On the use of real-time impulse response in non-linear optics

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Summary

- **Focus**:
  - Real-time impulse response cannot be used in non-linear optics. Is it true?
  - The case of excited-state absorption and reverse saturable absorption
- **Outline**:
  - Theory and analytical model
  - Applications to organic molecules

PhD Thesis Alberto Guandalini

Non-linear optics

Mathematical properties

•The response to a monochromatic field is no longer monochromatic

•Non-linear dependence of the induced polarization on the *exposure* (J m^{-2}) to the external field (also called *fluence*)

•Non-linear dependence of the induced polarization on the *irradiance* (W m^{-2}) of the external field

•Non-linear dynamics and chaos

Physical phenomena

•High harmonics generation

•Frequency mixing

•Saturable absorption (SA) and reverse saturable absorption (RSA)

•Multi-photon absorption

•Optical Kerr effect (irradiance dependent refractive index)

•Optical solitons (non-linear wave propagation)

Perturbation theory

Static perturbation theory

$$p_i = d_i^0 + \sum_j \alpha_{ij} E_j + \sum_{jk} \beta_{ijk} E_j E_k + \sum_{jkl} \gamma_{ijkl} E_j E_k E_l + \dots$$

Dynamic perturbation theory

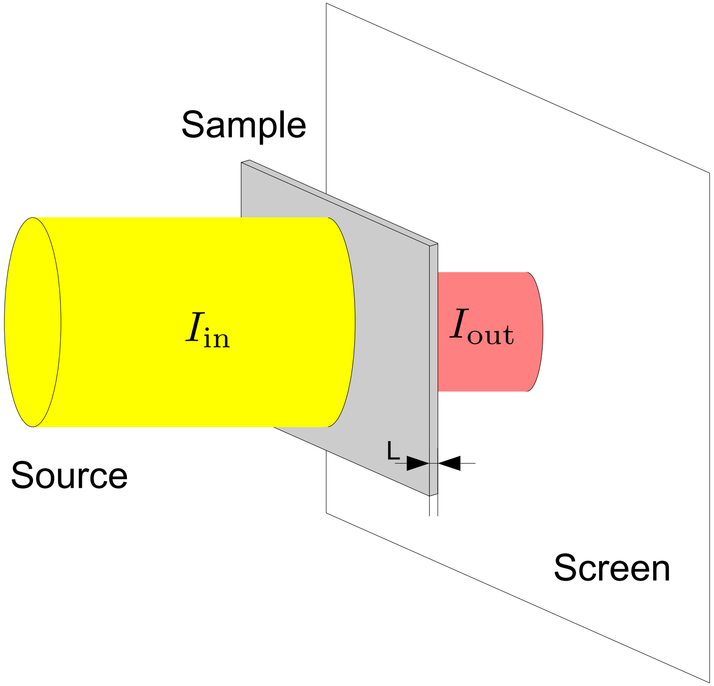
$$\begin{aligned} p_i(\omega) &= \sum_j \chi_j^{(1)}(\omega) E_j(\omega) \\ &+ \sum_{jk} \int \frac{d\omega'}{2\pi} \chi_{ijk}^{(2)}(\omega', \omega - \omega') E_j(\omega') E_k(\omega - \omega') \\ &+ \sum_{jkl} \int \frac{d\omega'}{2\pi} \int \frac{d\omega''}{2\pi} \chi_{ijkl}^{(3)}(\omega', \omega'', \omega - \omega' - \omega'') E_j(\omega') E_k(\omega'') E_l(\omega - \omega' - \omega'') \\ &+ \dots \end{aligned}$$

Requires unoccupied states
converges slowly with their number
calculation complexity increases quickly

A few known methods

Sternheimer's approach for TDDFT	Sternheimer, R. M. (1954), Phys. Rev. 96, 951 Andrade, X. et al. (2007), J. Chem. Phys. 126, 184106.
Dyson-like equation	Luppi, E. et al. (2010), J. Chem. Phys. 132, 241104
Finite differences	Vila, F. et al. (2010). J. Chem. Phys. 133, 034111 Goncharov, V. A. And Varga, K. (2012), J. Chem. Phys 137, 094111
Time propagation with ultrashort pulses	Takimoto et al. (2007), J. Chem. Phys. 127, 154114 Uemoto, M. et al. (2019). J. Chem. Phys. 150, 094101.
Two-steps perturbation theory	Fischer, S. et al. (2015), J. Chem. Theory Comput. 11, 4294

Absorption cross-section (stationary)



Transmittance $T = \frac{I_{\rm out}}{I_{\rm in}}$

Absorbance $A = \log\left(\frac{I_{\rm in}}{I_{\rm out}}\right)$

Total absorption cross section $\sigma = \frac{\Delta\mathcal{E}_{\rm abs}}{I_{\rm in}}$

Absorption coefficient $\alpha = \sigma n$

linear $\frac{dI(z)}{dz} = -\alpha I(z)$ Beer-Lambert law

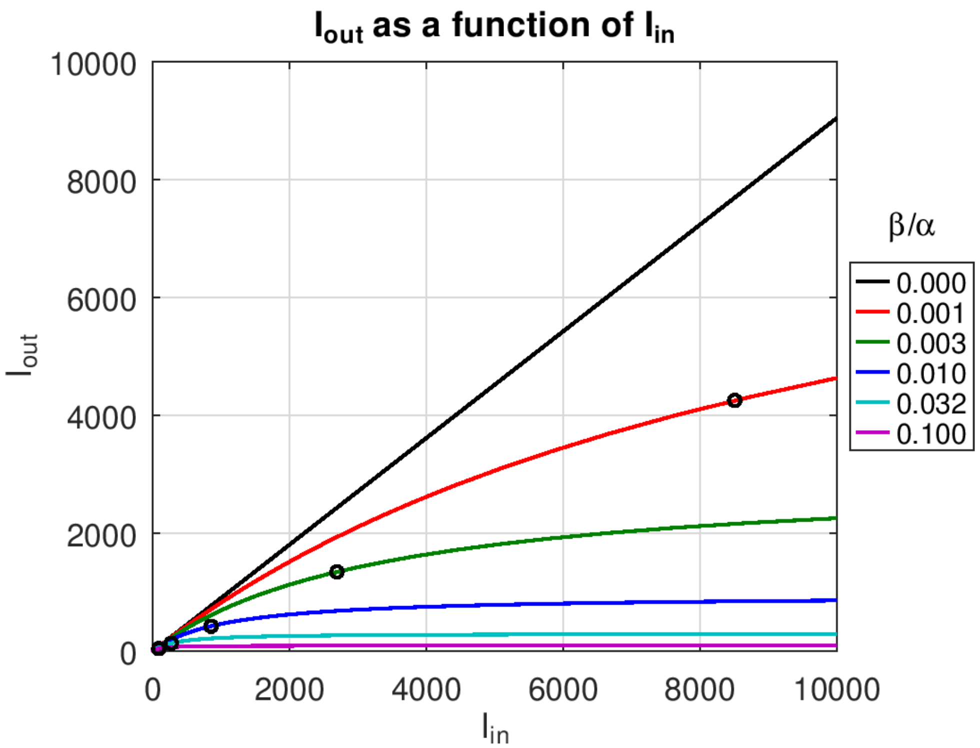
$$I_{\rm out} = I(L) = I_{\rm in} e^{-\alpha L}$$

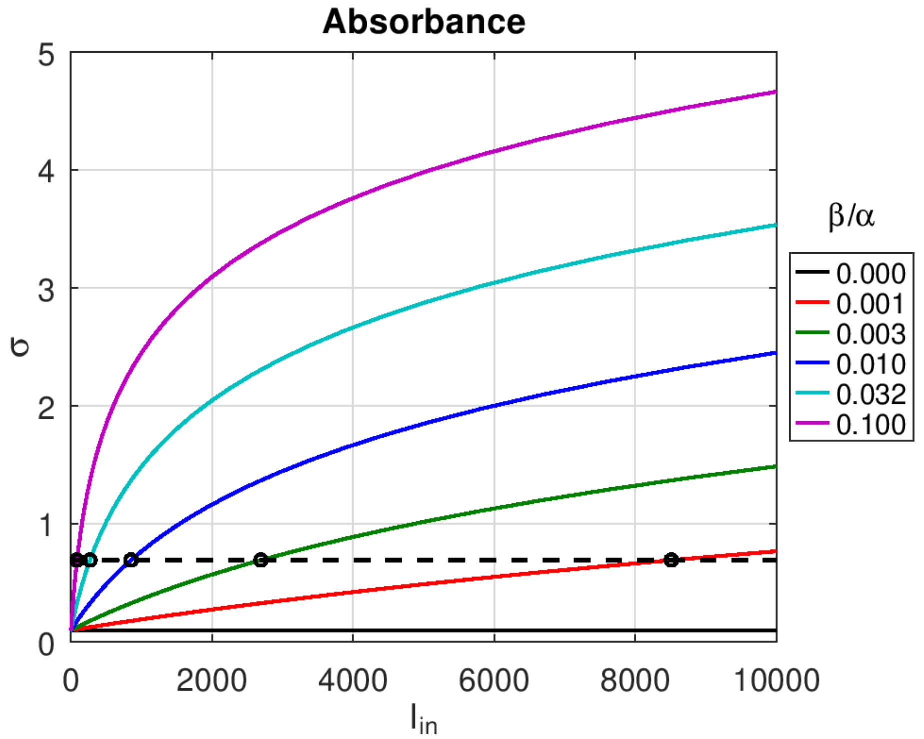
Linear and non-linear attenuation

non-linear

$$\frac{dI(z)}{dz} = -\alpha I(z) - \beta I^2(z)$$

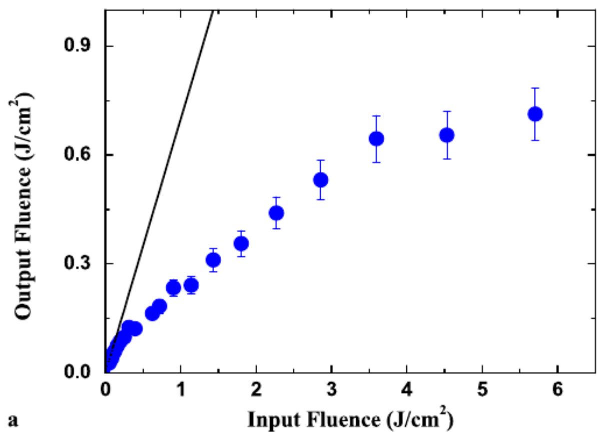
$$I_{\text{out}} = \frac{I_{\text{in}} e^{-\alpha L}}{1 + \beta \left(\frac{1-e^{-\alpha L}}{\alpha} \right) I_{\text{in}}}$$





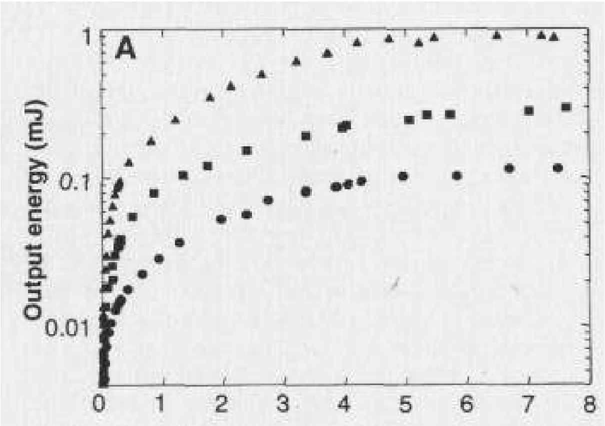
Optical limiting in organic molecules

Phtalocyanines

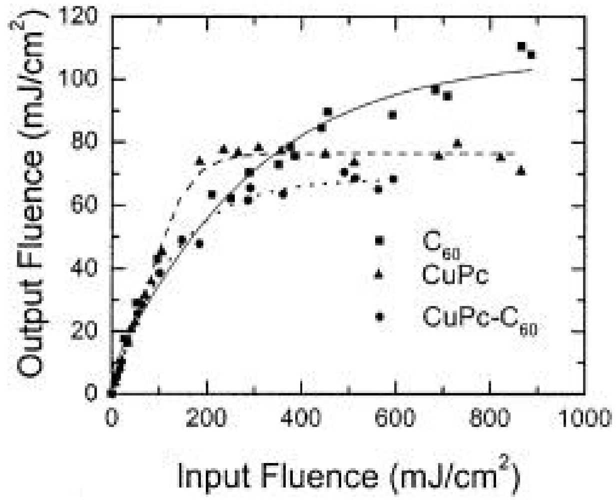


Venkatram, N. et al. (2008), Appl. Phys. B 91, 149

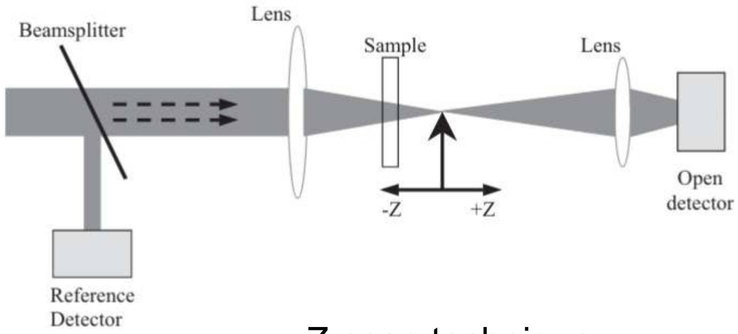
C60 in toluene



Perry, J. W. et al. (1996), Science 273, 1533

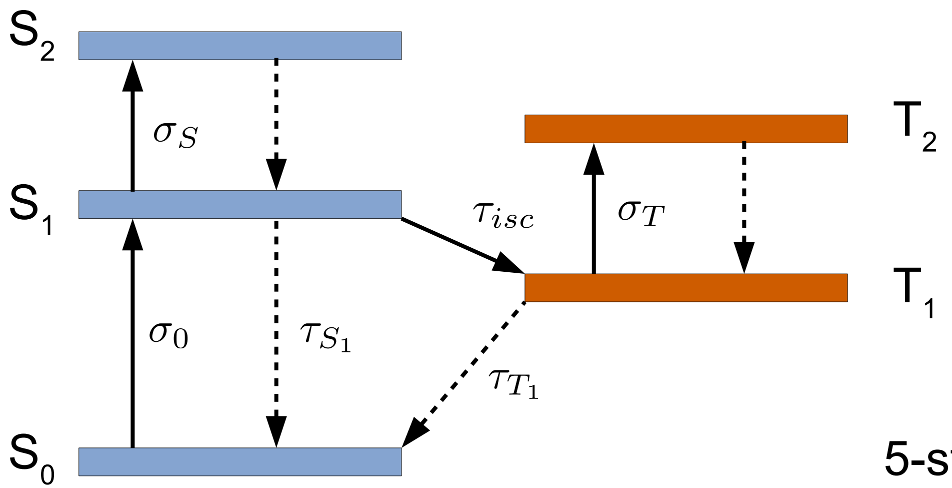


Zhu, P. et al. (2001) Appl. Phys. Lett. 78, 1319



Z-scan technique

Few-levels model



3-states model

$$\frac{\partial I}{\partial z} = -\alpha_0 I - \alpha_{\mathrm{S}} n_{\mathrm{S}} I$$

$$I = I(z,t)$$

$$n_{\mathrm{S}}(t) = \frac{\alpha_0 I(t)}{h\nu}$$

5-states model

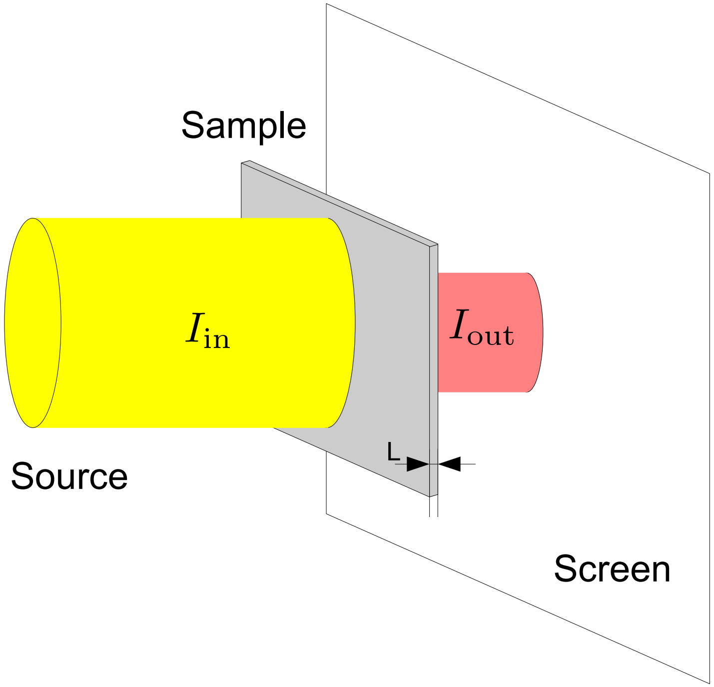
$$\frac{dn_{\mathrm{S}_0}(t)}{dt} = \frac{n_{\mathrm{S}_1}(t)}{\tau_{S_1}} + \frac{n_{\mathrm{T}_1}(t)}{\tau_{\mathrm{T}_1}} - \frac{\sigma_0(\nu)I}{h\nu} n_{\mathrm{S}_0}(t)$$

$$\frac{dn_{\mathrm{S}_1}(t)}{dt} = -\frac{n_{\mathrm{S}_1}(t)}{\tau_{S_1}} - \frac{n_{\mathrm{S}_1}(t)}{\tau_{\mathrm{isc}}} + \frac{\sigma_0(\nu)I}{h\nu} n_{\mathrm{S}_0}(t)$$

$$\frac{dn_{\mathrm{T}_1}(t)}{dt} = \frac{n_{\mathrm{S}_1}(t)}{\tau_{\mathrm{isc}}} - \frac{n_{T_1}(t)}{\tau_{\mathrm{T}_1}}$$

$$\frac{\partial I}{\partial z} = -[n_{\mathrm{S}_0}\sigma_0 + n_{\mathrm{S}_1}\sigma_S + n_{\mathrm{T}_1}\sigma_T] I = -\alpha(I) I$$

Absorption cross-section



Total absorption cross section $$\sigma = \frac{\Delta\mathcal{E}_{\text{abs}}}{I_{\text{in}}}$$

Energy exchanged with the field $$\Delta\mathcal{E}_{\text{abs}} = \int_0^\infty \mathcal{E}_{\text{abs}}(\omega)\, d\omega$$

Frequency dependent absorption cross section $$\sigma(\omega) = \frac{\mathcal{E}_{\text{abs}}(\omega)}{I_{\text{in}}(\omega)}$$

Absorption cross section

Plancherel (Parseval) identity

$$\Delta\mathcal{E}_{abs} = -\int_{-\infty}^{+\infty} \mathbf{d}(t) \cdot \frac{d\mathbf{E}(t)}{dt}\, dt = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{\mathbf{d}}(\omega) \cdot (i\omega)\tilde{\mathbf{E}}^*(\omega)\, d\omega$$

d*(t)* and ***E****(t)* are real

$$\mathcal{E}_{\rm abs}(\omega) = \frac{1}{\pi}\omega\, \mathrm{Im}\left[\tilde{\mathbf{d}}(\omega) \cdot \tilde{\mathbf{E}}^*(\omega)\right]$$

Definition of σ

$$\sigma(\omega) = \frac{\mathcal{E}_{\rm abs}(\omega)}{I_{\rm in}(\omega)}$$

Classical electrodynamics

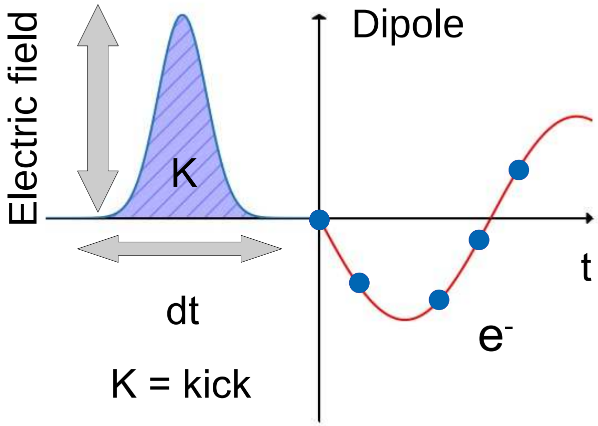
$$I_{\rm in}(\omega) = \frac{c}{4\pi^2}|\tilde{\mathbf{E}}(\omega)|^2$$

$$\sigma(\omega) = \frac{\mathcal{E}_{\rm abs}(\omega)}{I_{\rm in}(\omega)} = \frac{4\pi\omega}{c} \frac{\mathrm{Im}\left[\tilde{\mathbf{d}}(\omega) \cdot \tilde{\mathbf{E}}^*(\omega)\right]}{|\tilde{\mathbf{E}}(\omega)|^2}$$

This is independent of the constitutive equation that links ***d*** to ***E***

Impulse response

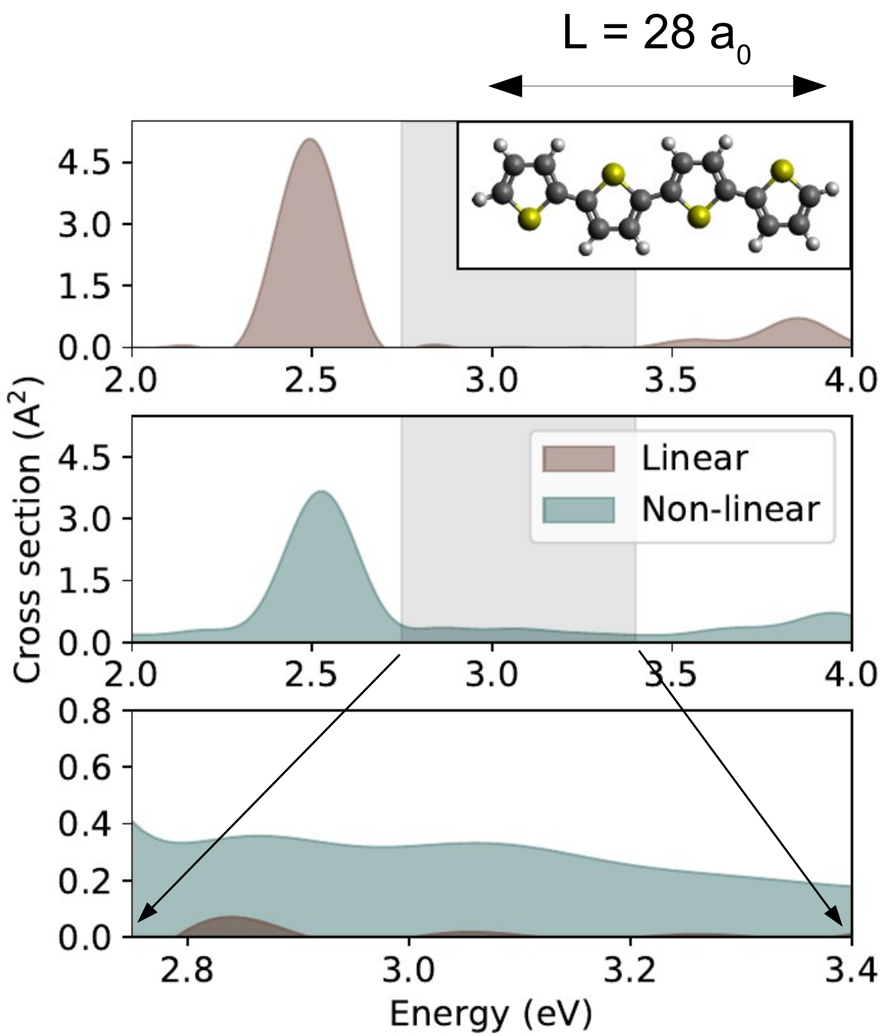
$$\mathbf{E}(t) = \mathbf{K}\delta(t) \longrightarrow \mathbf{E}(\omega) = \mathbf{K}$$



- For linear, time-invariant dynamical systems, the impulse response to an external perturbation is a property of the unperturbed system and is independent of the specific temporal shape of the perturbation
- Given the impulse response alone, it is possible to predict the response to perturbations of any shape by means of the convolution theorem
- In the linear regime, this procedure is equivalent to calculating the first-order polarizability
- Seminal application in real-time TDDFT: Yabana and Bertsch (1996), PRB 54, 4484

$$\phi_i(\mathbf{r}, 0^+) = e^{i\mathbf{K}\cdot\mathbf{r}}\phi_i(\mathbf{r}, 0)$$

4-tiophene example



K = *0.01* a_0^{-1}

K = *0.8* a_0^{-1}

Can impulse response be used to predict optical limiting?

Guandalini, A. et al. (2021). Phys. Chem. Chem. Phys. 23, 10059

Impulsive non-linear cross section

$$i\frac{\partial|\Psi(t)\rangle}{\partial t} = \left[\hat{H}_0 - \hat{\mathbf{d}}\cdot\mathbf{K}\delta(t)\right]|\Psi(t)\rangle$$

Assume centro-symmetric

$$|\Psi(t=0)\rangle = |\Psi_0\rangle$$

$$\mathbf{d}(t) = \langle\Psi(t)|\hat{\mathbf{d}}|\Psi(t)\rangle = \theta(t)\sum_{ij}^{+\infty} c_i^* c_j \mathbf{d}_{ij} e^{-i\omega_{ij}t}$$

$$c_i = \langle\Psi_i|e^{-i\hat{\mathbf{d}}\cdot\mathbf{K}}|\Psi_0\rangle$$

$$\sigma(\omega) = \frac{4\pi\omega}{c|\mathbf{K}|^2}\mathrm{Im}\left[\mathbf{d}(\omega)\cdot\mathbf{K}\right]$$

$$\mathbf{d}_{ij} = \langle\Psi_i|\hat{\mathbf{d}}|\Psi_j\rangle$$

General

$$\sigma(\omega) = \frac{4\pi^2\omega}{c|\mathbf{K}|^2}\sum_{i,j>i}^{+\infty} I_{ji}M_{ij}\delta(\omega-\omega_{ji})$$

Linear

$$\sigma^{(1)}(\omega) = \frac{4\pi^2\omega}{c|\mathbf{K}|^2}\sum_{j=0}^{+\infty} |M_{j0}|^2\delta(\omega-\omega_{j0})$$

Dipole matrix elements (selection rules)

$$M_{ij} = \langle\Psi_i|\hat{\mathbf{d}}\cdot\mathbf{K}|\Psi_j\rangle$$

$$I_{ij} = C_{0i}S_{j0} - S_{0i}C_{j0}$$

$$C_{ij} = \langle\Psi_i|\cos(\hat{\mathbf{d}}\cdot\mathbf{K})|\Psi_j\rangle$$

$$S_{ij} = \langle\Psi_i|\sin(\hat{\mathbf{d}}\cdot\mathbf{K})|\Psi_j\rangle$$

Guandalini, A. et al. (2021). Phys. Chem. Chem. Phys. 23, 10059

Recovering perturbation series

General

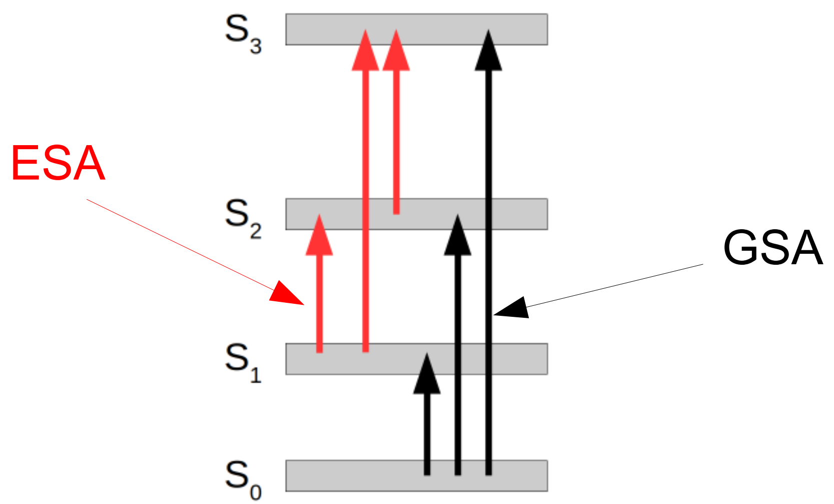
$$\sigma(\omega) = \frac{4\pi^2\omega}{c|\mathbf{K}|^2} \sum_{i,j>i}^{+\infty} I_{ji} M_{ij} \delta(\omega - \omega_{ji})$$

The TRK Sum rule holds for all regimes

$$\int_0^{+\infty} \sigma(\omega)\, d\omega = \frac{2\pi^2}{c} N$$

The linear limit is recovered for |***d*** · ***K***| ≪ *1*

$$\sigma^{(1)}(\omega) = \frac{4\pi^2\omega}{c|\mathbf{K}|^2} \sum_{j=0}^{+\infty} |M_{j0}|^2 \delta(\omega - \omega_{j0})$$



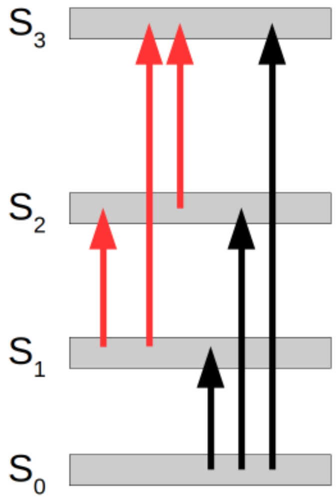
$$\sigma^{(3)}(\omega) = \sigma^{(3)}_{\text{GSA}}(\omega) + \sigma^{(3)}_{\text{ESA}}(\omega)$$

Guandalini, A. et al. (2021). Phys. Chem. Chem. Phys. 23, 10059

Non-linear impulse response

General

$$\sigma(\omega) = \frac{4\pi^2\omega}{c|\mathbf{K}|^2} \sum_{i,j>i}^{+\infty} I_{ji} M_{ij} \delta(\omega - \omega_{ji})$$



•*σ* includes terms *at all orders*

•excitations may occur between *any* levels (not only from the ground state)

•it is limited to a single spin manifold (no inter-system crossing) because M_{ij} enforces the same selection rules at all orders

•it holds *only* for the *impulsive* field, therefore, it is *not* suitable to describe phenomena dependent on the pulse shape

•if *L* is the system size the range for linear behaviour is defined by $|\boldsymbol{K}| \ll 1/L$

Two electrons in a 1D box

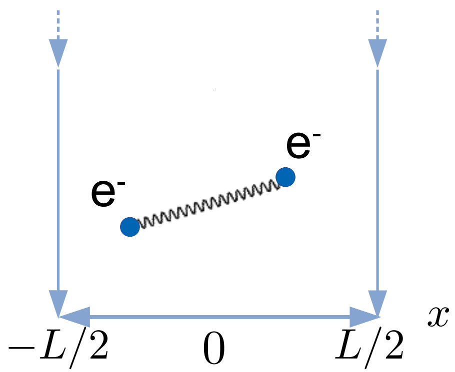
Two interacting particles in 1D

$$\hat{H}_0 = \hat{T} + \hat{V}_{ee}$$

$$\hat{T} = -\frac{\partial^2}{\partial x_1^2} - \frac{\partial^2}{\partial x_2^2}$$

$$\hat{V}_{ee} = \frac{1}{\sqrt{1 + (x_1 - x_2)^2}}$$

hard wall boundaries



$$x_1 \rightarrow x$$
$$x_2 \rightarrow y$$

One particle in 2D

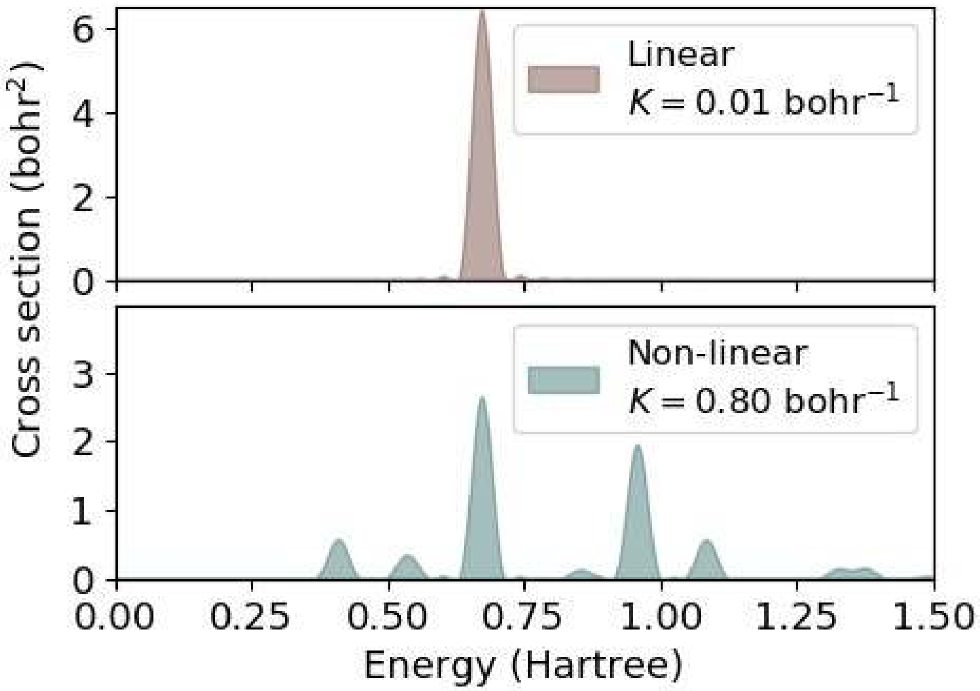
$$\hat{H}_0 = \hat{T} + \hat{V}_{ext}$$

$$\hat{T} = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2}$$

$$\hat{V}_{ext} = \frac{1}{\sqrt{1 + (x - y)^2}}$$

Guandalini, A. et al. (2021). Phys. Chem. Chem. Phys. 23, 10059

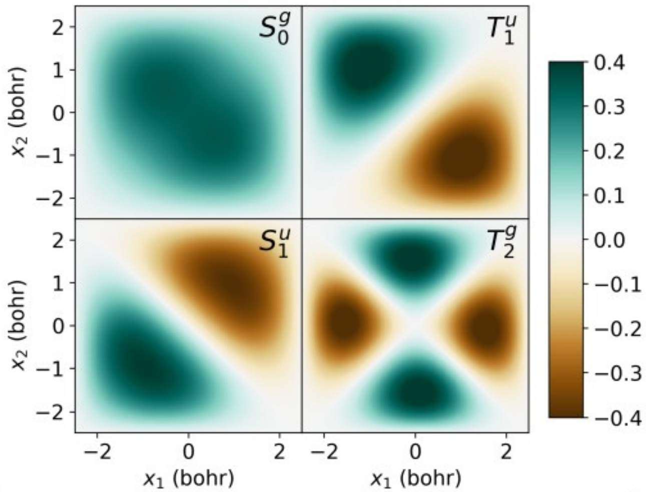
Linear vs non-linear cross sections



- Linear feature quenched
- New features appear

Box size: 4.4 a_0
Grid spacing: 0.015 a_0
Propagation time: T_{max} = 150 Ha^{-1}
Time step: dt = 0.002 Ha^{-1}
Broadening: 0.04 Ha

Two electrons in a box

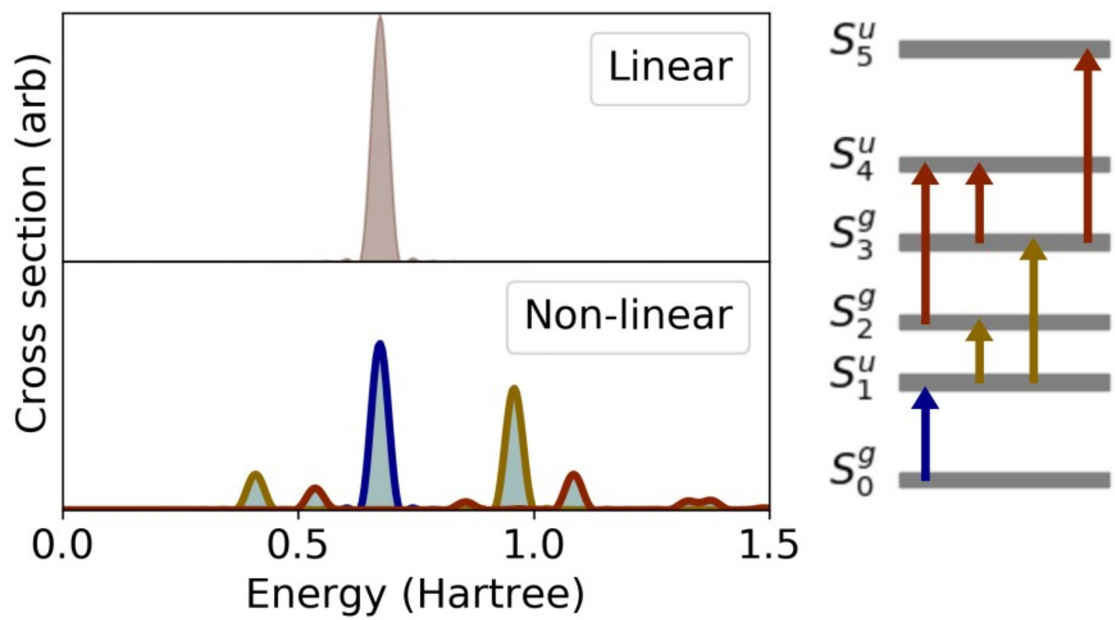


State	Energy (Ha)	State	Energy (Ha)
S_0^g	1.09		
S_1^u	1.76	T_1^u	1.47
S_2^g	2.17	T_2^g	2.53
S_3^g	2.72	T_3^u	3.05
S_4^u	3.26	T_4^u	3.95
S_5^u	4.05	T_5^g	4.49

obtained by real-time propagation

$$\sigma(\omega) = \frac{4\pi^2}{c|\mathbf{K}|^2} \sum_{i,j>i} I_{ji} M_{ij} \omega_{ji} \delta(\omega - \omega_{ji})$$

split using time-dependent exact orbitals



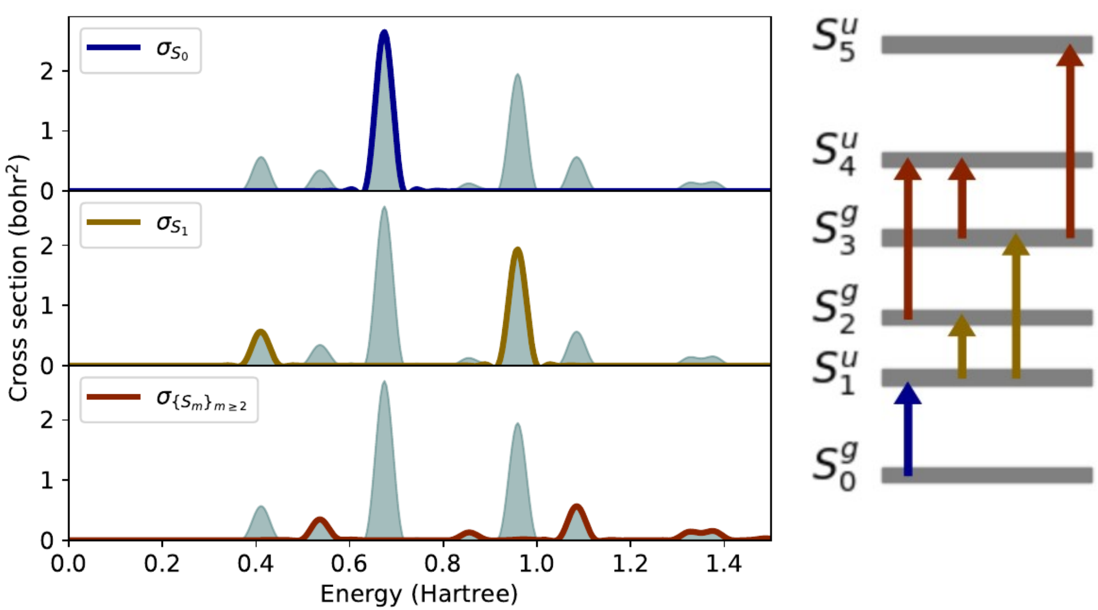
Non-linear excitations

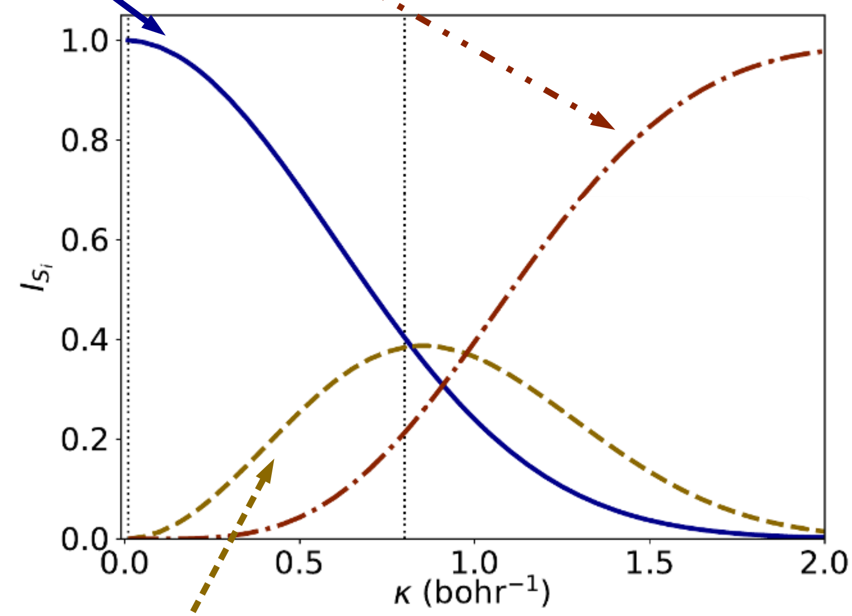
The relative weight of the features depends on the field strength

$K = 0.8\ a_0^{-1}$

$$I_{S_0} = \frac{c}{4\pi^2} \int d\omega\ \sigma_{S_0}(\omega)$$

$$I_{\{S_m\}_{m\geq 2}} = \frac{c}{4\pi^2} \int d\omega \sigma_{\{S_m\}_{m\geq 2}}(\omega)$$

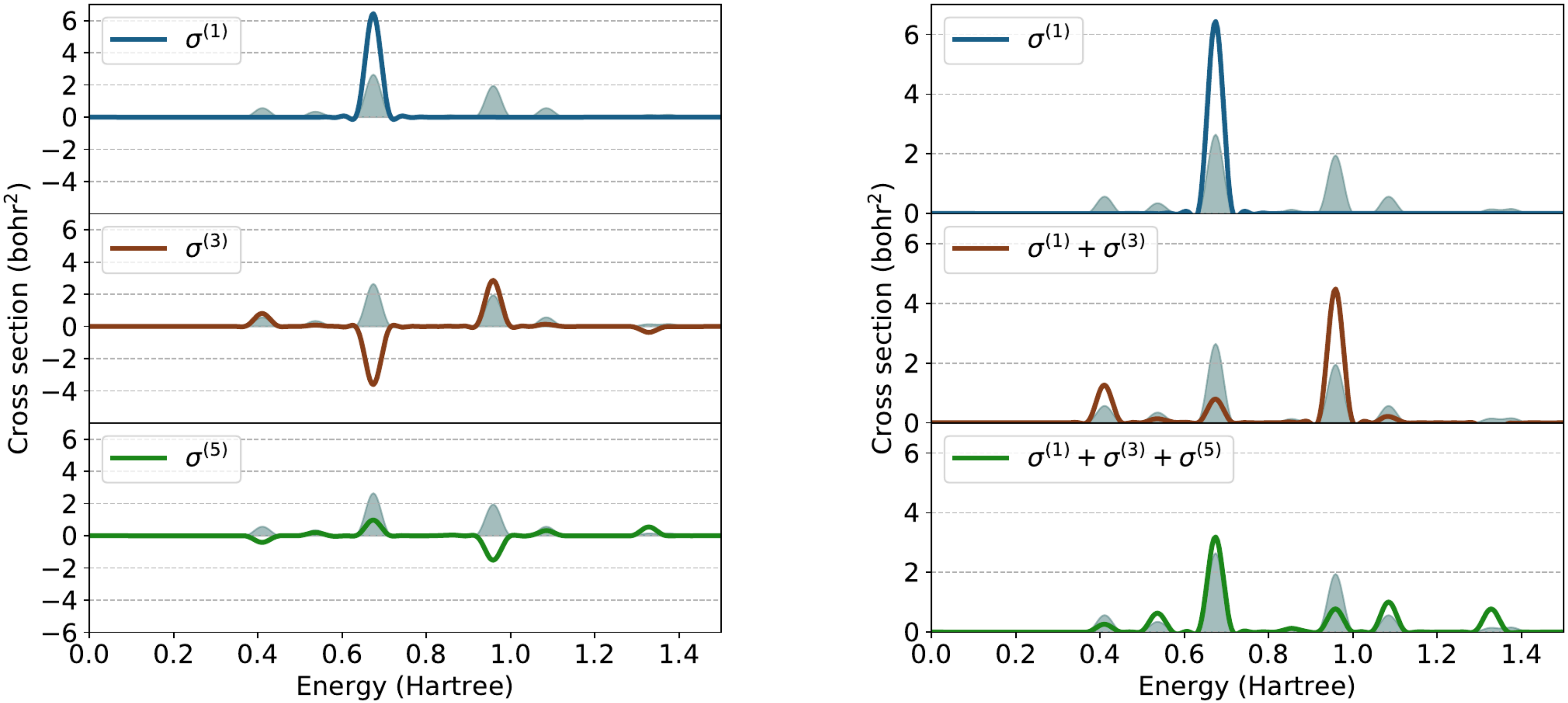




$$I_{S_1} = \frac{c}{4\pi^2} \int d\omega\ \sigma_{S_1}(\omega)$$

Back to perturbation expansion

NB: 5th order still observable here!



Dirac delta vs finite impulse

Octo-kick

The perturbation is a phase "kick"

$$\phi_i(\mathbf{r}, 0^+) = e^{i\mathbf{K}\cdot\mathbf{r}}\phi_i(\mathbf{r}, 0)$$

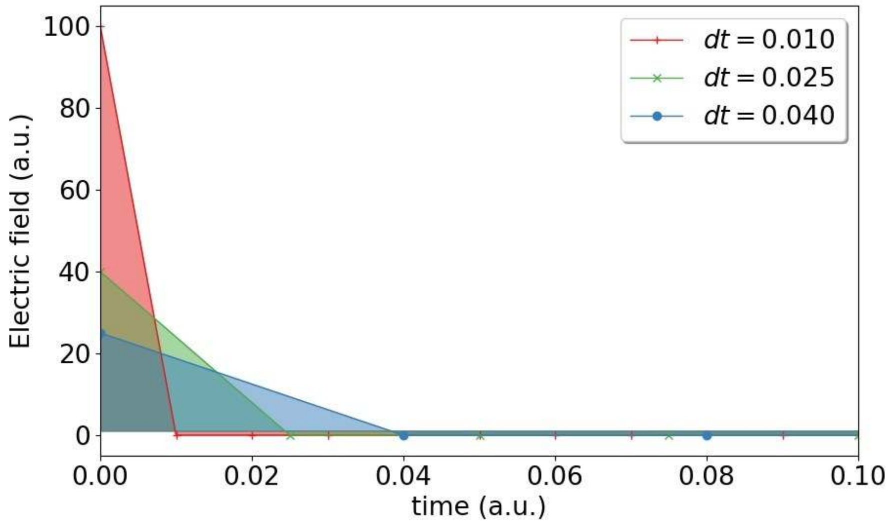
Yabana and Bertsch (1996), PRB 54, 4484

Octo-field

The perturbation is an external field

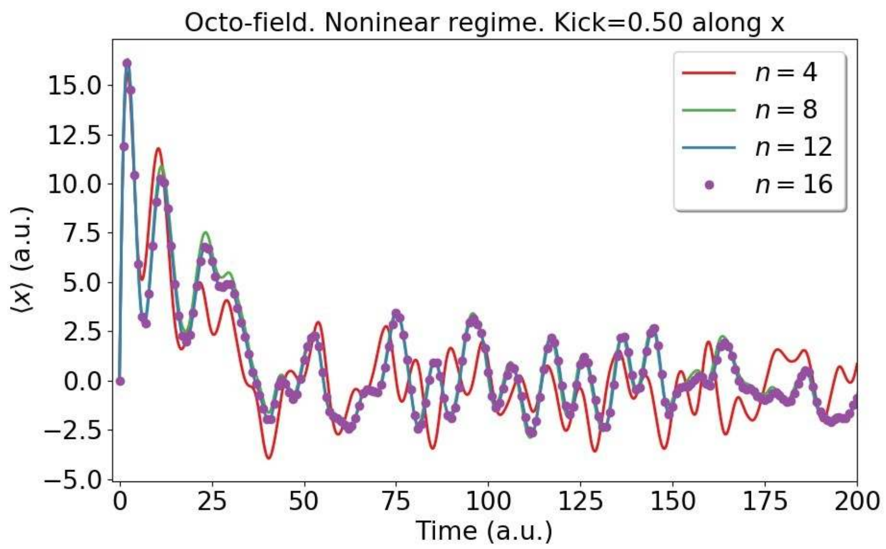
$$\hat{H}(t) = \hat{H}_0 - \hat{\mathbf{d}} \cdot \mathbf{E}(t)$$

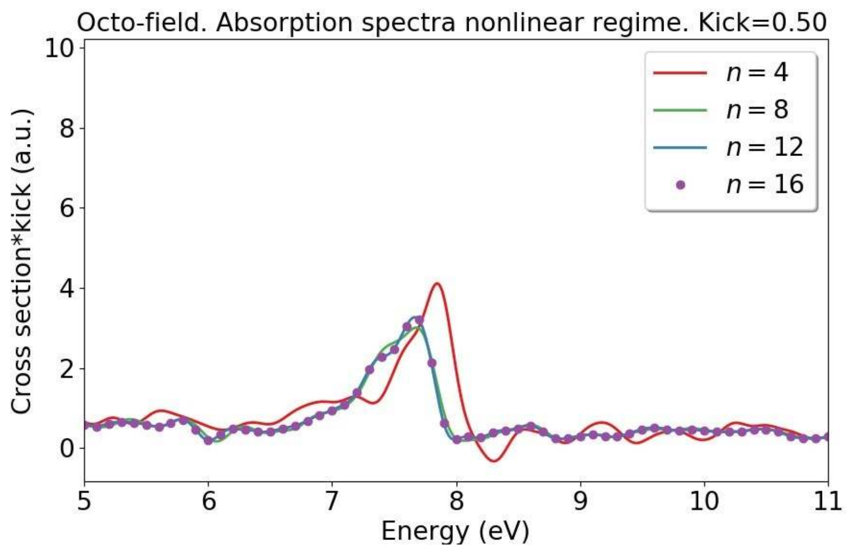
$$K \propto E_{\max} dt$$



Guandalini, A. (2021), PhD Thesis

Convergence for the propagator





Octo-kick

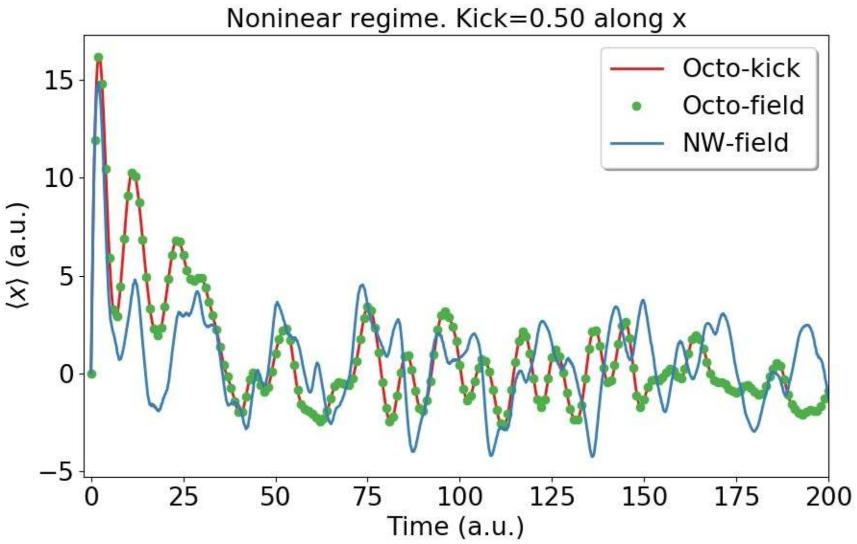
$$\phi_i(\mathbf{r}, dt) = e^{-i\hat{H}_0 dt + iKx}\phi_i(\mathbf{r}, 0) = e^{iKx}\sum_{m=0}^{n}\frac{(-i\hat{H}_0 dt)^m}{m!}\phi_i(\mathbf{r}, 0)$$

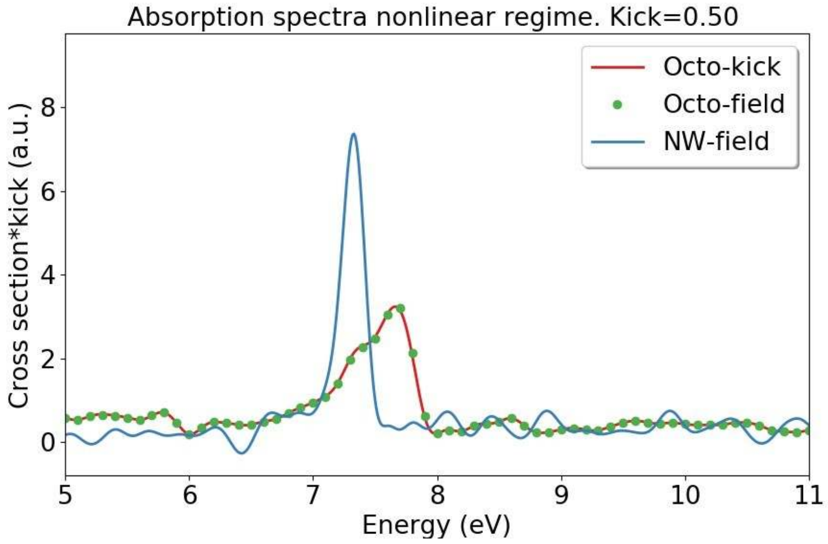
Octo-field

$$\phi_i(\mathbf{r}, dt) = e^{-i\hat{H}_0 dt + iE_{\max} x dt}\phi_i(\mathbf{r}, 0) = \sum_{m=0}^{n}\frac{(-i\hat{H}_0 dt + iE_{\max} x dt)^m}{m!}\phi_i(\mathbf{r}, 0)$$

- In Octo-field, when the impulse is high, the convergence with respect to n must be checked. This is not an issue in Octo-kick.

Beware of software implementations!

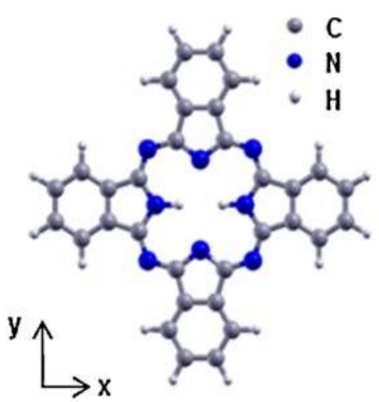




- Octo-kick and Octo-field are equivalent *in octopus* provided the propagator order is high enough
- differences may arise in different implementations of the propagator

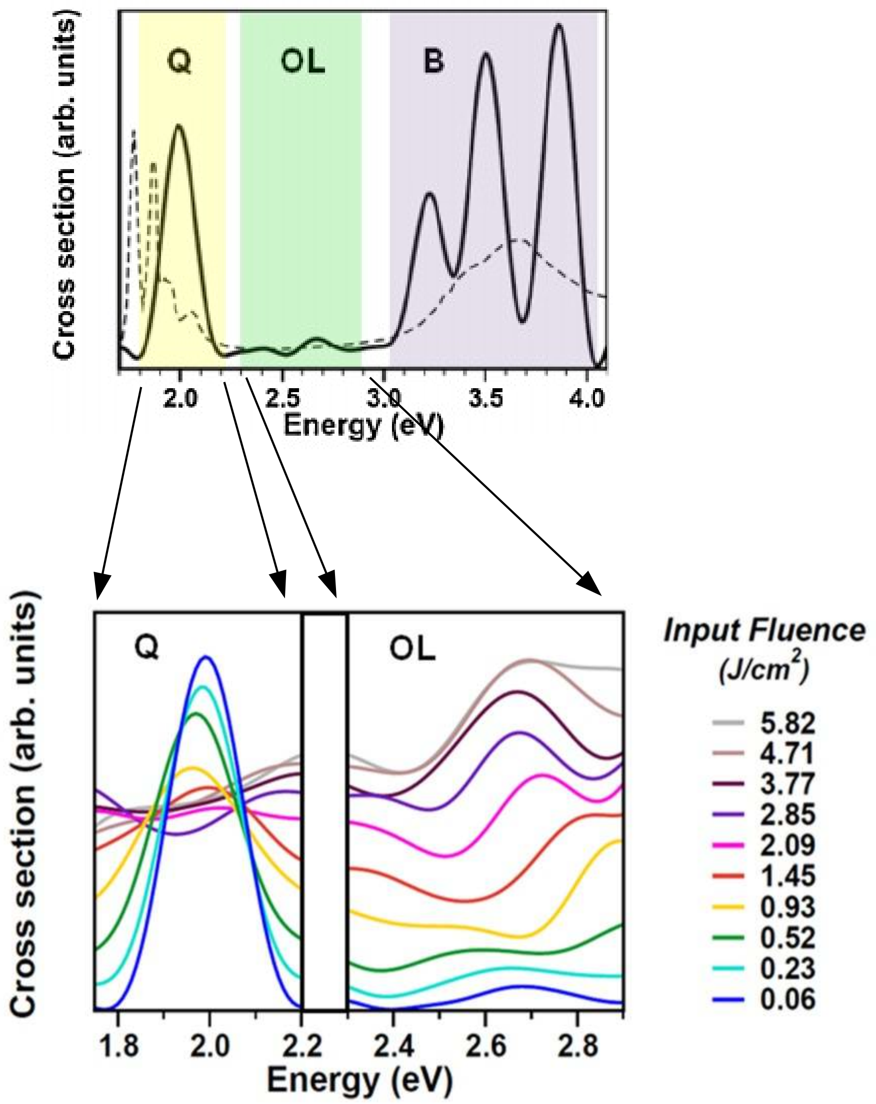
Optical limiting

Phthalocyanine



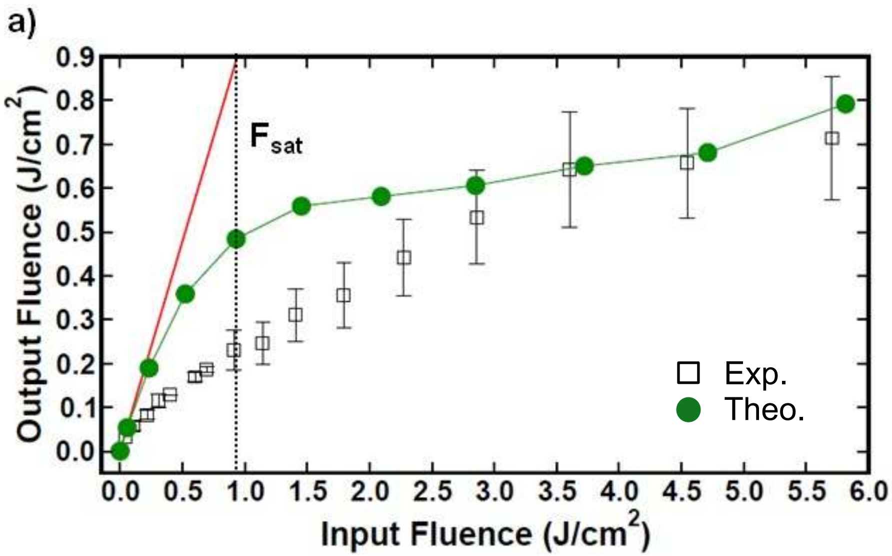
Linear

Fluence-dependent



Cocchi, C. et al. (2014), Phys. Rev. Lett. 112, 198303

Absorption in the OL band

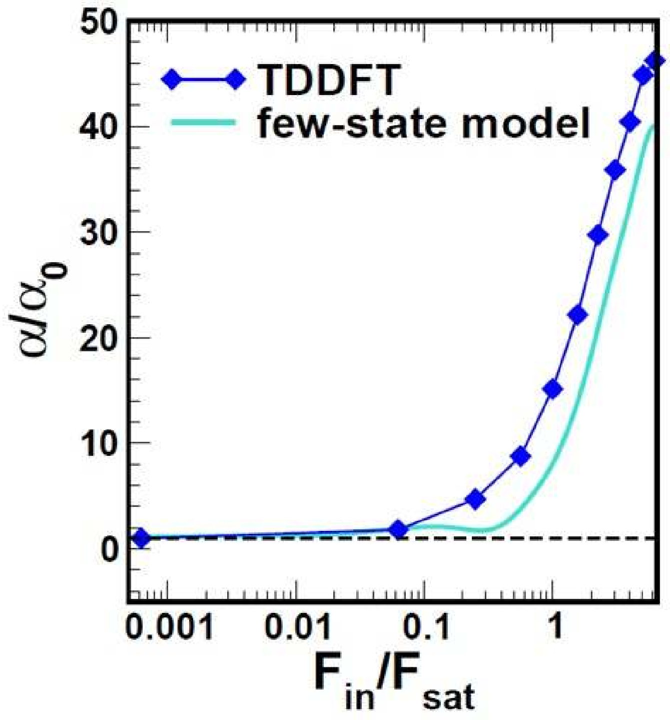


$$\alpha = \frac{\alpha_0}{1+\frac{I}{I_{\rm sat}}}\left(1+\kappa\frac{I}{I_{\rm sat}}\right)$$

$$\kappa = \frac{\sigma_{\rm S}}{\sigma_{\rm T}}\frac{\tau_{\rm ISC}}{\tau_{\rm ph}} + \frac{\sigma_{\rm T}}{\sigma_0} \approx \frac{\sigma_{\rm S}}{\sigma_{\rm T}}$$

$$\frac{I_{\rm out}}{I_{\rm in}} = e^{-\sigma n L}$$

$$\sigma = \int_{\omega\in{\rm OL}} \sigma(\omega) d\omega$$



n = 10^{-4} M
L = 1 mm
Z-scan with λ = 532 nm

Conclusions

- ~~Real-time impulse response cannot be used in non-linear optics.~~
- **Pros**:
  - it provides valuable information about excited state absorption;
  - it provides information at all orders for the whole spectral range at once;
  - it has (almost) the same computational cost of a real-time linear response calculation;
- **Cons**:
  - σ does not directly correspond to any observable obtained with finite bandwidth light;
  - not suitable for ultrafast optics because not sensitive to the pulse shape;
- These features render this method particularly suitable to perform quick screening of non-linear fluence-dependent properties (i.e. searching for good optical limiters).

Aknowledgments

- Theory
  - **Alberto Guandalini**, Caterina Cocchi, Alice Ruini, Stefano Pittalis

- Resources
  - **High Performance Computing:**
    - North-German Supercomputing Alliance (HLRN), project bep00060
    - High Performance Computing Center Stuttgart (HLRS)
  - **Financial support:**
    - DAAD grant n. 57440917
    - HPC Europa 3 grant n. HPC17AS2HO
    - DFG Project n. 182087777 – SFB 951
    - MIUR PRIN grant n. 2017RKWTMY
    - MIUR PRIN grant n. 201795SBA3