Linear and circular dichroism, trichroism, tetrachroism, pentachroism, hexachroism, heptachroism, octochroism, and enneachroism represented by a single tensor.

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In the previous example we've seen that the XAS spectra of NiO change according to the polarisation used. For a system with low enough symmetry the obtained absorption spectra will be different for each possible direction of the polarisation of the light, seemingly leading to infinichroism. (Infinite many different possible colors of the sample accrdoing to the direction one looks at the sample)

There are relations between the spectra measured in different directions. One could assume that the spectrum with polarisation parallel or perpendicular to the magnetisation in cubic symmetry would be different and all other spectra could be given as a linear combination of these two. In spherical symmetry (plus a magnetisation) that would definitely be true. As our previous example showed, it is not that simple if the crystal has cubic symmetry. (And even worse if the point-group symmetry is lower).

We can find the relations between the different polarisation directions by representing the absorption as a tensor (The conductivity tensor).

For an arbitrary polarisation direction $\vec{\varepsilon}=\alpha\hat{x}+\beta\hat{y}+\gamma\hat{z}$ we can define the absorption as:

$$I_{XAS}(\omega) = -\frac{1}{\pi}\mathrm{Im}\left\langle \psi_0 \left| T_{\vec{\varepsilon}}^\dagger G(\omega) T_{\vec{\varepsilon}} \right| \psi_0 \right\rangle, \qquad (1)$$

with $T_{\vec{\varepsilon}}$ the polarisation dependent dipole operator,

$$G(\omega) = \frac{1}{\omega - H + \mathrm{i}\Gamma/2} \qquad (2)$$

the Green's operator, H the Hamiltonian and Γ the lifetime of the excited states. The dipole operator for a polarization $\vec{\varepsilon}=\alpha\hat{x}+\beta\hat{y}+\gamma\hat{z}$ can be written as:

$$T_{\vec{\varepsilon}} = \alpha T_{\hat{x}} + \beta T_{\hat{y}} + \gamma T_{\hat{z}} \qquad (3)$$

resulting in the absorption given as:

$$\begin{aligned} I_{XAS}(\omega) = -\frac{1}{\pi}\mathrm{Im}[\quad & \alpha^*\alpha \left\langle \psi_0 \left| T_{\hat{x}}^\dagger G(\omega) T_{\hat{x}} \right| \psi_0 \right\rangle + \alpha^*\beta \left\langle \psi_0 \left| T_{\hat{x}}^\dagger G(\omega) T_{\hat{y}} \right| \psi_0 \right\rangle + \alpha^*\gamma \left\langle \psi_0 \left| T_{\hat{x}}^\dagger G(\omega) T_{\hat{z}} \right| \psi_0 \right\rangle \\ & + \beta^*\alpha \left\langle \psi_0 \left| T_{\hat{y}}^\dagger G(\omega) T_{\hat{x}} \right| \psi_0 \right\rangle + \beta^*\beta \left\langle \psi_0 \left| T_{\hat{y}}^\dagger G(\omega) T_{\hat{y}} \right| \psi_0 \right\rangle + \beta^*\gamma \left\langle \psi_0 \left| T_{\hat{y}}^\dagger G(\omega) T_{\hat{z}} \right| \psi_0 \right\rangle \\ & + \gamma^*\alpha \left\langle \psi_0 \left| T_{\hat{z}}^\dagger G(\omega) T_{\hat{x}} \right| \psi_0 \right\rangle + \gamma^*\beta \left\langle \psi_0 \left| T_{\hat{z}}^\dagger G(\omega) T_{\hat{y}} \right| \psi_0 \right\rangle + \gamma^*\gamma \left\langle \psi_0 \left| T_{\hat{z}}^\dagger G(\omega) T_{\hat{z}} \right| \psi_0 \right\rangle] \end{aligned}$$

or

$$I_{XAS}(\omega) = -\frac{1}{\pi}\mathrm{Im}\left[\begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix}^\dagger \cdot \begin{pmatrix} G_{xx} & G_{xy} & G_{xz} \\ G_{yx} & G_{yy} & G_{yz} \\ G_{zx} & G_{zy} & G_{zz}\end{pmatrix} \cdot \begin{pmatrix}\alpha\\ \beta\\ \gamma\end{pmatrix} \right] \qquad (4)$$

with

$$G_{i,j} = \left\langle \psi_0 \left| T_{\hat{i}}^\dagger G(\omega) T_{\hat{j}} \right| \psi_0 \right\rangle \qquad (5)$$

the x-ray absorption Green's function.

Any absorption spectra for any given polarisation can thus be given as a linear combination of nine different spectra. For different symmetries one finds that many of these components are zero or equivalent.

Quanty has two options to calculate this tensor. One can either calculate the absorption for x, y $x+y$ and $x+\mathrm{i}y$ polarised light and use linear combinations to recombine the old spectra, or use the option tensor=true in the input to get a full tensor output at once. The later is the numerical more stable and faster method.