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha} | \partial_{\beta\gamma}^2 u_{m\mathbf{k}}^{(0)} \rangle$$

$d^2 / dk_\beta dk_\gamma$  wave functions

$$\mathcal{A}_{\mathbf{k}}^{\alpha,\beta\gamma} = \frac{1}{2} \sum_m \epsilon_{\delta\beta\gamma} \langle u_{m\mathbf{k}}^{\mathcal{E}_\alpha} | u_{m\mathbf{k}}^{B_\delta} \rangle$$

Wave function response to a uniform orbital magnetic field,  $B_\delta$

- The  $u_{m\mathbf{k},\gamma}^{A_\beta}$  wave functions are obtained from the following Sternheimer equation:

$$(\hat{H}_{\mathbf{k}}^{(0)} + a\hat{P}_{\mathbf{k}} - \varepsilon_{m\mathbf{k}}^{(0)}) | u_{m\mathbf{k},\gamma}^{A_\beta} \rangle = -\hat{Q}_{\mathbf{k}} \hat{O}_{\mathbf{k}}^{\beta\gamma} | u_{m\mathbf{k}}^{(0)} \rangle$$

$$\hat{O}_{\mathbf{k}}^{\beta\gamma} = \partial_\gamma \hat{H}_{\mathbf{k}}^{(0)} \partial_\beta \hat{P}_{\mathbf{k}} - \partial_\gamma \hat{P}_{\mathbf{k}} \partial_\beta \hat{H}_{\mathbf{k}}^{(0)} + \frac{1}{2} \partial_{\beta\gamma}^2 \hat{H}_{\mathbf{k}}^{(0)}$$

Everything is already coded in Abinit, we just need to rearrange some pieces....

$$\partial_\gamma \equiv \partial / \partial k_\gamma \quad , \quad \hat{P}_{\mathbf{k}} = \sum_m | u_{m\mathbf{k}}^{(0)} \rangle \langle u_{m\mathbf{k}}^{(0)} | \quad , \quad \hat{Q}_{\mathbf{k}} = 1 - \hat{P}_{\mathbf{k}}$$



# Some formal aspects of the theory...

- **Non-uniqueness of the energy functional**

$$\eta_{\alpha\beta\gamma} = -\frac{4\pi}{\Omega} \text{Im} E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} \longrightarrow E_{\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} = 2s \int_{\text{BZ}} [d^3k] E_{\mathbf{k},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} + \int_{\Omega} \int n^{\mathcal{E}_{\alpha}}(\mathbf{r}) K_{\gamma}(\mathbf{r}, \mathbf{r}') n^{\mathcal{E}_{\beta}} d^3r d^3r'$$

***Electromagnetic gauge freedom:***

Distinct choices for the electromagnetic gauge can give rise to different energy functionals for the NOA.

$$E_{\mathbf{k},\gamma}^{\mathcal{E}_{\alpha}\mathcal{E}_{\beta}} - \lambda f(\mathbf{k}) \quad \text{with} \quad \int_{\text{BZ}} [d^3k] f(\mathbf{k}) = 0$$

Complex number

Any function whose integral over the whole BZ is zero

- **Our formalism recovers the expressions that are commonly used with molecules**

$$\tilde{\eta}_{\alpha\beta\gamma} = -\frac{4\pi}{\Omega} s \text{Im} \sum_{m,l}^{o,e} \tilde{\eta}_{\alpha\beta\gamma}^{ml}$$

The *tilde* symbol indicates that SCF are neglected  
 $m$  : occupied states  
 $l$  : empty states

$$\begin{aligned} \tilde{\eta}_{\alpha\beta\gamma}^{ml} = & \frac{1}{(\epsilon_l - \epsilon_m)^2} \left( \langle m | r_{\alpha} | l \rangle \langle l | (r_{\beta} v_{\gamma} - r_{\gamma} v_{\beta}) | m \rangle - \langle m | r_{\beta} | l \rangle \langle l | (r_{\alpha} v_{\gamma} - r_{\gamma} v_{\alpha}) | m \rangle \right) \\ & + \frac{i}{(\epsilon_l - \epsilon_m)} \left( \langle m | r_{\beta} | l \rangle \langle l | r_{\alpha} r_{\gamma} | m \rangle - \langle m | r_{\alpha} | l \rangle \langle l | r_{\beta} r_{\gamma} | m \rangle \right) \end{aligned}$$



# Example of an input file

ndtset 5

**#Set 1 : ground state self-consistency**

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getwfk1 0  
kptopt1 1  
tolvrs1 1.0d-18

**#Set 2: Response function calculation of d/dk wave function**

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kptopt2 2  
iscf2 -3  
rfelfd2 2  
tolwfr2 1.0d-20

**#Set 3: Response function calculation of d2/dkdk wave function**

\*\*\*\*\*

kptopt3 2  
getddk3 2  
iscf3 -3  
rf2\_dkdk3 3  
tolwfr3 1.0d-20

**#Set 4 : Response function calculation of electric field**

\*\*\*\*\*

getddk4 2  
kptopt4 2  
rfelfd4 3  
tolvrs4 1.0d-8  
**prepalw4 4**

**#Set 5 : Natural optical activity calculation**

\*\*\*\*\*

optdriver5 10  
kptopt5 2  
getlwf5 4  
getlden5 4  
getddk5 2  
getdkdk5 3  
**lw\_natopt5 1**

**#Common input variables**

\*\*\*\*\*

getwfk 1  
useylm 1

$$\beta \leftrightarrow \gamma$$

→ {  
rf2\_dkdk = 1, symmetric  
rf2\_dkdk = 2, antisymmetric  
rf2\_dkdk = 3, total response

$$u_{m\mathbf{k},\gamma}^{A_\beta}$$

This term is also needed for the calculation of the flexoelectric tensor: until its implementation, the strategy had been to select materials where the antisymmetric part vanishes by symmetry.

→ lw\_natopt = 1, Natural Optical Activity calculation

→ useylm = 1, spherical harmonics

# Testing the implementation: chiral crystals

- We will assume that the system under study is a time-reversal (TR) symmetric insulator. Even in most general case, only 9 of the 27 components are independent,

$$\eta_{\alpha\beta\gamma}(\omega) = -\eta_{\beta\alpha\gamma}(\omega) \longrightarrow g_{\alpha\beta}(\omega) = \frac{1}{2} \epsilon_{\gamma\delta\alpha} \eta_{\gamma\delta\beta}(\omega)$$

antisymmetric under  $\alpha \leftrightarrow \beta$  Levi-Civita symbol

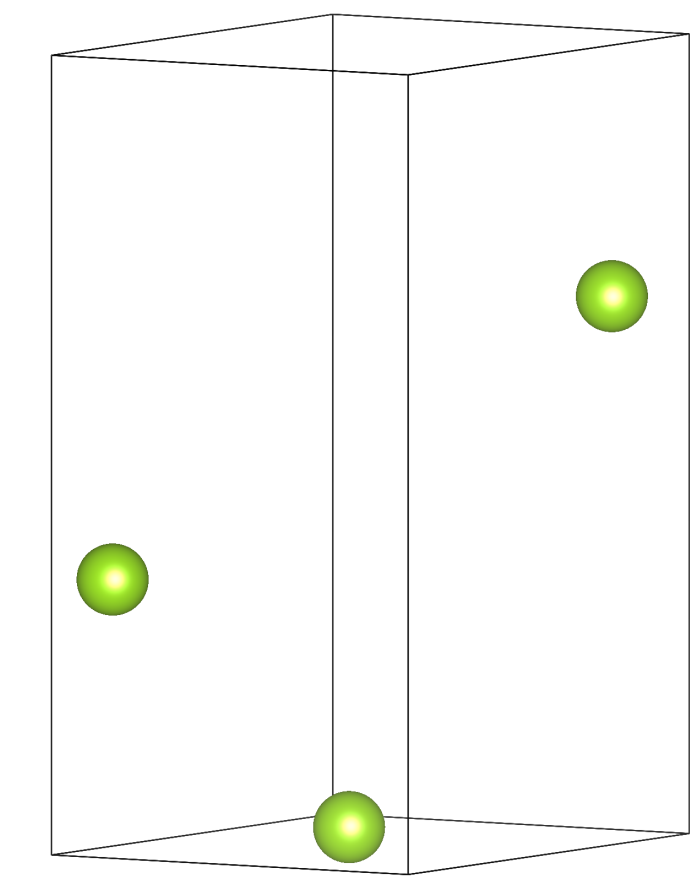
$$\mathbf{g}(\omega) = \begin{pmatrix} g_{11}(\omega) & 0 & 0 \\ 0 & g_{11}(\omega) & 0 \\ 0 & 0 & g_{33}(\omega) \end{pmatrix} \longleftarrow \text{For crystal structures with the point group 32 (trigonal axis oriented along the z Cartesian direction)}$$

- Optical rotatory power

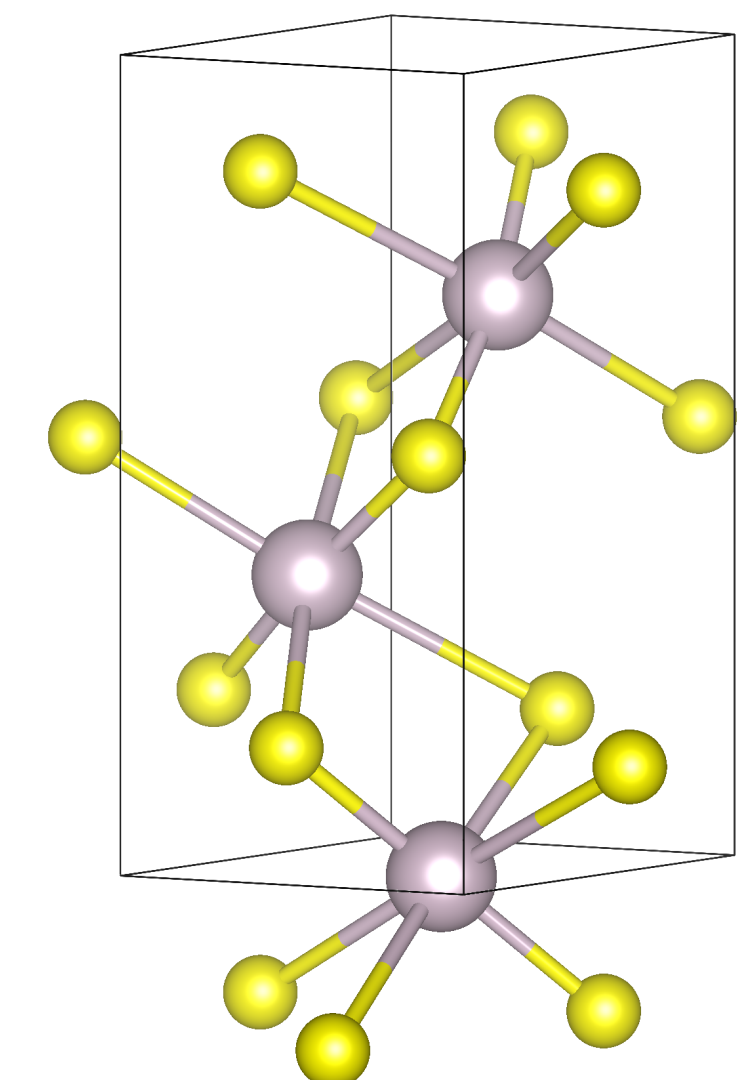
$$\rho(\omega) = \frac{\omega^2}{2c^2} g_{33}(\omega) \xrightarrow[\substack{\omega \rightarrow 0 \\ g_{33}(\omega \rightarrow 0) = g_{33}}]{\quad} \rho(\omega) \simeq (\hbar\omega)^2 \bar{\rho}$$

speed of light reduced Planck constant

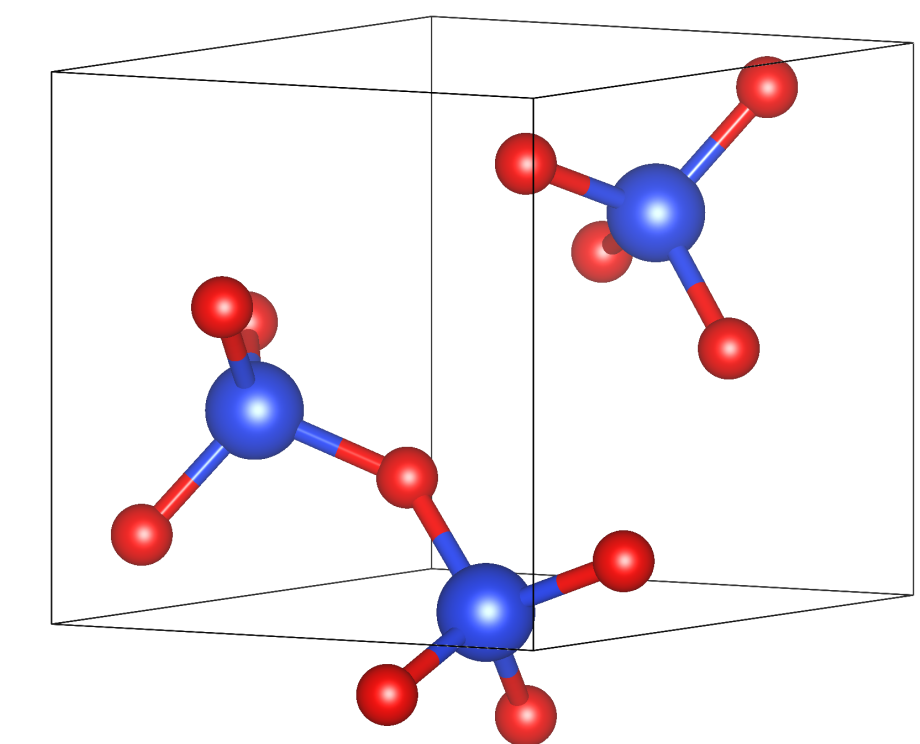
$$\bar{\rho} = \frac{g_{33}}{2(\hbar c)^2}$$



Trigonal Se



$\alpha$ -HgS



$\alpha$ -SiO<sub>2</sub>



# Results: trigonal Se, $\alpha$ -HgS and $\alpha$ -SiO<sub>2</sub>

## • Results with LDA

	$g_{11}$	$g_{33}$	$\bar{\rho}$
Se	-1.307 (-1.547)	-1.913 (-0.458)	-74.5 (-17.8)
$\alpha$ -HgS	0.775 (0.554)	-1.861 (-1.274)	-72.5 (-49.6)
$\alpha$ -SiO <sub>2</sub>	-0.071 (-0.001)	0.125 (0.019)	4.9 (0.7)

Calculated independent components of the gyration tensor (in bohr) and the optical rotatory power (in deg/[mm (eV)<sup>2</sup>] units). Values in brackets are computed neglecting the SCF terms.

## • Comparison with literature results

$\bar{\rho}$	This work	Phys. Rev. Lett. <b>76</b> , 1372 (1996)		Experiment
Se	-74.5	-131 ( $\Delta = 0$ )	-55 ( $\Delta = 1.1$ eV)	$\pm 56 \pm 30^a$
$\alpha$ -HgS	-72.5	—	—	-83 <sup>b</sup>
$\alpha$ -SiO <sub>2</sub>	4.9	6.8 ( $\Delta = 0$ )	5.6 ( $\Delta = 1.8$ eV)	$\pm 4.6 \pm 0.1^a$

$\Delta$  is an *ad-hoc* correction to the conduction band energies coming from a scissor operator.

<sup>a</sup> Phys. Rev. Lett. **76**, 1372 (1996)

<sup>b</sup> Acta Crystallogr. A **42**, 560 (1986), with  $\hbar\omega \sim 1.959$  eV

## • Effect of the exchange and correlation functional: LDA vs PBE

Structure	$g_{11}$ (bohr)		$g_{33}$ (bohr)	
	LDA	PBE	LDA	PBE
Se(exp)	-1.307	-1.301	-1.913	-1.329
Se(PBE)	-1.408	-1.431	-1.802	-1.216
$\alpha$ -HgS (LDA)	0.775	0.663	-1.861	-1.645
$\alpha$ -HgS (PBE)	-0.716	-0.692	-0.065	-0.065
$\alpha$ -SiO <sub>2</sub> (LDA)	-0.071	-0.071	0.125	0.125
$\alpha$ -SiO <sub>2</sub> (PBE)	-0.085	-0.085	0.168	0.167

• Our results are in good agreement with literature values, both with experiments and with other computationally more demanding methods, and confirm the ***crucial importance of SCF terms***.

• Different schemes for the exchange-correlation functional have a minimal impact on the results for the natural optical activity, while the structural geometry of the crystal plays a significant role.



# Conclusions and outlook

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*We have presented an efficient and accurate methodology for computing the natural optical activity within the framework of DFPT.*

- Only occupied states are included in our equations.
- SCF terms are naturally included in the formalism.
- Differentiation with respect to the wave vector  $\mathbf{q}$  is taken analytically.
- Only response functions to uniform field perturbations are needed.
- Our methodology is equally applicable to both solids and molecules.

## *Future work*

- Generalize our method to finite frequencies.
- Magnetic materials with broken time-reversal symmetry.
- Include spin-orbit coupling.

## *Formal aspects of the theory*

Non-uniqueness of the energy functional for the NOA: electromagnetic gauge freedom