Atomic-orbital based real-time TDDFT for circular dichroism spectroscopy

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Wednesday, March 16, 4:05pm

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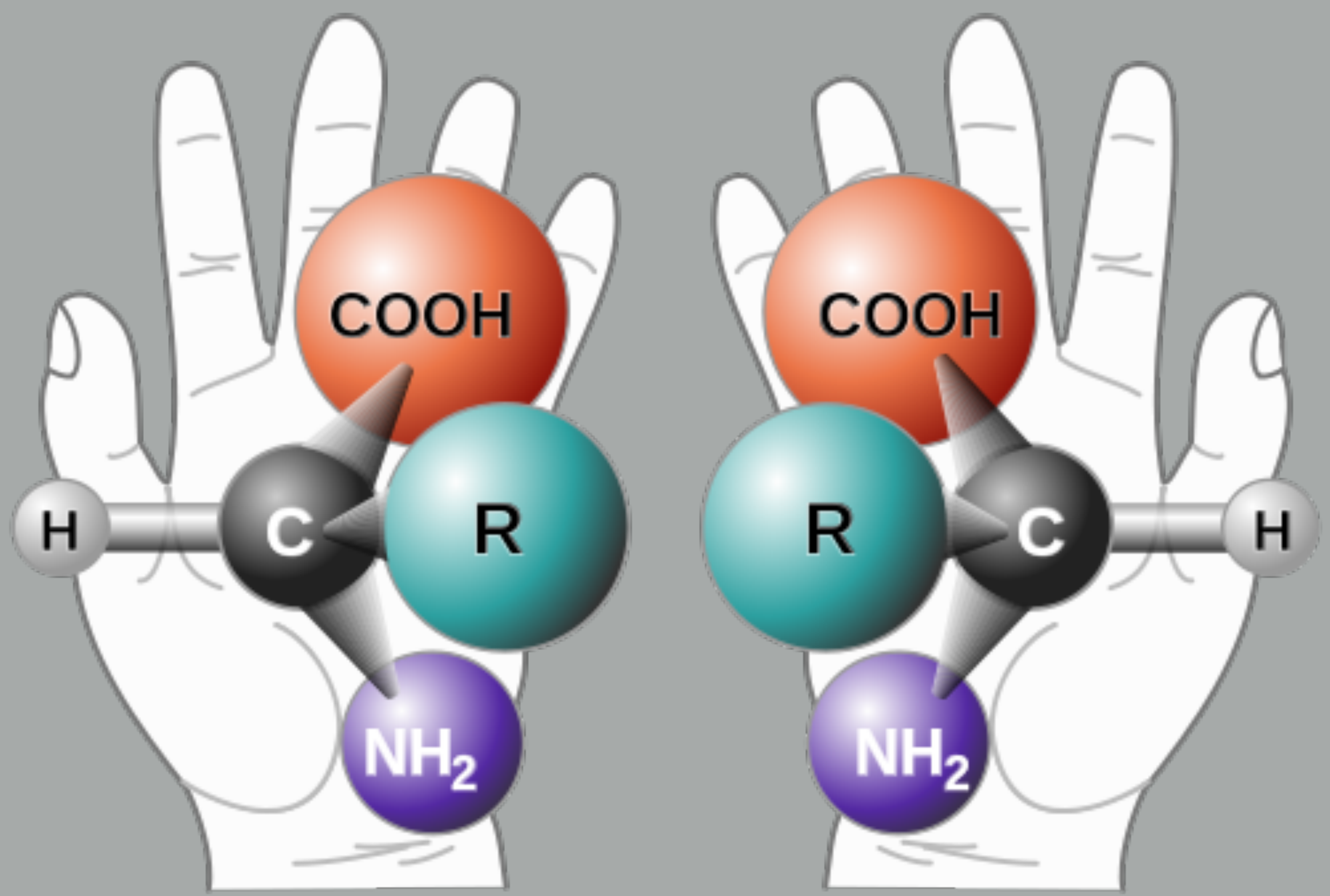
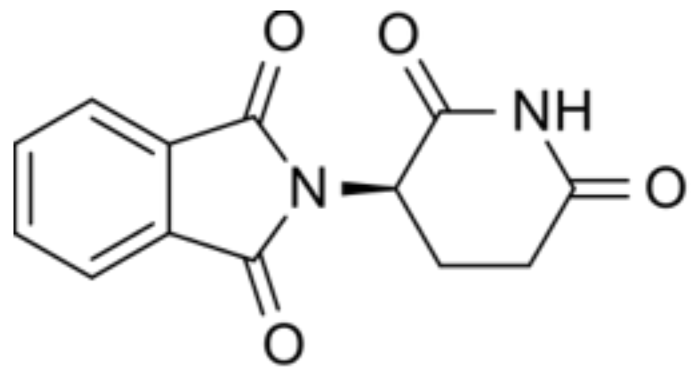
Natural circular dichroism

Differential absorption of circularly polarized light by chiral molecules

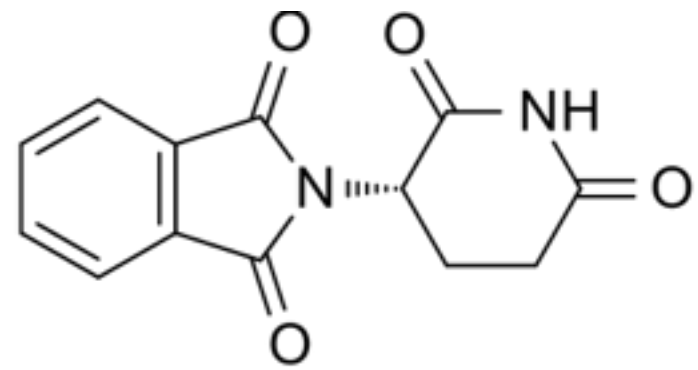


Source: NASA (http://www.nai.arc.nasa.gov/)

Thalidomide tragedy



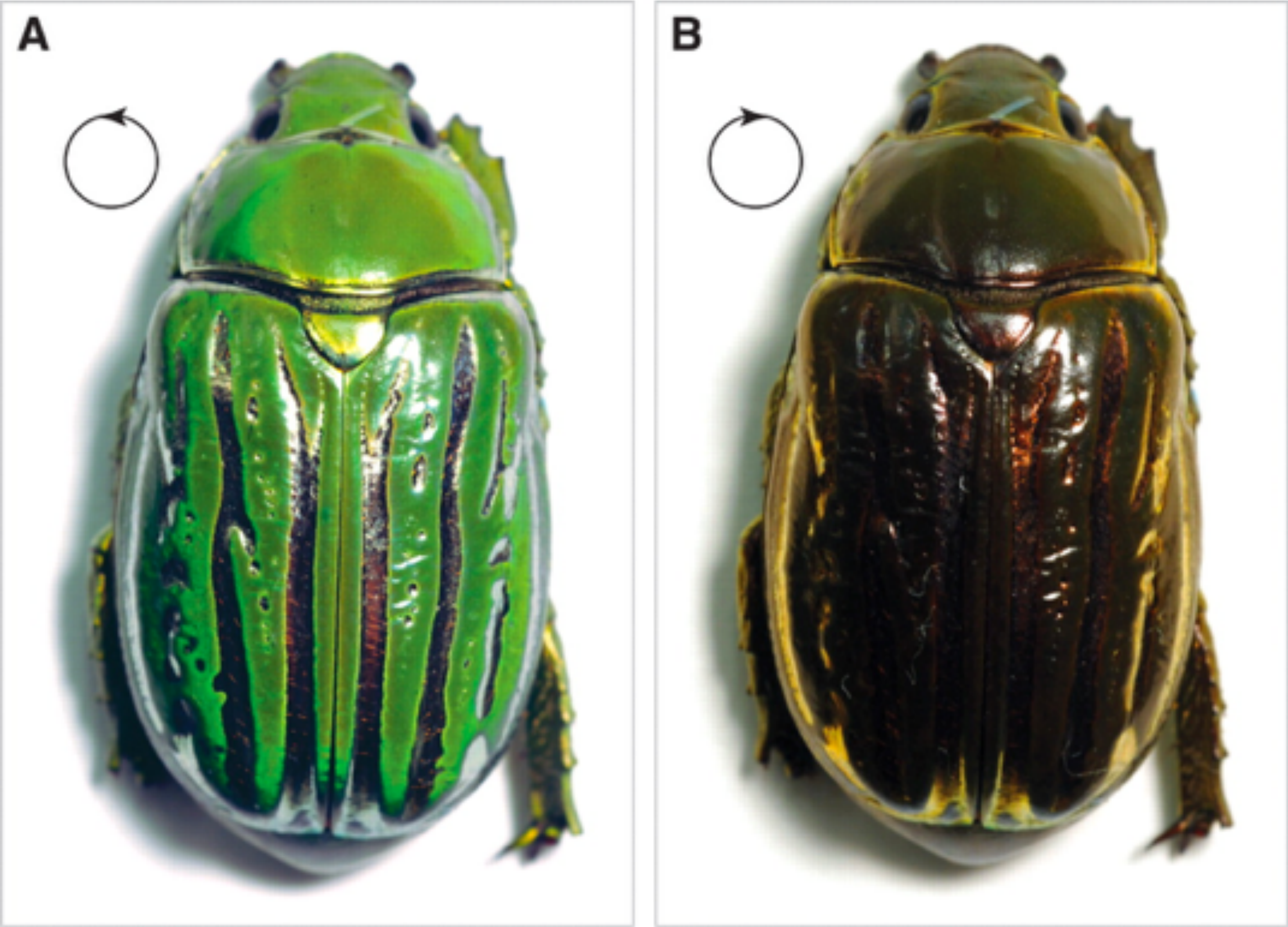
(R)-thalidomide



(S)-thalidomide

Source: Otis Historical Archives National Museum of Health and Medicine

Iridescence of the scarab beetle



Left CP　　　　Right CP

Sharma, Vivek, et al. "Structural origin of circularly polarized iridescence in jeweled beetles." Science 325.5939 (2009): 449-451.

In CD spectroscopy,
we usually care about rotary strength

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

Which characterizes the intensity of an isotropic CD transition

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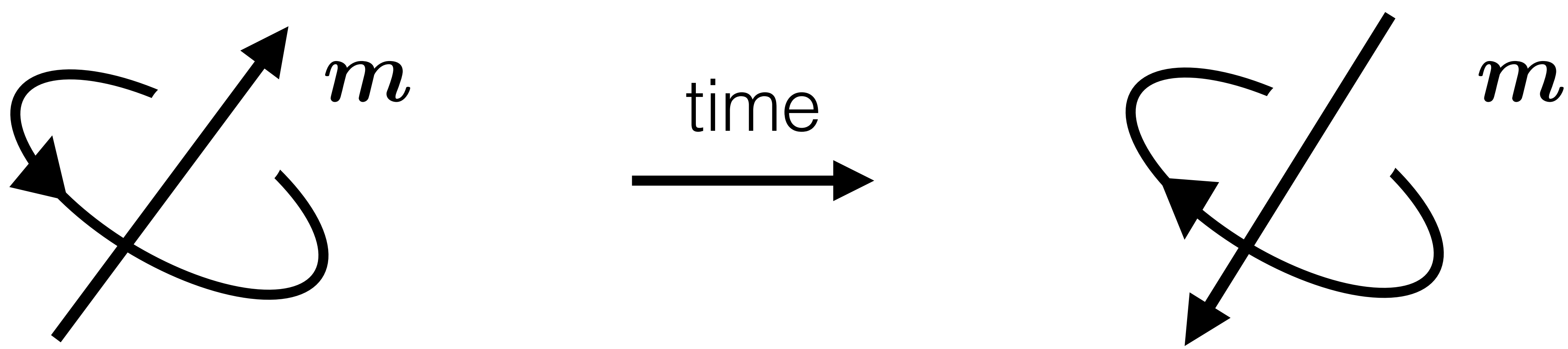
$\boldsymbol{\mu}$	electric dipole
$\boldsymbol{m}$	magnetic dipole

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

$\boldsymbol{\mu}$ electric dipole $\quad$ $\boldsymbol{m}$ magnetic dipole

Chiral molecules can support an oscillating current density, which arises as a result of a perturbing electric field



It’s important to note that

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

Only holds for isotropic (non-oriented) systems

For oriented systems,
(especially in X-ray CD spectroscopy)
we must also include the induced
electric dipole — electric quadrupole

Getting good (experimentally meaningful) CD spectra is not a trivial task

CD spectra can take positive and negative values

CD very sensitive to geometry, functional / wave function, and basis

Vibronic effects (and VCD) further complicate interpretation of spectra

Linear response:

TDDFT: Furche, 2001;
Autschbach, *et al.* 2002;
Stephens, *et al.* 2002;
Diedrich and Grimme 2003;
Caricato, 2014, 2015;
many more!

CC: Crawford, 2006;

Great if you want to study a specific transition,
gets expensive if you want the full band spectrum

Since we are often interested in CD bands,
real-time (RT) propagation is advantageous

Current RT-ECD methods are **grid-based**

Yabana and Bertsch, 1999;

Varsano, Daniele, *et al.*, 2009;

We have implemented an atomic-orbital based real-time method for computing the ECD band spectrum

Pros:

- No pseudopotential
- Variational ground state
- Can easily extend to X-ray regime
- No nuclear origin dependence

Cons:

- Not nearly as parallel as grid-based
- Still have gauge-origin dependencies

Working in the dipole length gauge
leads to gauge-origin dependencies.

RT-TDDFT and LR-TDDFT share this problem.

Despite this, Diedrich and Grimme (2003)
recommend length gauge due to robustness.

Ideally, we'd use London orbitals (GIAOs).

In RT-TDDFT we compute rotary strength

$$R(\omega) = \frac{\omega}{\pi c} \mathrm{Im} \left[\mathrm{Tr} \left(\boldsymbol{\beta}(\omega) \right) \right]$$

With a delta field, e.g. $E(t) = \delta(t)\kappa$

$$\beta_{\alpha\alpha}(\omega) = \frac{ic}{\omega \kappa_\alpha} m_\alpha(\omega)$$

Measure how much the magnetic dipole changes
as a function of perturbing electric dipole

To propagate, start with Kohn-Sham matrix

$$\mathbf{K} = \mathbf{h} + \mathbf{G}_{xe}[\mathbf{P}] + \alpha \cdot \mathbf{V}_{xc}[\mathbf{P}]$$

Time evolution (in orthonormal basis) governed by

$$i\frac{\partial \mathbf{P}'}{\partial t} = [\mathbf{K}', \mathbf{P}']$$

Modified Midpoint Unitary Update (MMUT)

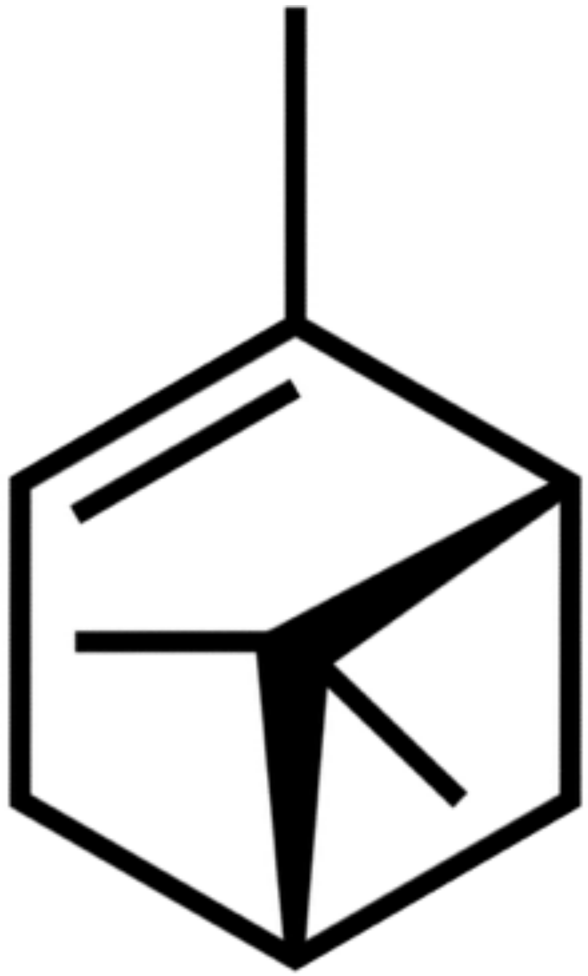
$$\mathbf{C}^\dagger(t_n)\cdot\mathbf{K}(t_n)\cdot\mathbf{C}(t_n) = \boldsymbol{\epsilon}(t_n)$$

$$\begin{aligned}\mathbf{U}(t_n) &= \exp\big[-i\cdot 2\Delta t\cdot\mathbf{K}(t_n)\big]\\ &= \mathbf{C}(t_n)\cdot\exp\big[-i\cdot 2\Delta t\cdot\boldsymbol{\epsilon}(t_n)\big]\cdot\mathbf{C}^\dagger(t_n)\end{aligned}$$

This allows for us to propagate density

$$\mathbf{P}(t_{n+1}) = \mathbf{U}(t_n)\cdot\mathbf{P}(t_{n-1})\cdot\mathbf{U}^\dagger(t_n)$$

Example: RT-ECD with alpha-1,3-(R,R)-pinene



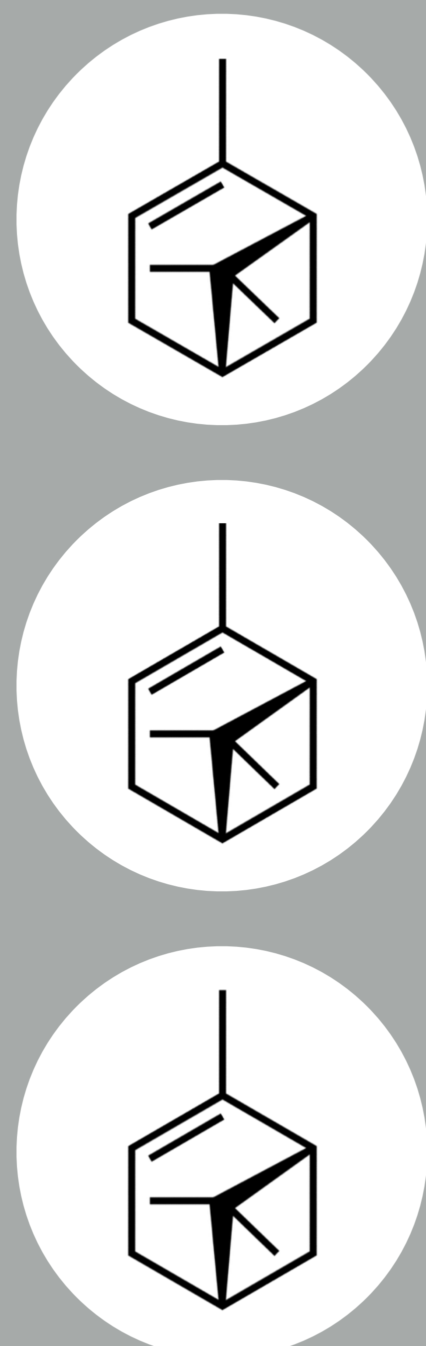
Perturb with delta $E(t)$

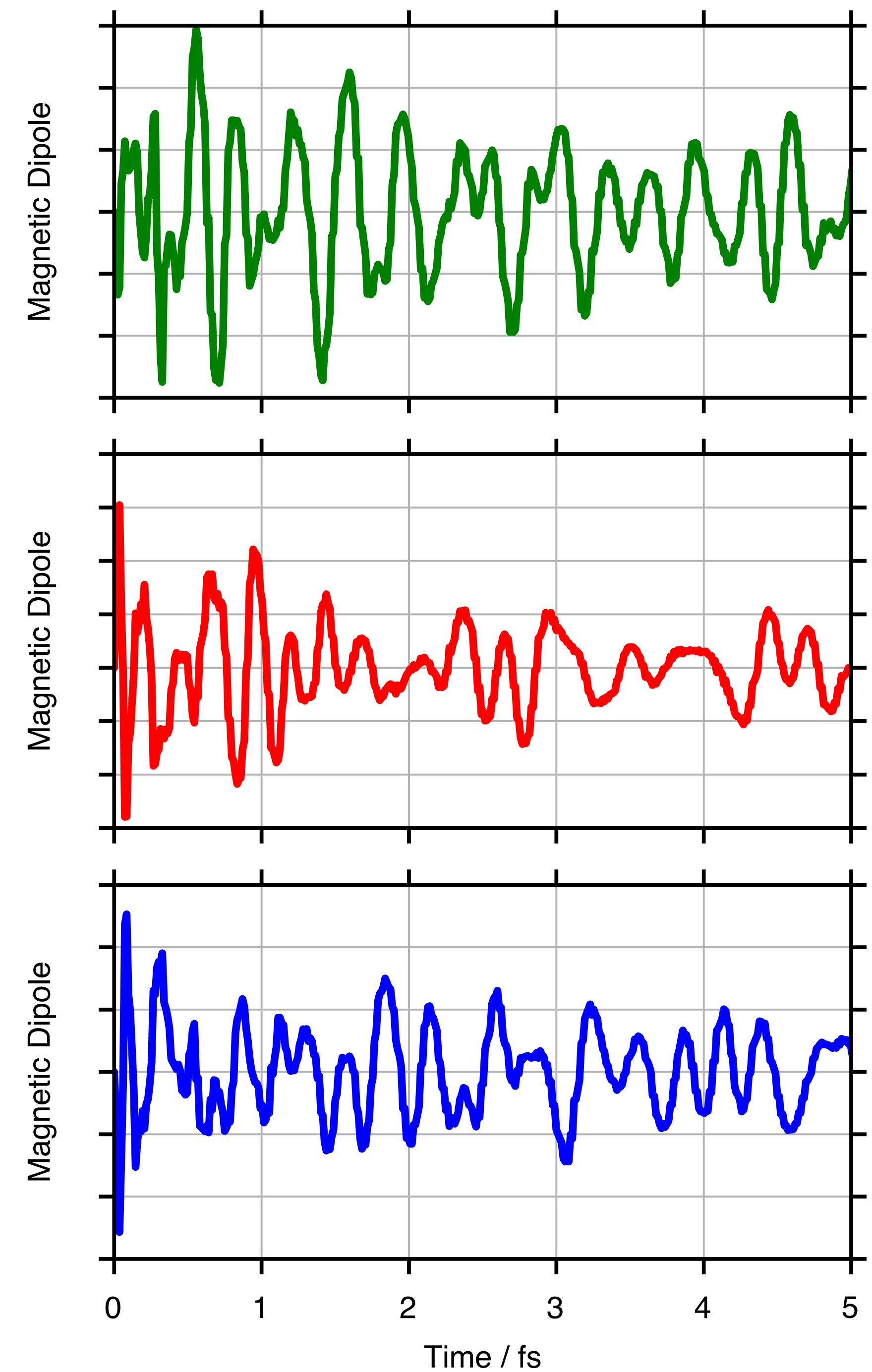
Measure $\boldsymbol{m}(t)$

$\delta(t)\kappa_x$

$\delta(t)\kappa_y$

$\delta(t)\kappa_z$





$m_x(t)$

$m_y(t)$

$m_z(t)$

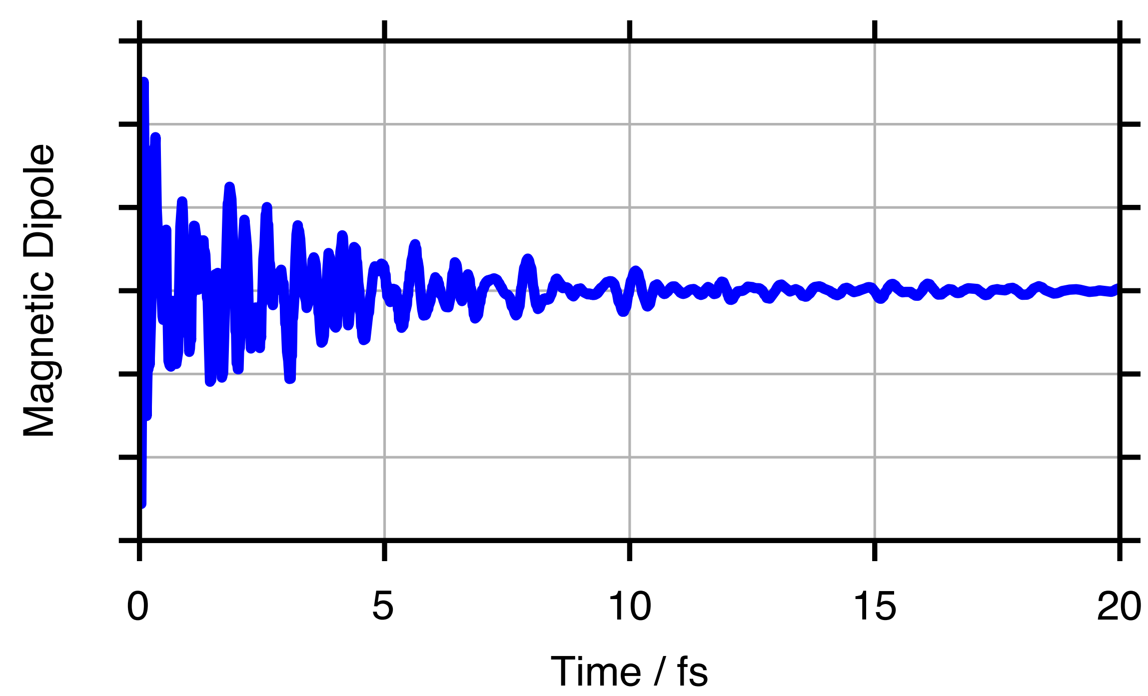
Fourier transforming TD magnetic dipole, substitute components

$$
\begin{aligned}
R(\omega) &= \frac{i}{\pi}\mathrm{Im}\left[\mathrm{Tr}\left(\frac{m_\alpha(\omega)}{\kappa_\alpha}\right)\right] \\
&= \frac{1}{\pi}\mathrm{Re}\left[\mathrm{Tr}\left(\frac{m_\alpha(\omega)}{\kappa_\alpha}\right)\right]
\end{aligned}
$$

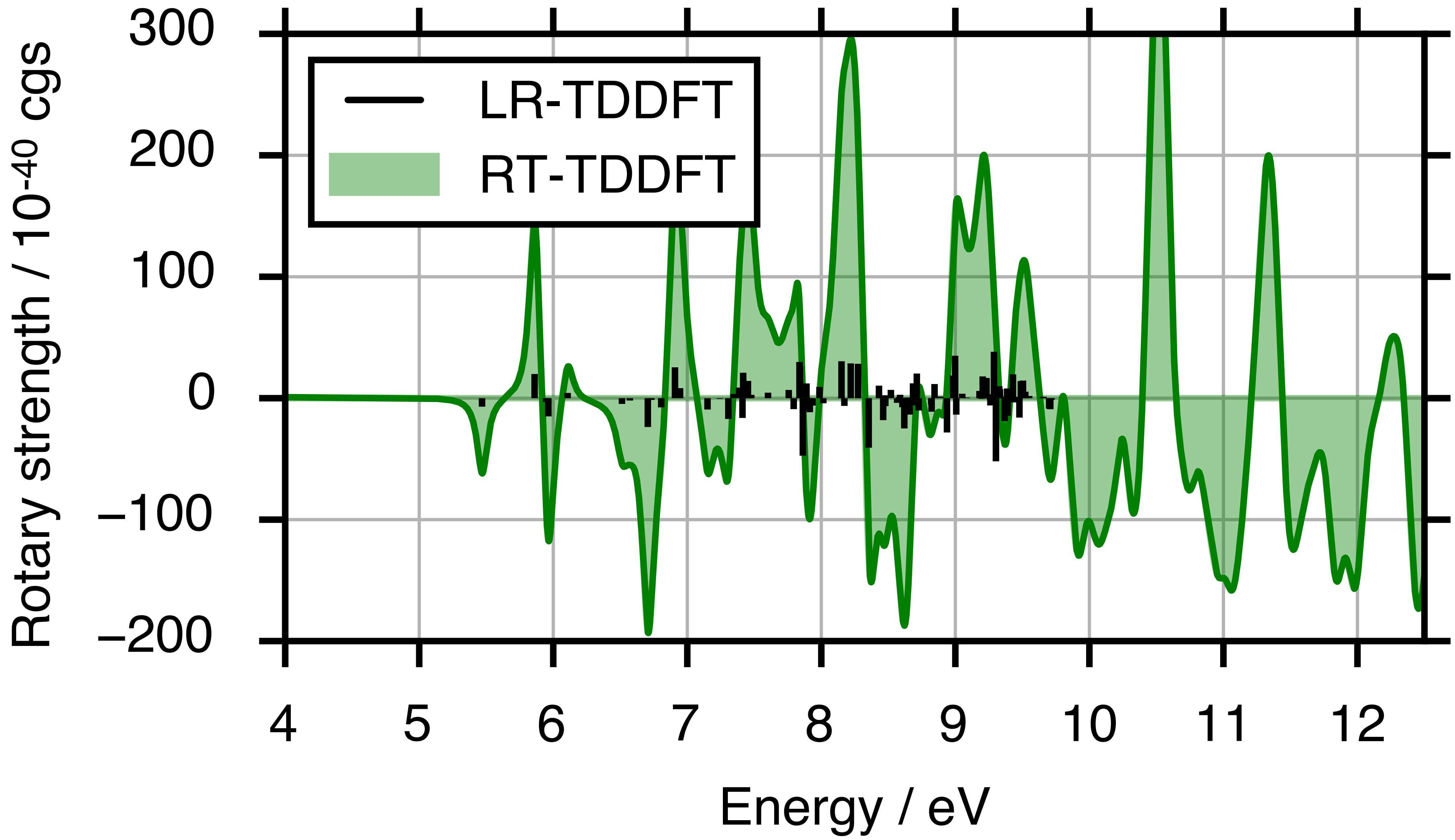
To give each peak a finite width,
we artificially damp by an exponential

$$\boldsymbol{m}'(t) = \boldsymbol{m}(t)e^{-t/a}$$

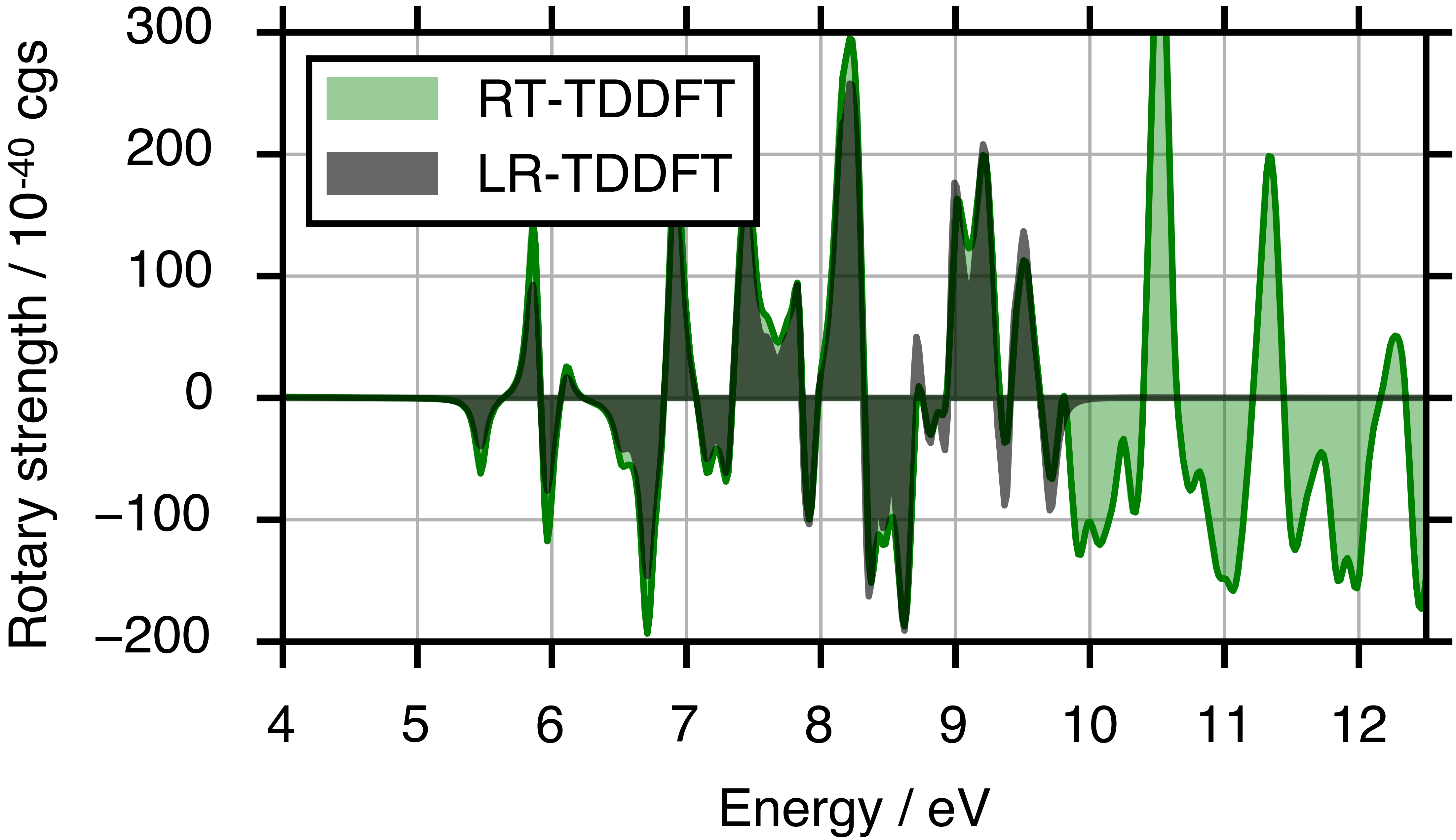
This effectively "dresses" each peak as a Lorentzian



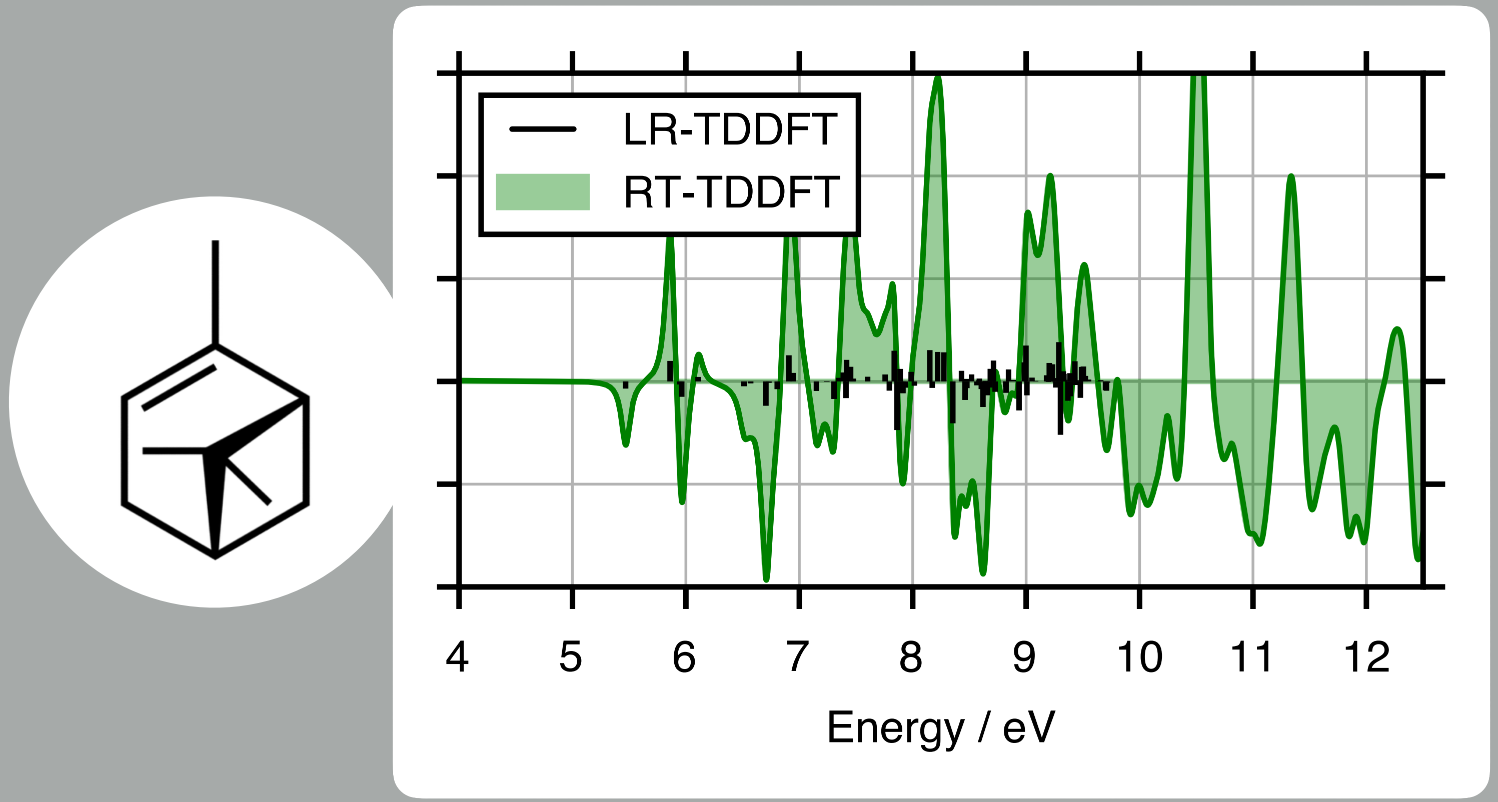
We damp to give a
FWHM of 0.05 eV



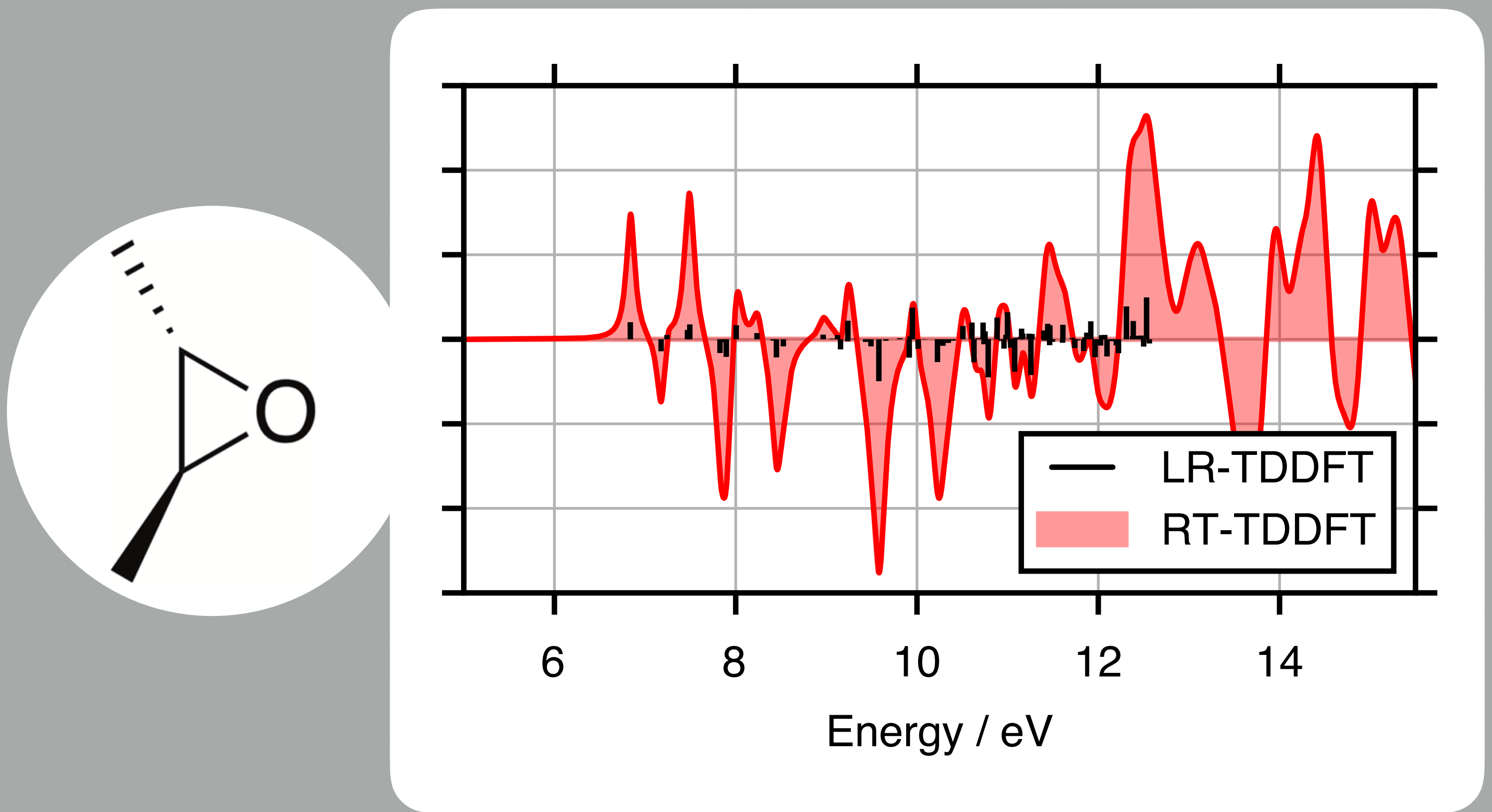
With a weak delta field, we can recover LR-TDDFT



With a weak delta field, we can recover LR-TDDFT alpha-1,3-(R,R)-pinene



2,3-(S,S)-dimethyloxirane



B3LYP/6-31+G*

Compare to first 100 LR-TDDFT states

Resolution limited by propagation time

Here, at least 100 fs, 0.012 fs time step

Since we have the full ECD spectrum, integrating over should give the sum rules of Condon (1937)

$$\sum_{n \neq 0} R(n \leftarrow 0) = \sum_{n \neq 0} \mathrm{Im}\left(\langle 0|\boldsymbol{\mu}|n\rangle \langle n|\boldsymbol{m}|0\rangle\right) = 0$$

We expect

$$\int_0^\infty d\omega R(\omega) = 0$$

In practice, we find sums

$$0.00001 < \int_0^\infty d\omega R(\omega) < 1.0$$

Signals inadequate basis set and numerical noise

pinene: TZVP two orders of magnitude less than 6-31+G*

AO-based Real Time TDSCF in `ChronusQ`

https://github.com/liresearchgroup/chronusq_public

Real Time TDSCF

1. Free & open source!
2. RHF, UHF, GHF, complex
3. Various types of fields
4. C++/Python

DFT and ECD,
soon to be released
on public branch!

Thank you!

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

$$R(\omega) = \frac{\omega}{\pi c}\mathrm{Im}\left[\mathrm{Tr}\left(\boldsymbol{\beta}(\omega)\right)\right]$$

$$\beta_{\alpha\alpha}(\omega) = \frac{ic}{\omega\kappa_\alpha} m_\alpha(\omega)$$

$$\begin{aligned} R(\omega) &= \frac{i}{\pi}\mathrm{Im}\left[\mathrm{Tr}\left(\frac{m_\alpha(\omega)}{\kappa_\alpha}\right)\right] \\ &= \frac{1}{\pi}\mathrm{Re}\left[\mathrm{Tr}\left(\frac{m_\alpha(\omega)}{\kappa_\alpha}\right)\right] \end{aligned}$$

$$R(\omega) = \frac{1}{\pi}\mathrm{Re}\left[\mathrm{Tr}\left(\frac{m_\alpha(\omega)}{\kappa_\alpha}\right)\right]$$

$$\mathbf{K} = \mathbf{h} + \mathbf{G}_{xe}[\mathbf{P}] + \alpha \cdot \mathbf{V}_{xc}[\mathbf{P}]$$

$$i\frac{\partial \mathbf{P}'}{\partial t} = [\mathbf{K}', \mathbf{P}']$$

$$\begin{aligned}
\mathbf{C}^\dagger(t_n) \cdot \mathbf{K}(t_n) \cdot \mathbf{C}(t_n) &= \boldsymbol{\epsilon}(t_n) \\
\mathbf{U}(t_n) &= \exp\left[-i \cdot 2\Delta t \cdot \mathbf{K}(t_n)\right] \\
&= \mathbf{C}(t_n) \cdot \exp\left[-i \cdot 2\Delta t \cdot \boldsymbol{\epsilon}(t_n)\right] \cdot \mathbf{C}^\dagger(t_n)
\end{aligned}$$

$$\mathbf{P}(t_{n+1}) = \mathbf{U}(t_n) \cdot \mathbf{P}(t_{n-1}) \cdot \mathbf{U}^\dagger(t_n)$$