Optical and vibrational spectroscopy of (chiral) systems with RT-TDDFT: Gauge dependence and linear response

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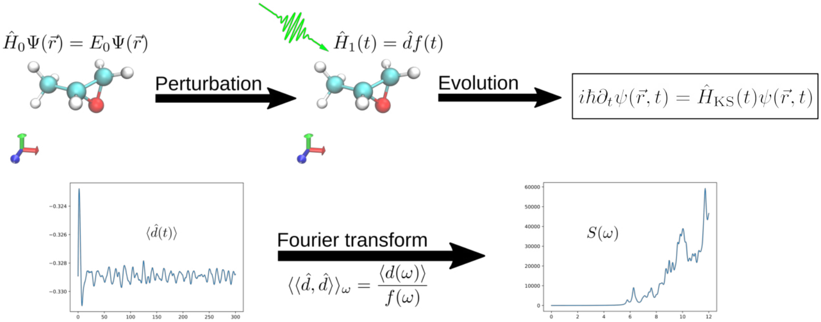
Outline

1. Real-time TDDFT
2. Linear response theory and gauge dependence
3. Applications to optical spectroscopy
    - UV-VIS absorption
    - Electric circular dichroism
    - Non-, resonance Raman
    - Non-, resonance Raman optical activity

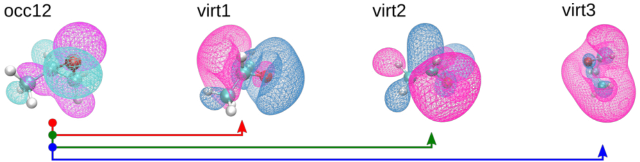
Optical response with RT-TDDFT

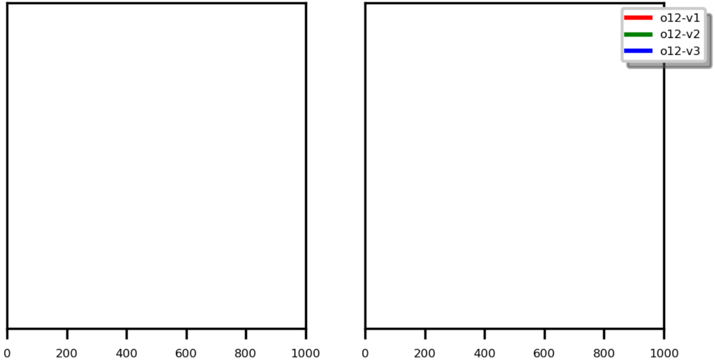


- δ-pulse to excite the full spectrum.
- Different combinations of perturbation $\hat{A}$ and 'measurement' $\hat{B}$.
- Construct linear response function (LRF) implicitly

$$\langle\langle\hat{B};\hat{A}\rangle\rangle_\omega E(\hbar\omega) = \langle\hat{B}(\hbar\omega)\rangle = \lim_{\epsilon\to 0^+}\int_{-\infty}^{\infty}\mathrm{d}t\ \left(\langle\hat{B}(t)\rangle - \langle\hat{B}\rangle_0\right)e^{i\omega t}e^{-\epsilon t}$$

Illustration





Length and velocity gauge Hamiltonians

- Long wavelength approximation

$$\vec{A}(\vec{r},t) \approx \vec{A}(t) \qquad U(\vec{r},t) \approx U(t)$$

  Implies $\vec{B}(t) = 0$
- Length gauge Hamiltonian

$$\hat{H}^{\text{len}} = \frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) - \hat{\vec{d}} \cdot \vec{E}(t)$$

- Velocity gauge Hamiltonian (Göppert-Mayer gauge transformation)

$$\hat{H}^{\text{vel}} = \frac{1}{2m}\left(\hat{\vec{p}} + \frac{e}{c}\vec{A}(t)\right)^2 + V(\vec{r})$$

- In *theory* the time-dependent Kohn–Sham equations (TDKS) are *gauge invariant.*
- Not in practice ...

Sources of gauge dependence

Finite basis sets

- Gauge transformation:

$$\phi_i'(\vec{r},t) = \sum_i^N c_{i\nu}(t) e^{\frac{ie}{c\hbar}\theta(\vec{r},t)} \chi_\nu(\vec{r})$$

- Expand into the same basis set

$$\phi_i'(\vec{r},t) = \sum_i^N c_{i\nu}'(t) \chi_\nu(\vec{r})$$

- For a finite basis there will always be a choice of $\theta(\vec{r},t)$ that will take $e^{\frac{ie}{c\hbar}\theta(\vec{r},t)} \chi_\nu(\vec{r})$ outside its linear span.
- Remedy: Approach complete basis set limit.

Non-local potentials

- Explicit gauge transformation

$$\hat{V}_{\mathrm{nl}}' = e^{\frac{ie}{c\hbar}\theta(\vec{r},t)}\ \hat{V}_{\mathrm{nl}}\ e^{-\frac{ie}{c\hbar}\theta(\vec{r},t)}$$

- Linear order

$$-\frac{i}{c\hbar}[\hat{V}_{\mathrm{nl}}, \hat{\vec{d}}] \cdot \vec{A}$$

- Velocity operator

$$\hat{\vec{v}} = \frac{i}{\hbar}[\hat{H}, \hat{\vec{r}}] = \frac{\hat{\vec{p}}}{m} + \frac{i}{\hbar}\left[\hat{V}_{\mathrm{nl}}, \hat{\vec{r}}\right] + \frac{e}{mc}\vec{A}$$

- Non-local terms carry explicit dependence on $\vec{A}$

Ding, et al., *J. Chem. Phys.*, **135**, 164101 (2011); Ismail-Beigi, et al., *Phys. Rev. Lett.*, **87**, 087402 (2001)

Linear response in time and energy domain

- Linear response of $\hat{B}$ to $\hat{H}_1 = -\hat{A}f(t)$

$$\langle \hat{B}(t) \rangle - \langle \hat{B} \rangle_0 = \int_{-\infty}^{t} \mathrm{d}t' \ \langle\langle \hat{B}(t); \hat{A}(t') \rangle\rangle f(t')$$

- Energy domain, inserting eigen states of $\hat{H}_0$, $|k\rangle$

$$\langle\langle \hat{B}; \hat{A} \rangle\rangle_\omega = \lim_{\epsilon \to 0} \sum_k \frac{1}{\hbar} \left[\frac{\langle 0|\hat{B}|k\rangle \ \langle k|\hat{A}|0\rangle}{\omega - (\omega_k - \omega_0) + i\epsilon} - \frac{\langle 0|\hat{A}|k\rangle \ \langle k|\hat{B}|0\rangle}{\omega - (\omega_0 - \omega_k) - i\epsilon} \right]$$

- Properties of linear response functions

$$\hbar\omega \langle\langle \hat{B}; \hat{A} \rangle\rangle_\omega = \langle [\hat{B}, \hat{A}] \rangle_0 + \langle\langle [\hat{B}, \hat{H}]; \hat{A} \rangle\rangle_\omega \qquad \text{(complete basis)}$$

$$\langle\langle \hat{B}; \hat{A} \rangle\rangle_\omega^* = \langle\langle \hat{B}; \hat{A} \rangle\rangle_{-\omega} = \langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega \qquad \text{(finite basis)}$$

Length and velocity representations

- First order perturbation operators in length and velocity *gauge*

$$\hat{H}_1^{\text{len}} = e\ \hat{\vec{r}} \cdot \vec{E}(t)$$
$$\hat{H}_1^{\text{vel}} = \frac{e}{c}\ \hat{\vec{v}} \cdot \vec{A}(t)$$

- Length and velocity *representations*

$$\left\langle a \middle| [\hat{H}, \hat{\vec{r}}] \middle| b \right\rangle = (E_a - E_b) \left\langle a \middle| \hat{\vec{r}} \middle| b \right\rangle = \left\langle a \middle| \hat{\vec{v}} \middle| b \right\rangle$$

- Linear response functions, e. g. electric-dipole–electric-dipole response

$$\hbar\omega\langle\langle\hat{r};\hat{r}\rangle\rangle_\omega = \langle\langle[\hat{r},\hat{H}];\hat{r}\rangle\rangle_\omega = i\hbar\langle\langle\hat{v};\hat{r}\rangle\rangle_\omega$$

- 4 possible LRF: len-len, len-vel, vel-len, vel-vel

Zoo of linear response functions

- $\langle\langle \text{measurement}; \text{perturbation} \rangle\rangle_\omega$

propagator	response tensor	simplified notation	experiment	ref point dependence
$\langle\langle \hat{d}_\beta; \hat{d}_\alpha \rangle\rangle_\omega$	l,l	$\alpha_{\alpha\beta}$	UV-VIS, Raman, ROA	no
$\langle\langle \hat{d}_\beta; \dot{\hat{d}}_\alpha \rangle\rangle_\omega$	l,v	$\alpha_{\alpha\beta}$	UV-VIS, Raman, ROA	no
$\langle\langle \dot{\hat{d}}_\beta; \hat{d}_\alpha \rangle\rangle_\omega$	v,l	$\alpha_{\alpha\beta}$	UV-VIS, Raman, ROA	no
$\langle\langle \dot{\hat{d}}_\beta; \dot{\hat{d}}_\alpha \rangle\rangle_\omega$	v,v	$\alpha_{\alpha\beta}$	UV-VIS, Raman, ROA	no
$\langle\langle \hat{m}^{\mathrm{nl}}_\beta; \hat{d}_\alpha \rangle\rangle_\omega$	m,l	$G_{\alpha\beta}$	ECD, ROA	yes
$\langle\langle \hat{m}^{\mathrm{nl}}_\beta; \dot{\hat{d}}_\alpha \rangle\rangle_\omega$	m,v	$G_{\alpha\beta}$	ECD, ROA	yes
$\langle\langle \hat{q}_{\beta\gamma}; \hat{d}_\alpha \rangle\rangle_\omega$	q,l	$A_{\alpha,\beta\gamma}$	ROA	yes
$\langle\langle \hat{q}_{\beta\gamma}; \dot{\hat{d}}_\alpha \rangle\rangle_\omega$	q,v	$A_{\alpha,\beta\gamma}$	ROA	yes
$\langle\langle \dot{\hat{q}}_{\beta\gamma}; \hat{d}_\alpha \rangle\rangle_\omega$	qv,l	$A_{\alpha,\beta\gamma}$	ROA	yes
$\langle\langle \dot{\hat{q}}_{\beta\gamma}; \dot{\hat{d}}_\alpha \rangle\rangle_\omega$	qv,v	$A_{\alpha,\beta\gamma}$	ROA	yes

- LRF are connected to spectroscopy via spectroscopic **invariants**
- Moments:

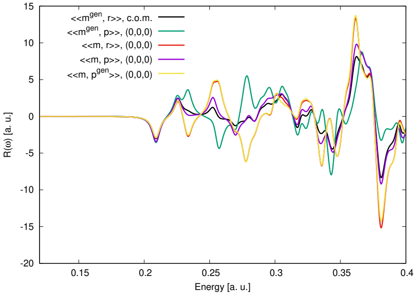
$$\hat{d}_\alpha = -e\hat{r}_\alpha, \quad \hat{m}_\alpha = -\frac{e}{2c}\epsilon_{\alpha\beta\gamma}\hat{r}_\beta\hat{v}_\gamma, \quad \hat{q}_{\alpha\beta} = -e\hat{r}_\alpha\hat{r}_\beta$$

- Implemented in `CP2K`.

Electric circular dichroism – reference point dependence

Two sources of error:

- Finite basis sets.
- Non-local commutator term.



Dependent on choice of representation:

- E. g. for ECD invariant:

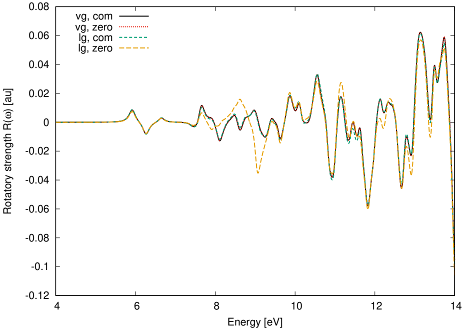
$$
\begin{aligned}
&\sum_\alpha \langle\langle \hat{m}^{\mathrm{nl}}_\alpha(\vec{R}+\vec{a}); \hat{d}_\alpha \rangle\rangle_\omega = \\
&\sum_\alpha \langle\langle \hat{m}^{\mathrm{nl}}_\alpha(\vec{R}); \hat{d}_\alpha \rangle\rangle_\omega \\
&+ \sum_j \frac{1}{2c}\left(a_y \langle\langle \dot{\hat{d}}_z; \hat{d}_x \rangle\rangle_\omega - a_z \langle\langle \dot{\hat{d}}_y; \hat{d}_x \rangle\rangle_\omega \right) \\
&+ \sum_j \frac{1}{2c}\left(a_z \langle\langle \dot{\hat{d}}_x; \hat{d}_y \rangle\rangle_\omega - a_x \langle\langle \dot{\hat{d}}_z; \hat{d}_y \rangle\rangle_\omega \right) \\
&+ \sum_j \frac{1}{2c}\left(a_x \langle\langle \dot{\hat{d}}_y; \hat{d}_z \rangle\rangle_\omega - a_y \langle\langle \dot{\hat{d}}_x; \hat{d}_z \rangle\rangle_\omega \right)
\end{aligned}
$$

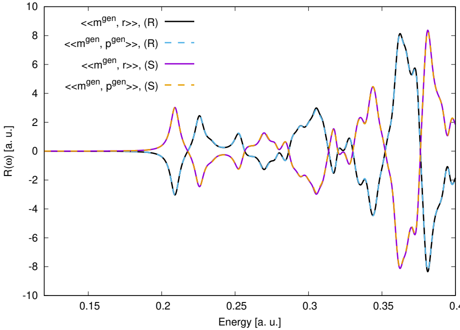
- $\langle\langle \dot{\hat{d}}_\beta; \hat{d}_\alpha \rangle\rangle_\omega \approx \langle\langle \dot{\hat{d}}_\alpha; \hat{d}_\beta \rangle\rangle_\omega$ only approximately fulfilled for finite basis sets

Mattiat, Luber, *Chem. Phys.*, **527**, 110464, (2019)

Electric circular dichroism – Results

(R)-methyloxirane





- Differences between length and velocity gauge vanish with increasing basis set.
- Velocity gauge is inherently reference point independent for finite basis sets.
- Magnetic dipole moment couples via velocity operator and includes non-local commutator.

Mattiat, Luber, *Chem. Phys.*, **527**, 110464, (2019)

Raman/ROA with RT-TDDFT

- **Static approach** (Double harmonic approximation):
  - Normal mode analysis, finite differences.

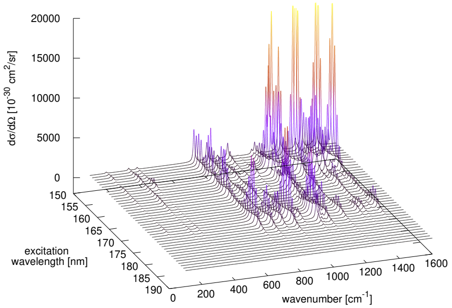
$$\hat{\alpha}^{\mathrm{PtP}}_{\alpha\beta}(\omega_I, q) = \hat{\alpha}^{\mathrm{PtP}}_{\alpha\beta}(\omega_I, q_0) + \left(\frac{\partial \hat{\alpha}^{\mathrm{PtP}}_{\alpha\beta}(\omega_I, q)}{\partial q_k}\right)_{q=q_0} q_k + \cdots$$

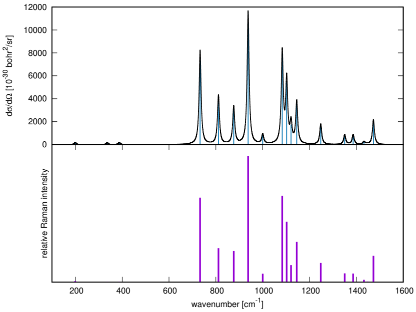
- **Dynamic approach**:
  - Time autocorrelation function of polarizabilities [nuclear time scale].

$$I_{\alpha\beta} = \int_{-\infty}^{\infty} \mathrm{d}t \sum_i p_i \, \langle i|\hat{\alpha}^{\mathrm{PtP}}_{\alpha\beta}\, \hat{\alpha}^{\mathrm{PtP}}_{\alpha\beta}(t)|i\rangle \exp\{-i\tilde{\omega}t\}$$

- **Born-Oppenheimer** and **short time approximation** (STA):
  - Decoupled electronic and nuclear degrees of freedom.
  - Treat nuclear degrees of freedom classically.
    $\rightarrow$ Full separation of electronic and nuclear time scales
- With RT-TDDFT cover non-resonance and resonance regimes simultaneously [electronic time scale].

Raman, static: Uracil

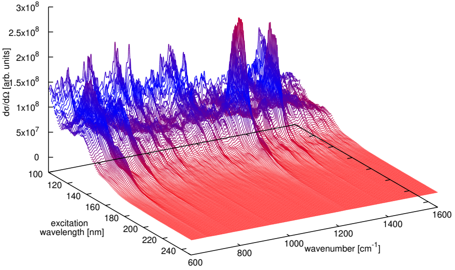


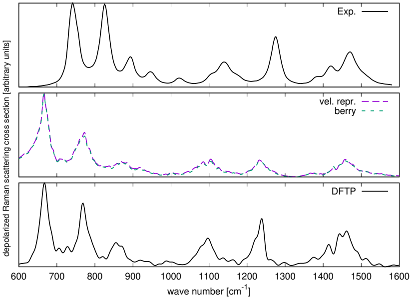


- Finite difference derivatives of $\alpha(\omega)$ along normal modes.
- All combinations of representations agree well.
- The STA corresponds to excited state gradient method.

Mattiat, Luber, *J. Chem. Phys.*, **149**, 174108, (2018)

Raman, dynamic: Liquid (S)-methyloxirane

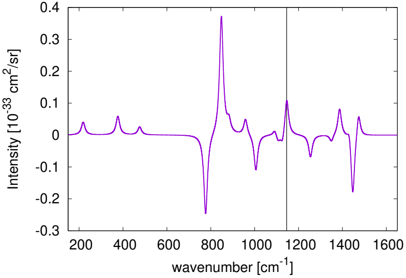


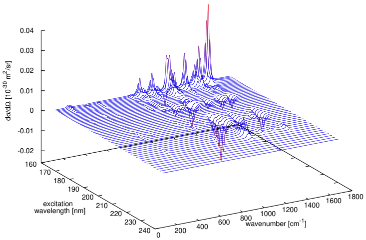


- Electronic time scale: RT-TDDFT.
- Nuclear time scale: Ab initio molecular dynamics.
- Periodic boundary conditions.

Mattiat, Luber, *J. Chem. Theory Comput.*, **17**, 1, 344–356, (2021)

Raman optical activity, static

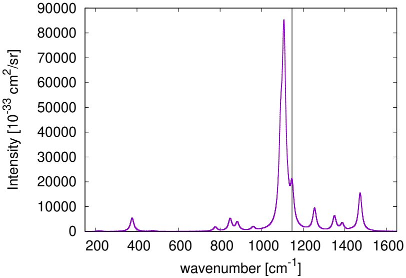


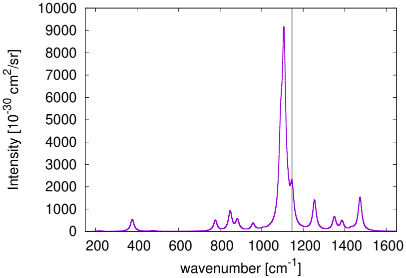


- Spectroscopic invariants $\alpha\mathbf{G}$, $\beta(\mathbf{G})^2$, and $\beta(\mathbf{A})^2$.
- Certain combinations of representations are reference point independent.

Mattiat, Luber, *J. Chem. Phys.*, **151**, 234110, (2019)

Resonance Raman optical activity: Two state limit



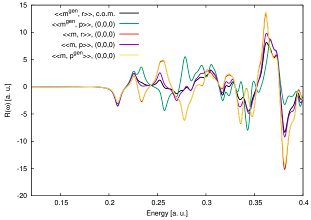


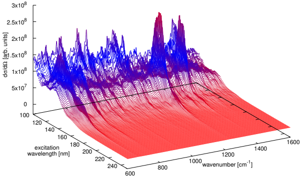
- If only one excited state is involved the ROA spectrum matches the Raman spectrum in form up to the sign (which is determined by the ECD intensity).

Mattiat, Luber, *J. Chem. Phys.*, **151**, 234110, (2019)

Conclusions

- RT-TDDFT allows clear distinction between *perturbation* and *measurement* for the construction of LRF.
- Gauge and reference point dependence:
    - Length and velocity gauges are only equivalent in the complete basis set limit.
    - Non-local potentials require explicit gauge transformation.
    - Spectroscopic invariants are truly invariant only for certain representations of linear response functions.
- Non-resonance and resonance Raman/ROA spectra for non-periodic and periodic systems, combining AIMD + RT-TDDFT





Thanks!

University of Zurich[UZH]

URPP LightChEC

Swiss National Science Foundation

CSCS Centro Svizzero di Calcolo Scientifico Swiss National Supercomputing Centre

CP2K

- `www.luber-group.com`
- Thanks for your attention!