Introduction to time-dependent density-functional perturbation theory

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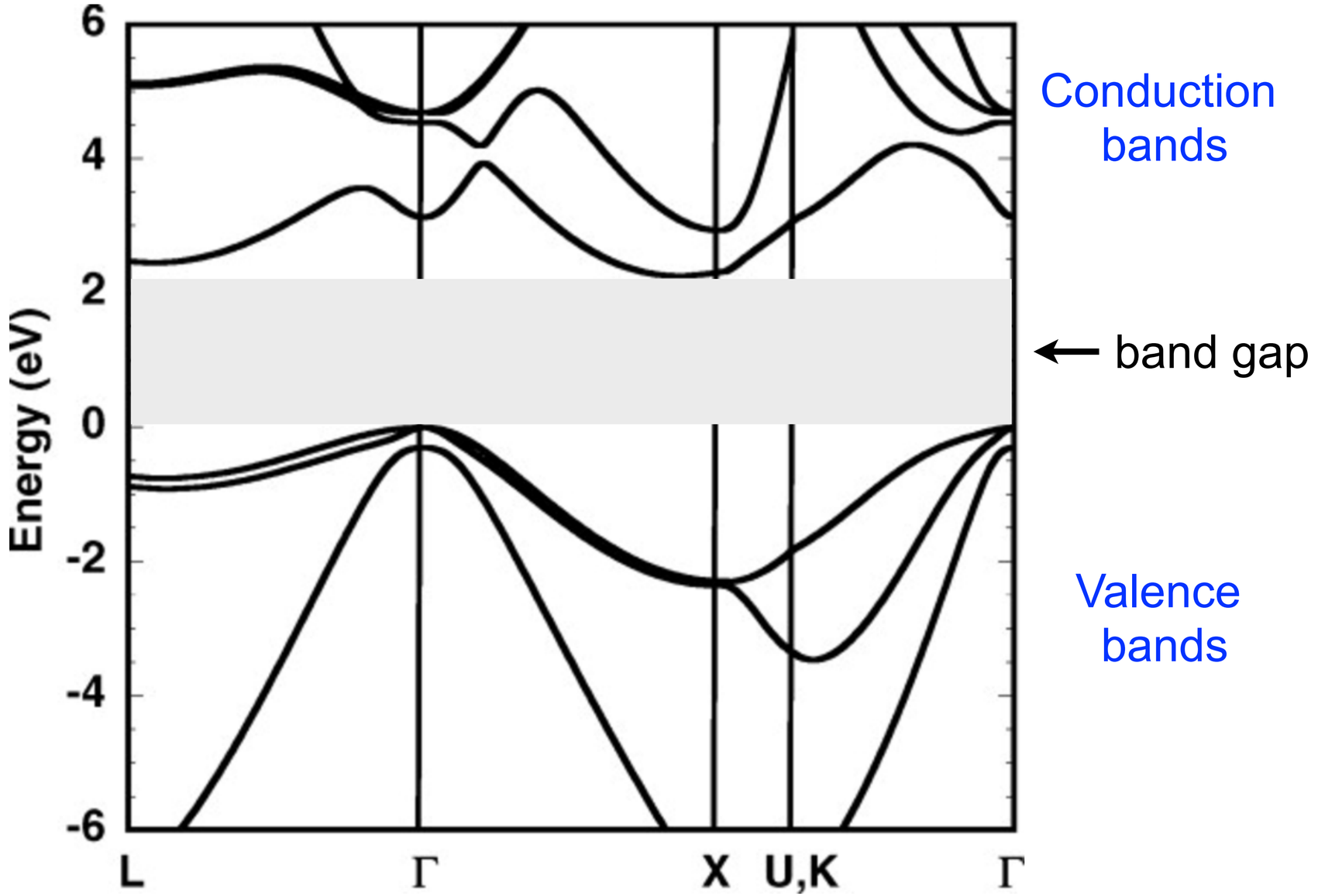
Computational spectroscopy: from ground state to excited state



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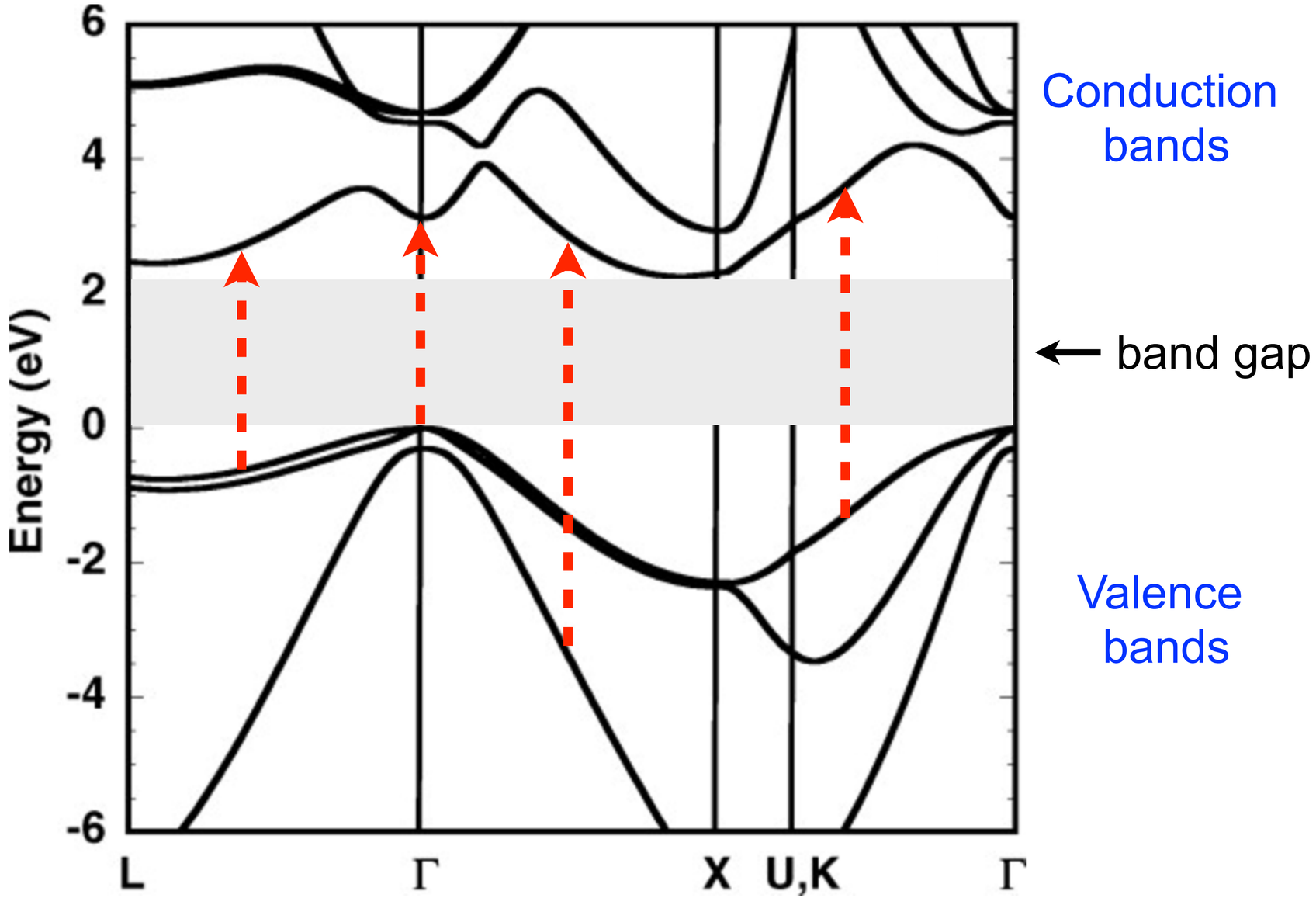
photon



Outline

- Basics of TDDFT: Two Runge-Gross theorems
- “Linear-response TDDFT” or “TDDFPT”
  - Dyson method
  - Sternheimer method
  - Liouville-Lanczos method
- Various spectroscopies from TDDFPT
  - Electron energy loss
  - Inelastic neutron scattering

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Time-dependent Schrödinger equation

The evolution of a non-relativistic interacting many-electron system is governed by the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\Psi_{\mathrm{el}}(\{\mathbf{r}_i\},t) = \hat{H}(\{\mathbf{r}_i\},t)\,\Psi_{\mathrm{el}}(\{\mathbf{r}_i\},t)$$

$$\hat{H}(\{\mathbf{r}_i\},t) = -\frac{\hbar^2}{2m_0}\sum_i \boldsymbol{\nabla}_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|} + \sum_i V_{ext}(\mathbf{r}_i,t)$$

By analogy to the static case, instead of considering the electronic wavefunction of 3*N*+1 variables we can consider the electronic charge density which is a function of only 4 variables:

$$n(\mathbf{r},t) = N\int |\Psi_{\mathrm{el}}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N,t)|^2\,d\mathbf{r}_2\ldots d\mathbf{r}_N$$

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DFT: one-to-one mapping between static charge density and static external potential (minimization principle of the total energy).

TDDFT: straightforward extension of this idea to the time-dependent domain is not possible, because the total energy is no longer a conserved quantity.

Runge-Gross Theorems I and II

For any system of interacting particles in an external time-dependent potential $V_{ext}(\mathbf{r}, t)$, *which can be expanded in Taylor series with respect to time, and given an initial state* $\Psi(\mathbf{r}, t_0) = \Psi_0(\mathbf{r})$, *there is a one-to-one correspondence between* $V_{ext}(\mathbf{r}, t)$ *and the time-dependent density* $n(\mathbf{r}, t)$, *apart from a trivial function of time.*

A quantum-mechanical action functional

$$\mathcal{A}[n] = \int_{t_0}^{t_1} dt \, \langle \Psi(t) | i\hbar \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle,$$

becomes stationary at the exact time-dependent density $n_0(\mathbf{r}, t)$ *which corresponds to the external potential* $V_{ext}(\mathbf{r}, t)$ *given the initial state* $\Psi_0(\mathbf{r})$ *at* t_0*:*

$$\left. \frac{\delta \mathcal{A}[n]}{\delta n(\mathbf{r}, t)} \right|_{n_0} = 0.$$

Quantum-mechanical action functional and TD Kohn-Sham equations

$$\mathcal{A}[n] = \mathcal{T}_0[n] + \mathcal{A}_H[n] + \mathcal{A}_{\rm xc}[n] - \int_{t_0}^{t_1} dt \int d\mathbf{r}\, V_{ext}(\mathbf{r},t) n(\mathbf{r},t)$$

$$\mathcal{A}_H[n] = -\frac{e^2}{2} \int_{t_0}^{t_1} dt \iint \frac{n(\mathbf{r},t)\, n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}'$$

Time-dependent Kohn-Sham equations:

$$i\hbar \frac{\partial}{\partial t} \varphi_i(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m_0} \nabla^2 + V_{KS}(\mathbf{r},t) \right) \varphi_i(\mathbf{r},t)$$

$$\begin{aligned} V_{KS}(\mathbf{r},t) &= V_H(\mathbf{r},t) + V_{\rm xc}(\mathbf{r},t) + V_{ext}(\mathbf{r},t) \\ &= e^2 \int \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}' + \frac{\delta \mathcal{A}_{\rm xc}[n]}{\delta n(\mathbf{r},t)} + V_{ext}(\mathbf{r},t) \end{aligned}$$

$$n(\mathbf{r},t) = \sum_i^N |\varphi_i(\mathbf{r},t)|^2$$

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Linear-response TDDFT (TDDFPT)

Let us assume that the time-dependent external potential is weak, and that it can be written as:

$$V_{ext}(\mathbf{r},t) = V^0_{ext}(\mathbf{r}) + V'_{ext}(\mathbf{r},t)$$

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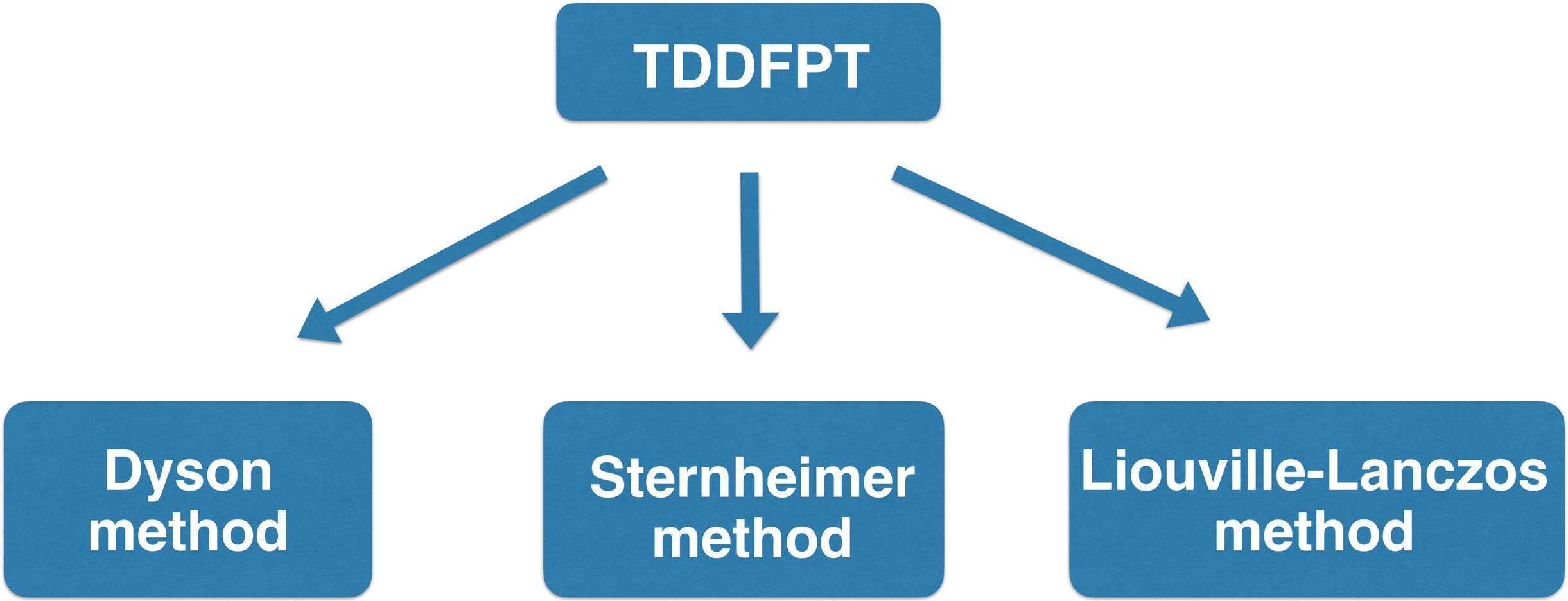
Time-dependent density functional **perturbation** theory (TDDF**P**T) is TDDFT in conjunction with perturbation theory. If we keep only the first-order term in the Taylor expansion, then this is linear-response TDDFT.

Different ways how to compute the susceptibility from TDDFPT



Dyson method

The Dyson-like matrix equation in the reciprocal space:

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) + \sum_{\mathbf{G}_1,\mathbf{G}_2} \chi^0_{\mathbf{G},\mathbf{G}_1}(\mathbf{q},\omega)\left[v_{\mathbf{G}_1}(\mathbf{q})\delta_{\mathbf{G}_1,\mathbf{G}_2} + f^{\mathrm{xc}}_{\mathbf{G}_1,\mathbf{G}_2}(\mathbf{q},\omega)\right]\chi_{\mathbf{G}_2,\mathbf{G}'}(\mathbf{q},\omega)$$

$v_{\mathbf{G}}(\mathbf{q}) = 4\pi e^2/|\mathbf{q}+\mathbf{G}|^2$ is the Fourier transform of the Coulomb potential

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- 😕 Sum over numerous empty states n' in the calculation of $\chi^0_{\mathbf{G},\mathbf{G}'}$
- 😕 Multiplication and inversion of large matrices
- 😕 The matrices $\chi^0_{\mathbf{G},\mathbf{G}'}$ and $\chi_{\mathbf{G},\mathbf{G}'}$ must be computed for every value of frequency

Sternheimer method

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The Kohn-Sham Hamiltonian:

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The time-dependent Kohn-Sham wavefunctions are: $\varphi_v(\mathbf{r},t) = e^{-i\varepsilon_v t/\hbar}\left[\varphi^0_v(\mathbf{r}) + \varphi'_v(\mathbf{r},t)\right]$

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This allows us to write the time-dependent linear-response Kohn-Sham equations (Sternheimer eqs.) as:

$$i\hbar\frac{\partial\varphi'_v(\mathbf{r},t)}{\partial t} = (\hat{H}^0 - \varepsilon_v)\varphi'_v(\mathbf{r},t) + \left[V'_{ext}(\mathbf{r},t) + V'_{H\mathrm{xc}}(\mathbf{r},t)\right]\varphi^0_v(\mathbf{r})$$

$$-i\hbar\frac{\partial\varphi'^*_v(\mathbf{r},t)}{\partial t} = (\hat{H}^0 - \varepsilon_v)\varphi'^*_v(\mathbf{r},t) + \left[V'_{ext}(\mathbf{r},t) + V'_{H\mathrm{xc}}(\mathbf{r},t)\right]\varphi^{0*}_v(\mathbf{r})$$

Sternheimer method

By performing a Fourier transformation from the time domain to the frequency domain we obtain:

$$(\hat{H}^0 - \varepsilon_v - \hbar\omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\tilde{V}'_{H\mathrm{xc}}(\mathbf{r},\omega)\varphi^0_v(\mathbf{r}) = -\hat{P}_c\tilde{V}'_{ext}(\mathbf{r},\omega)\varphi^0_v(\mathbf{r}),$$

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SELF-CONSISTENT PROBLEM

Solved iteratively

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Projector on empty states:

$\hat{P}_c = \sum_c |\varphi^0_c\rangle\langle\varphi^0_c|$

$\hat{P}_c = 1 - \hat{P}_v$

$$\tilde{V}'_{H\mathrm{xc}}(\mathbf{r},\omega) = \int \left[\frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')\right] \tilde{n}'(\mathbf{r}',\omega)\, d\mathbf{r}'$$

$$\tilde{n}'(\mathbf{r},\omega) = 2\sum_v \left[\tilde{\varphi}'_v(\mathbf{r},\omega)\varphi^{0\,*}_v(\mathbf{r}) + \tilde{\varphi}'^*_v(\mathbf{r},-\omega)\varphi^0_v(\mathbf{r})\right]$$

SELF-CONSISTENT PROBLEM

Solved iteratively

Sternheimer method

By performing a Fourier transformation from the time domain to the frequency domain we obtain:

$$(\hat{H}^0 - \varepsilon_v - \hbar\omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\tilde{V}'_{H\mathrm{xc}}(\mathbf{r},\omega)\varphi^0_v(\mathbf{r}) = -\hat{P}_c\tilde{V}'_{ext}(\mathbf{r},\omega)\varphi^0_v(\mathbf{r}),$$

$$(\hat{H}^0 - \varepsilon_v + \hbar\omega)\tilde{\varphi}'^*_v(\mathbf{r},-\omega) + \hat{P}_c\tilde{V}'_{H\mathrm{xc}}(\mathbf{r},\omega)\varphi^0_v(\mathbf{r}) = -\hat{P}_c\tilde{V}'_{ext}(\mathbf{r},\omega)\varphi^0_v(\mathbf{r})$$

Projector on empty states:

$\hat{P}_c = \sum_c |\varphi^0_c\rangle\langle\varphi^0_c|$

$\hat{P}_c = 1 - \hat{P}_v$

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SELF-CONSISTENT PROBLEM

Solved iteratively

🙂 No need in empty states (thanks to the projector $\hat{P}_c$)

🙁 The Sternheimer equations must be solved for every value of frequency

Liouville-Lanczos method

The quantum Liouville equation describes the time evolution of the charge density matrix operator:

$$i\hbar\frac{\partial\hat{\rho}(t)}{\partial t} = [\hat{H}_{KS}(t), \hat{\rho}(t)]$$

B. Walker, A.M. Saitta, R. Gebauer, and S. Baroni, Phys. Rev. Lett. **96**, 113001 (2006).
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$$\rho(\mathbf{r}, \mathbf{r}'; t) = 2 \sum_v \varphi_v(\mathbf{r}, t)\, \varphi_v^*(\mathbf{r}', t)$$

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Using the linear response theory, we can rewrite the quantum Liouville equation to first order as:

$$i\hbar\frac{\partial\hat{\rho}'(t)}{\partial t} = [\hat{H}^0, \hat{\rho}'(t)] + [\hat{V}'_{H\mathrm{xc}}(t), \hat{\rho}^0] + [\hat{V}'_{ext}(t), \hat{\rho}^0]$$

$$\rho'(\mathbf{r}, \mathbf{r}'; t) = 2\sum_v \left[\varphi'_v(\mathbf{r}, t)\varphi_v^{0*}(\mathbf{r}') + \varphi'^*_v(\mathbf{r}', t)\varphi_v^0(\mathbf{r})\right]$$

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Liouville-Lanczos method

Let use rewrite the linear-response quantum Liouville equation by defining the Liouville superoperator:

$$i\hbar\frac{\partial\hat{\rho}'(t)}{\partial t} = \hat{\mathcal{L}}\cdot\hat{\rho}'(t) + [\hat{V}'_{ext}(t), \hat{\rho}^0]$$

$$\hat{\mathcal{L}}\cdot\hat{\rho}' = [\hat{H}^0, \hat{\rho}'] + \left[V'_{H\mathrm{xc}}[\hat{\rho}'], \hat{\rho}^0\right]$$

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Now let us perform a Fourier transform from the time domain to the frequency domain:

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$$\chi_A(\omega) = \mathrm{Tr}[\hat{A}\,\hat{\rho}'(\omega)]$$

Liouville-Lanczos method

How to solve the linear-response quantum Liouville equation in practice? → Lanczos recursion algorithm

O.B. Malcioglu, R. Gebauer, D. Rocca, and S. Baroni, Comput. Phys. Comun. **182**, 1744 (2011).
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$$q_v(\mathbf{r}) = \frac{1}{2}\left[\tilde{\varphi}'_v(\mathbf{r},\omega) + \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)\right] \qquad p_v(\mathbf{r}) = \frac{1}{2}\left[\tilde{\varphi}'_v(\mathbf{r},\omega) - \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)\right]$$

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Lanczos recursion algorithm

Let us define two two-component Lanczos vectors:

$$\mathbf{V}_i = \begin{pmatrix} q_v^i \\ p_v^i \end{pmatrix} \qquad \mathbf{U}_i = \begin{pmatrix} \tilde{q}_v^i \\ \tilde{p}_v^i \end{pmatrix}$$

Liouville-Lanczos method

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Tridiagonal matrix:

$$\hat{T}^N = \begin{pmatrix} 0 & \gamma_2 & 0 & \dots & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \gamma_N \\ 0 & \dots & 0 & \beta_N & 0 \end{pmatrix}$$

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Susceptibility is computed in a postprocessing step:

$$\chi_A(\omega) = \langle \zeta^N | \left(\hbar\omega \hat{I}^N - \hat{T}^N \right)^{-1} \cdot e_1^N \rangle$$

Liouville-Lanczos method

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→ Lanczos recursion algorithm

- 🙂 No need in empty states
- 🙂 The tridiagonal matrix $\hat{T}^N$ must be computed only once (independently of frequency)
- 🙂 The postprocessing is inexpensive; extrapolation of Lanczos coefficients allows us to speed up the convergence enormously

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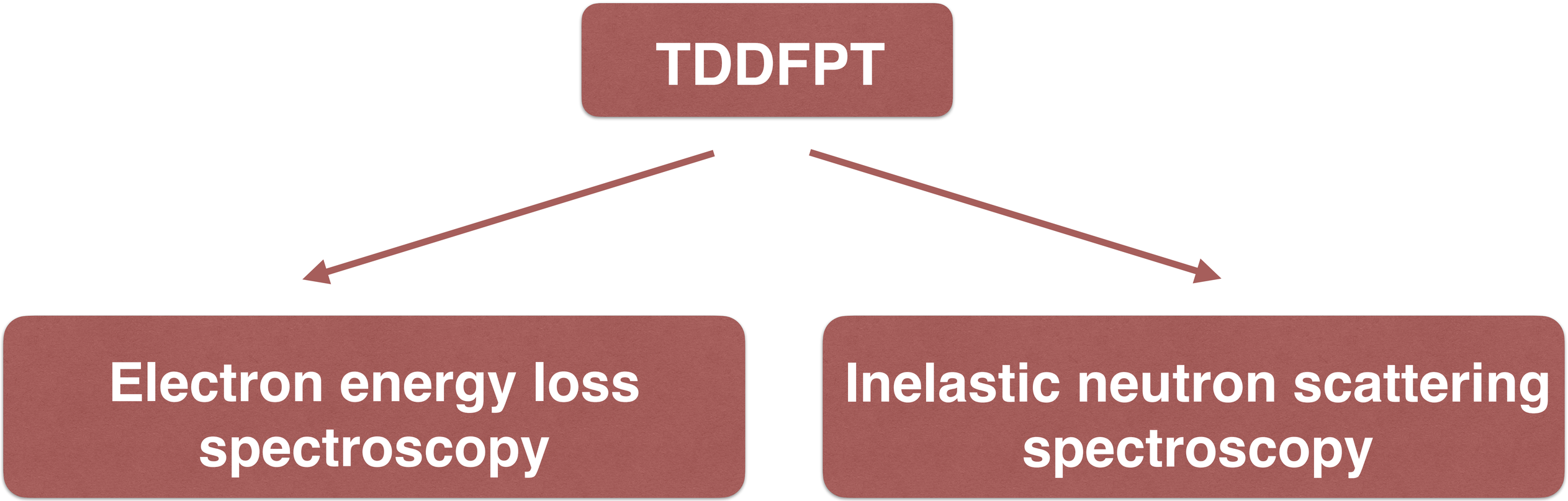
Outline

- Basics of TDDFT: Two Runge-Gross theorems
- “Linear-response TDDFT” or “TDDFPT”
  - Dyson method
  - Sternheimer method
  - Liouville-Lanczos method
- Various spectroscopies from TDDFPT
  - Electron energy loss
  - Inelastic neutron scattering

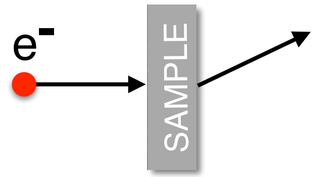
Various spectroscopies from TDDFPT



Electron energy loss in solids

Let us consider an external perturbation which is an incoming electron (i.e. a plane wave):

$$\tilde{V}'_{ext,\mathbf{q}}(\mathbf{r},\omega) = e^{i\mathbf{q}\cdot\mathbf{r}}$$



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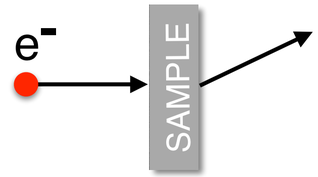

The charge-density susceptibility (density-density response function) reads:

$$\chi_{\mathrm{n}}(\mathbf{q},\omega) = \langle \hat{\mathbf{n}}_{\mathbf{q}} | (\hbar\omega - \hat{\mathcal{L}}_{\mathbf{q}})^{-1} \cdot [\hat{\mathbf{n}}_{\mathbf{q}}, \hat{\rho}^{0}] \rangle$$

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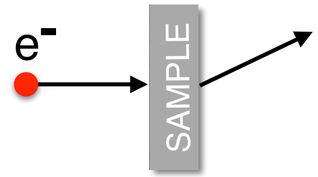

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This allows us to compute the inverse dielectric function:

$$\epsilon^{-1}(\mathbf{q},\omega) = 1 + \frac{4\pi e^2}{|\mathbf{q}|^2} \chi_{\mathrm{n}}(\mathbf{q},\omega)$$

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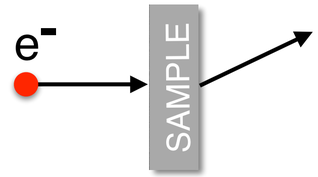

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Double-differential cross section:

$$\frac{d^2\sigma}{d\Omega d\varepsilon} \propto -\mathrm{Im}\left[\epsilon^{-1}(\mathbf{q},\omega)\right]$$

Loss function $-\mathrm{Im}\left[\epsilon^{-1}(\mathbf{q},\omega)\right]$: **Liouville-Lanczos (**turbo_eels.x**)**

turboEELS code

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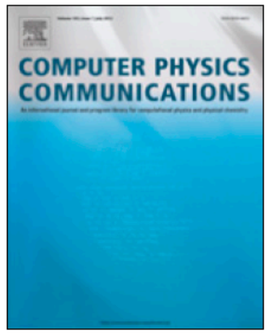
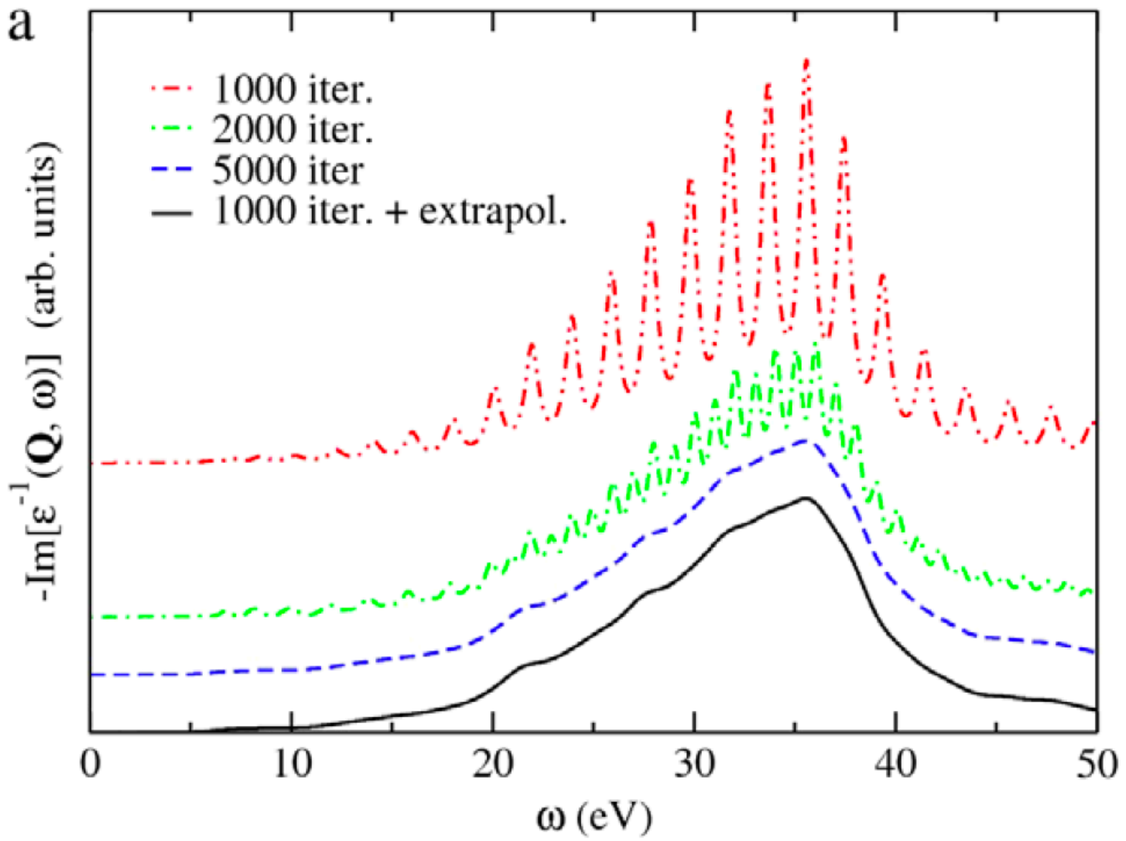


turboEELS—A code for the simulation of the electron energy loss and inelastic X-ray scattering spectra using the Liouville–Lanczos approach to time-dependent density-functional perturbation theory☆

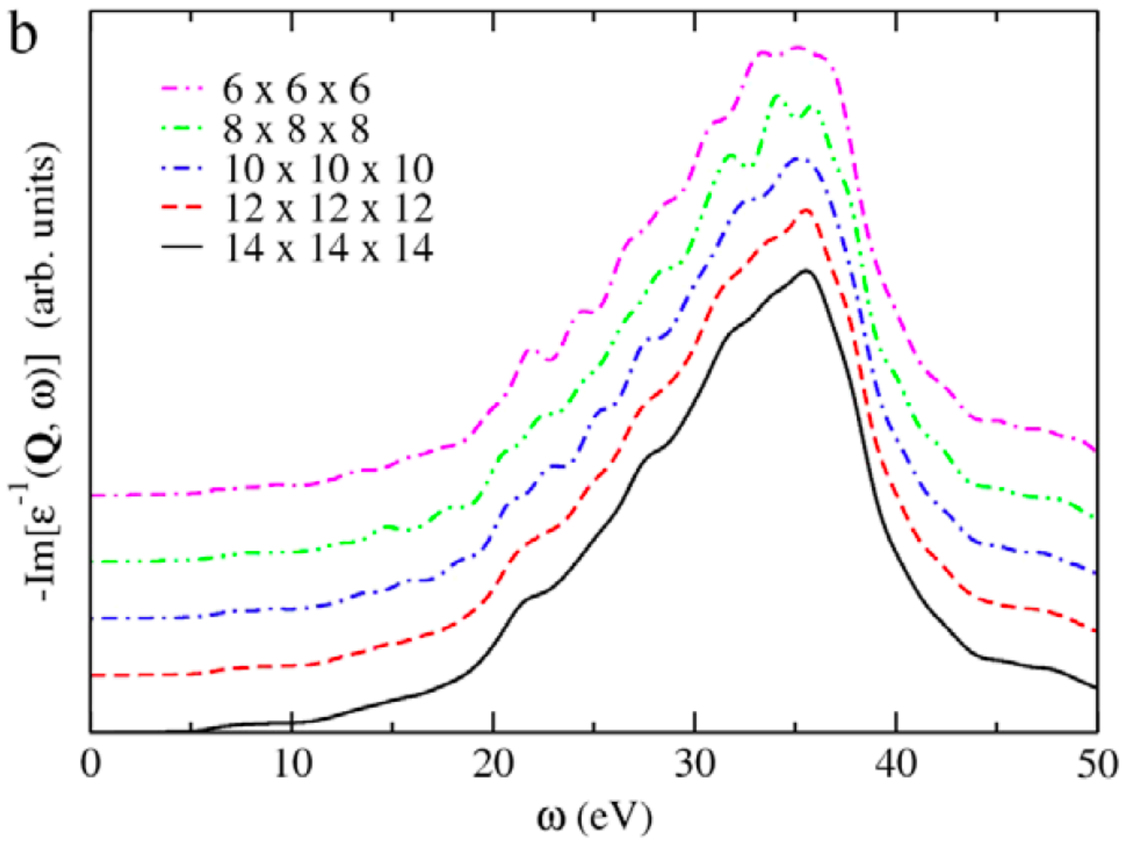
Iurii Timrov[a,b,1], Nathalie Vast[a], Ralph Gebauer[c], Stefano Baroni[b,*]

Loss function of bulk diamond

Convergence w.r.t. Lanczos iterations



Convergence w.r.t. **k** points mesh

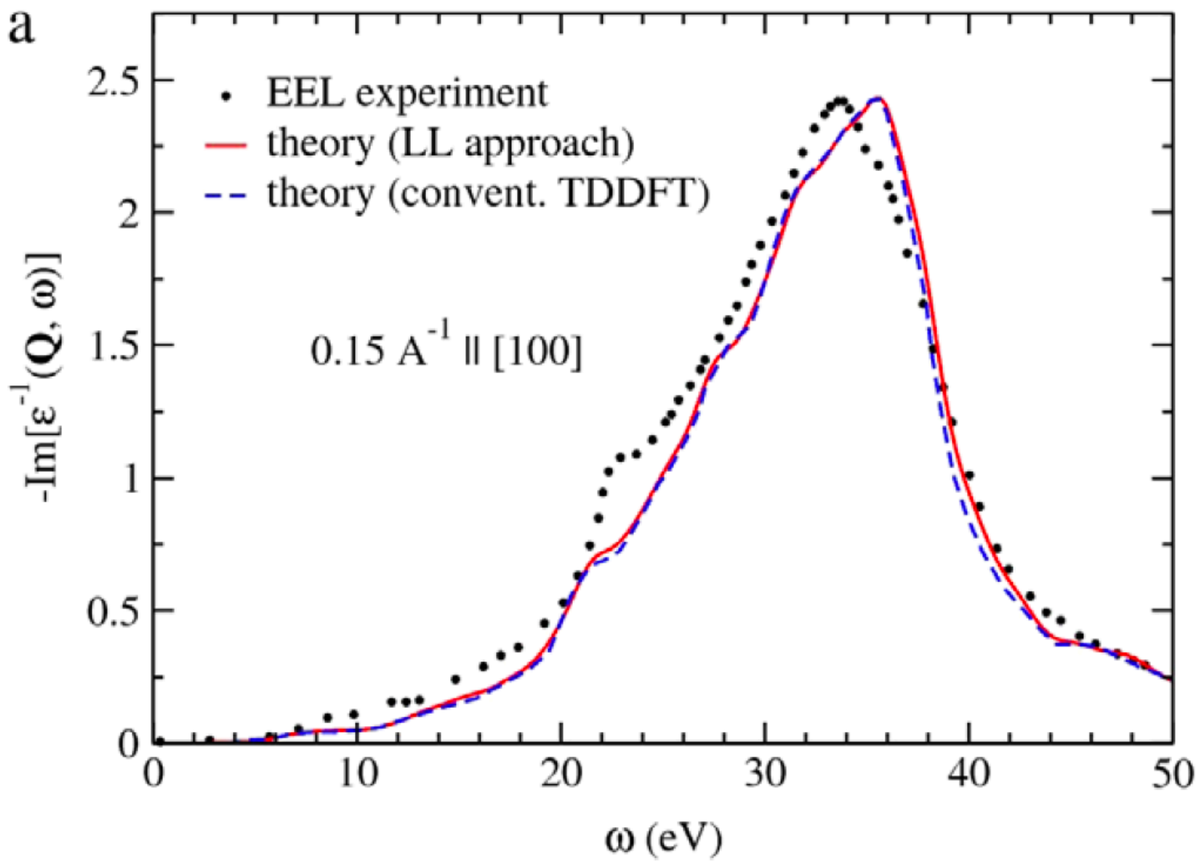


The loss function is computed for q = 0.15 (A^{-1}) along the [100] direction

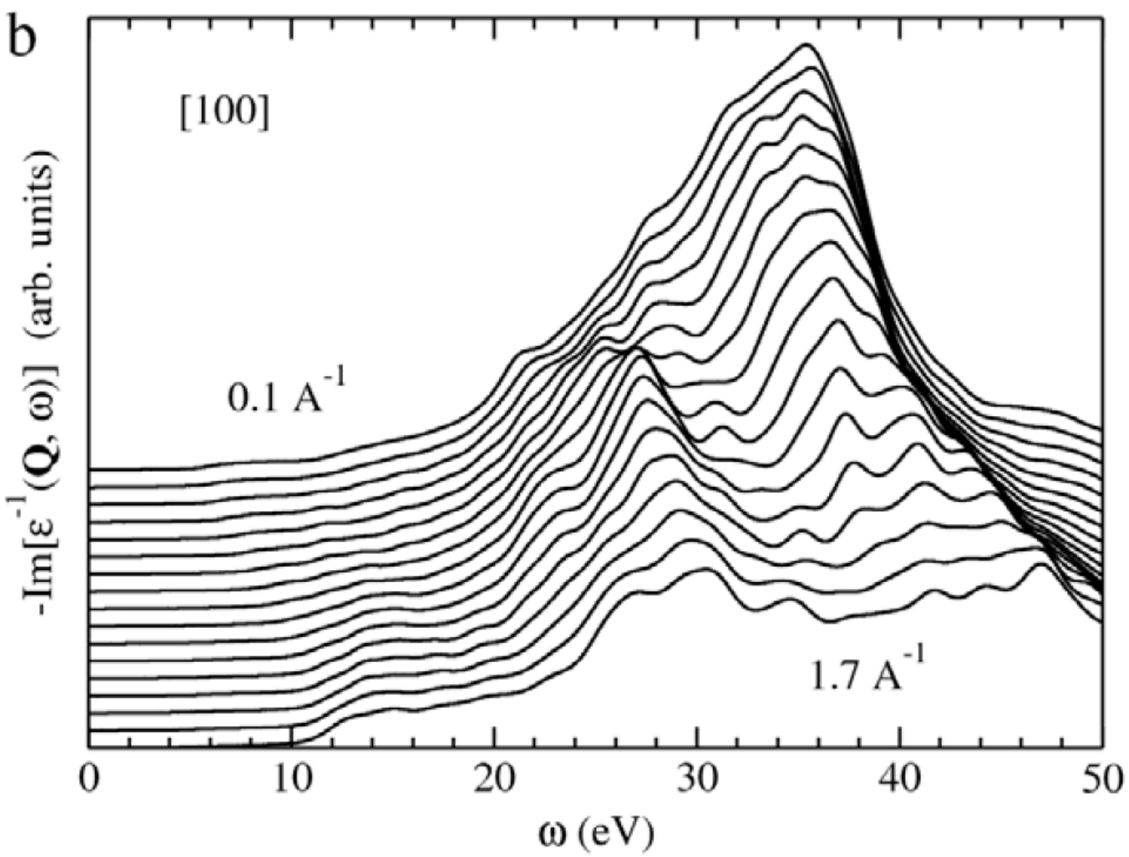
I. Timrov, N. Vast, R. Gebauer, and S. Baroni, Comput. Phys. Commun. 196, 460 (2015).

Loss function of bulk diamond

Comparison with experiment



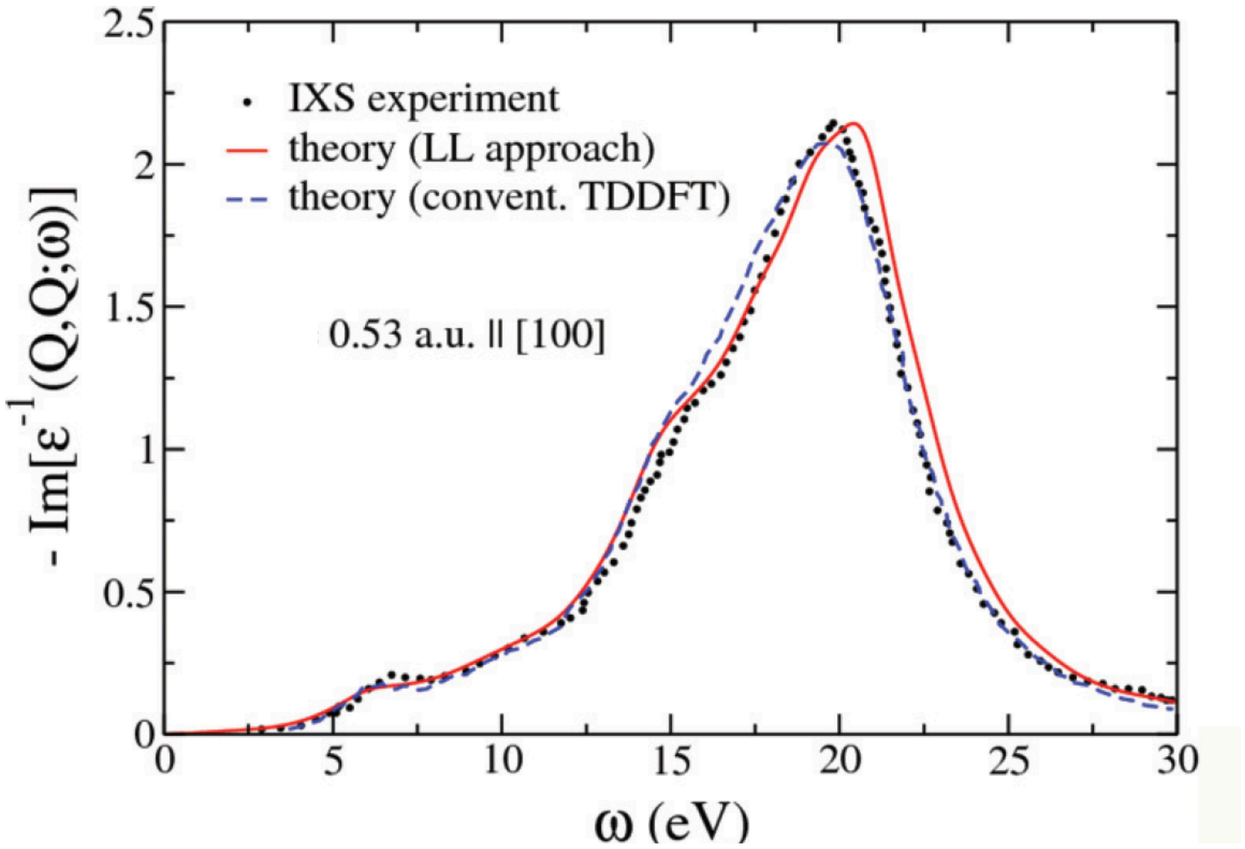
Evolution as a function of **q**



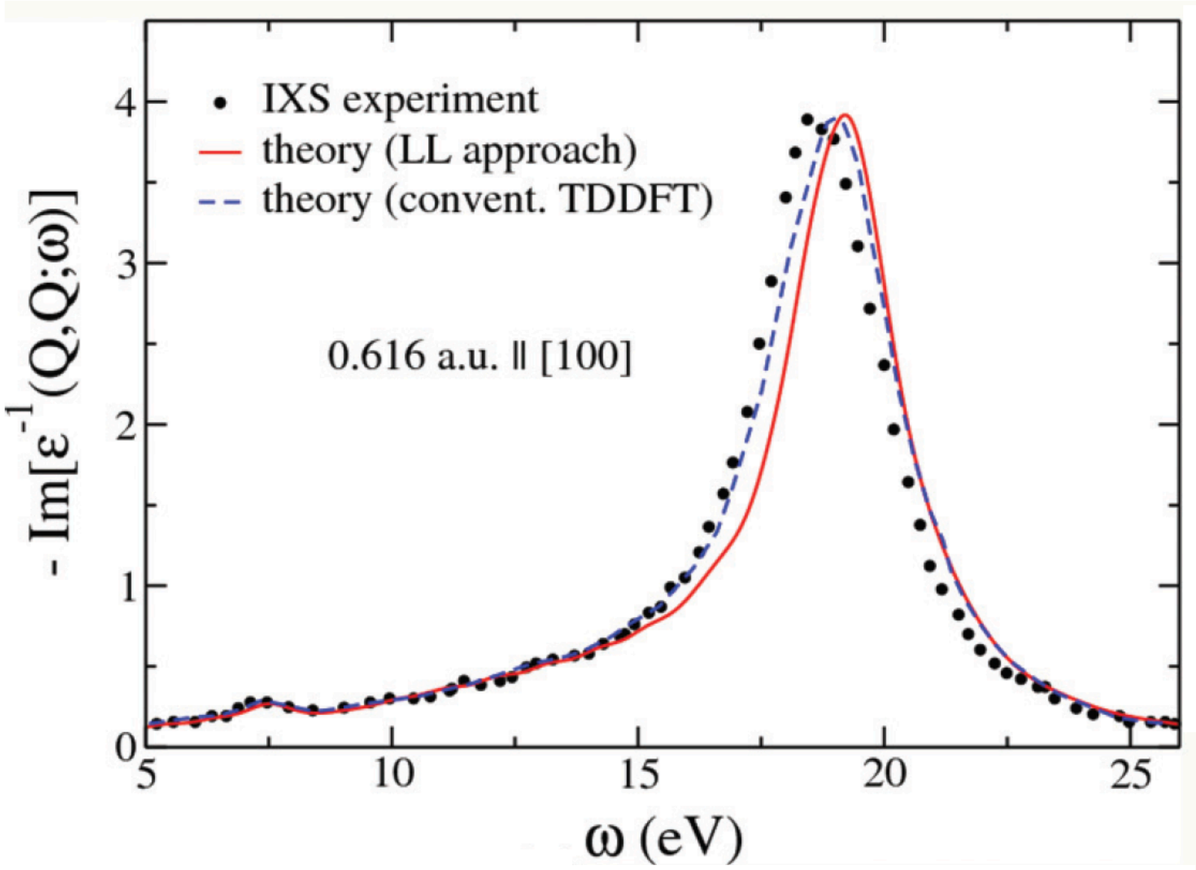
I. Timrov, N. Vast, R. Gebauer, and S. Baroni, Comput. Phys. Commun. 196, 460 (2015).

Loss function of bulk silicon and aluminum

Silicon



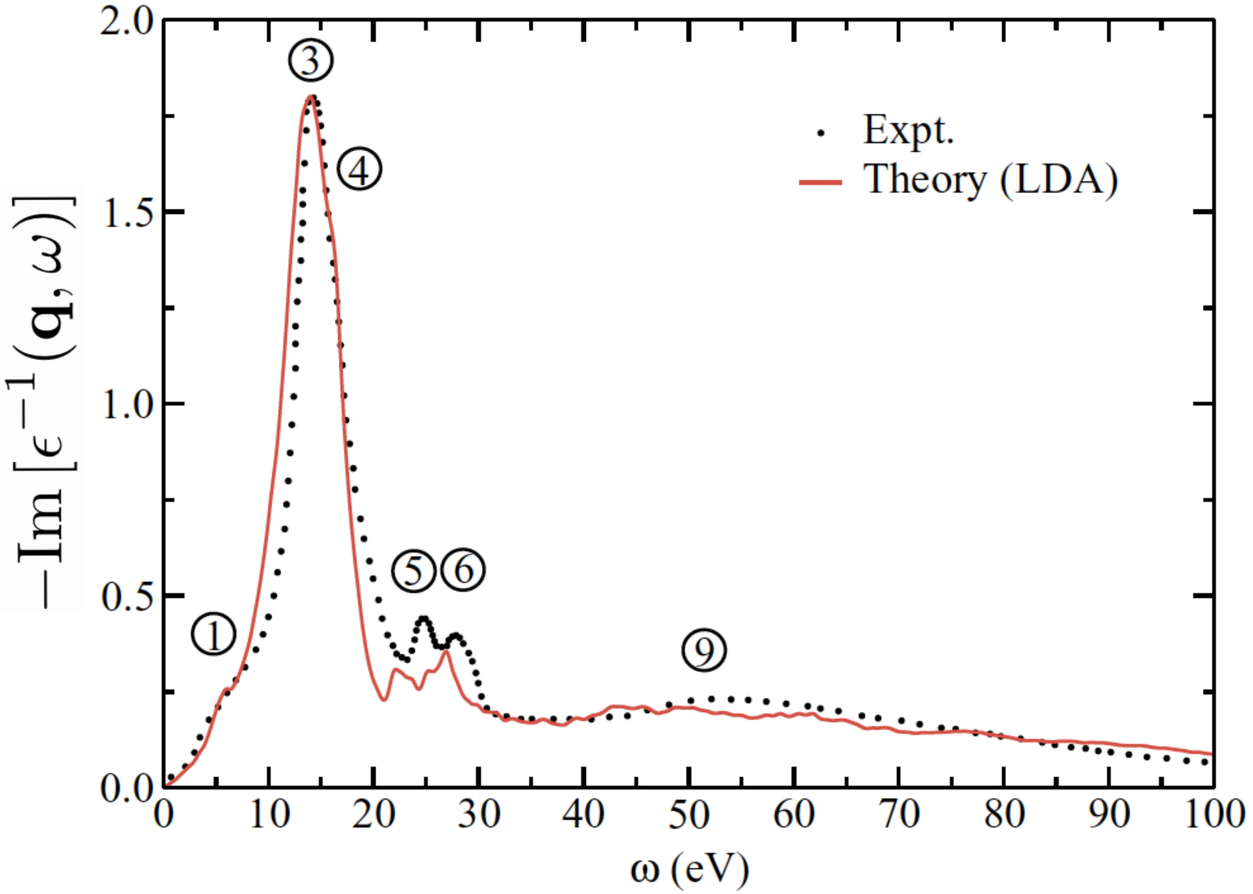
Aluminum



I. Timrov, N. Vast, R. Gebauer, and S. Baroni, Phys. Rev. B 88, 064301 (2013).

Loss function of bulk bismuth

EELS spectrum of bulk bismuth



I. Timrov, M. Markov, T. Gorni, M. Raynaud, O. Motornyi, R. Gebauer, and S. Baroni, and N. Vast, Phys. Rev. B **95**, 094301 (2017).

Loss function of bulk bismuth

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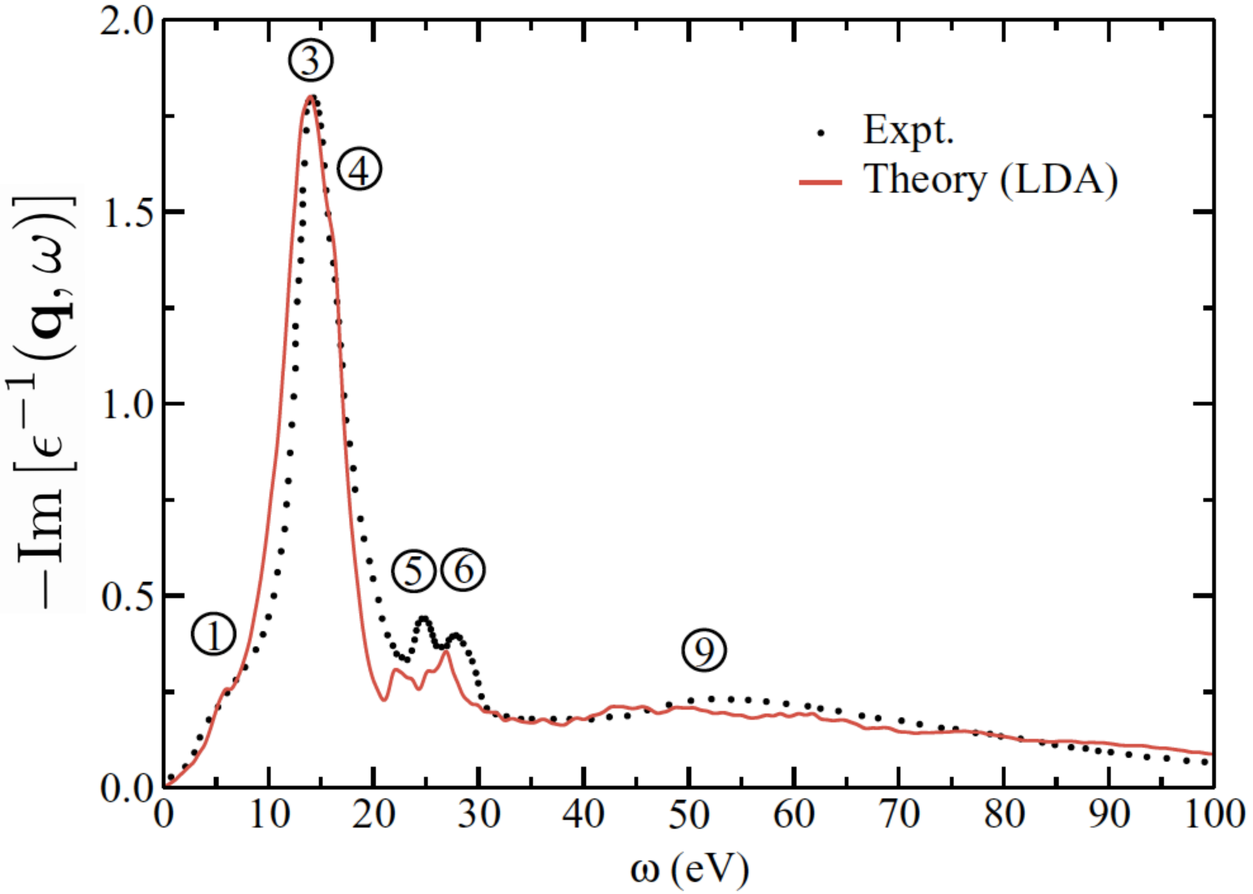
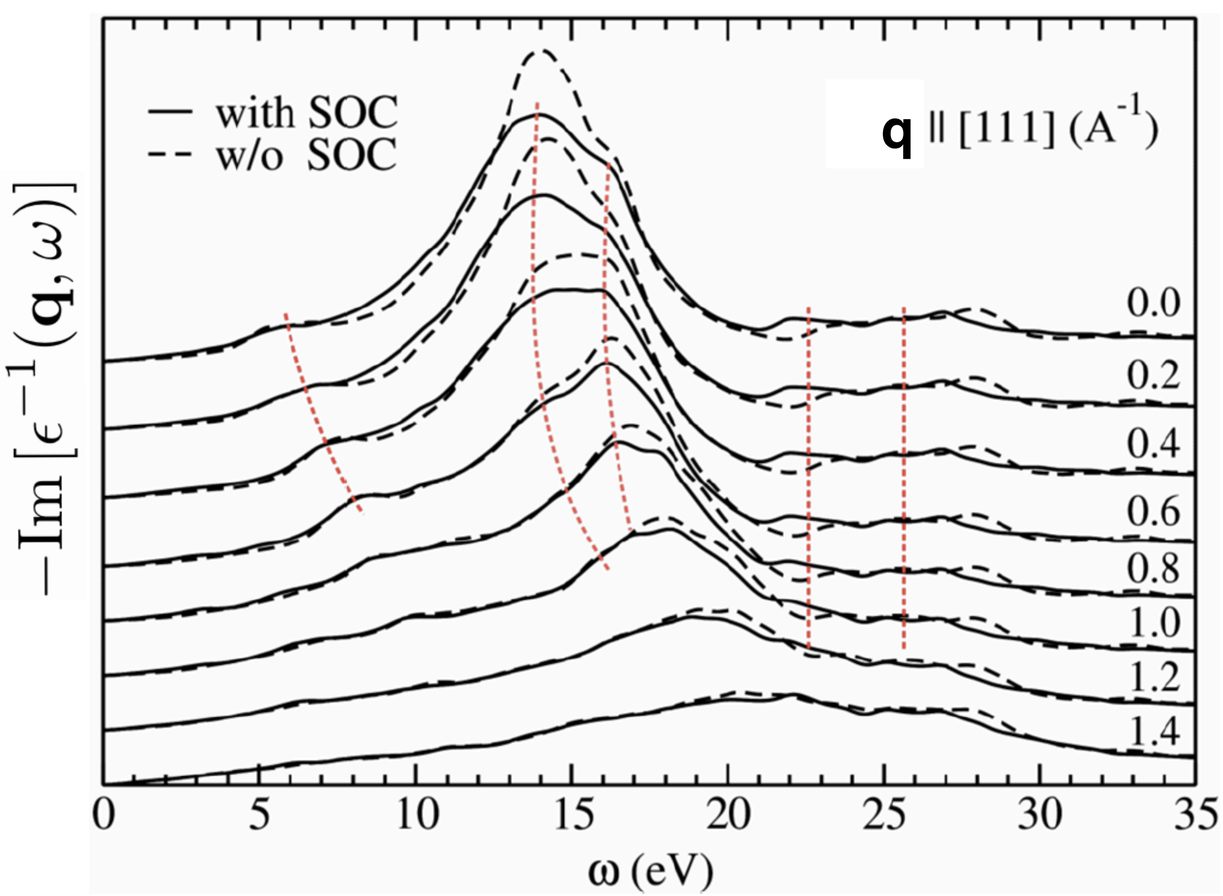


Peaks dispersion as a function of **q**



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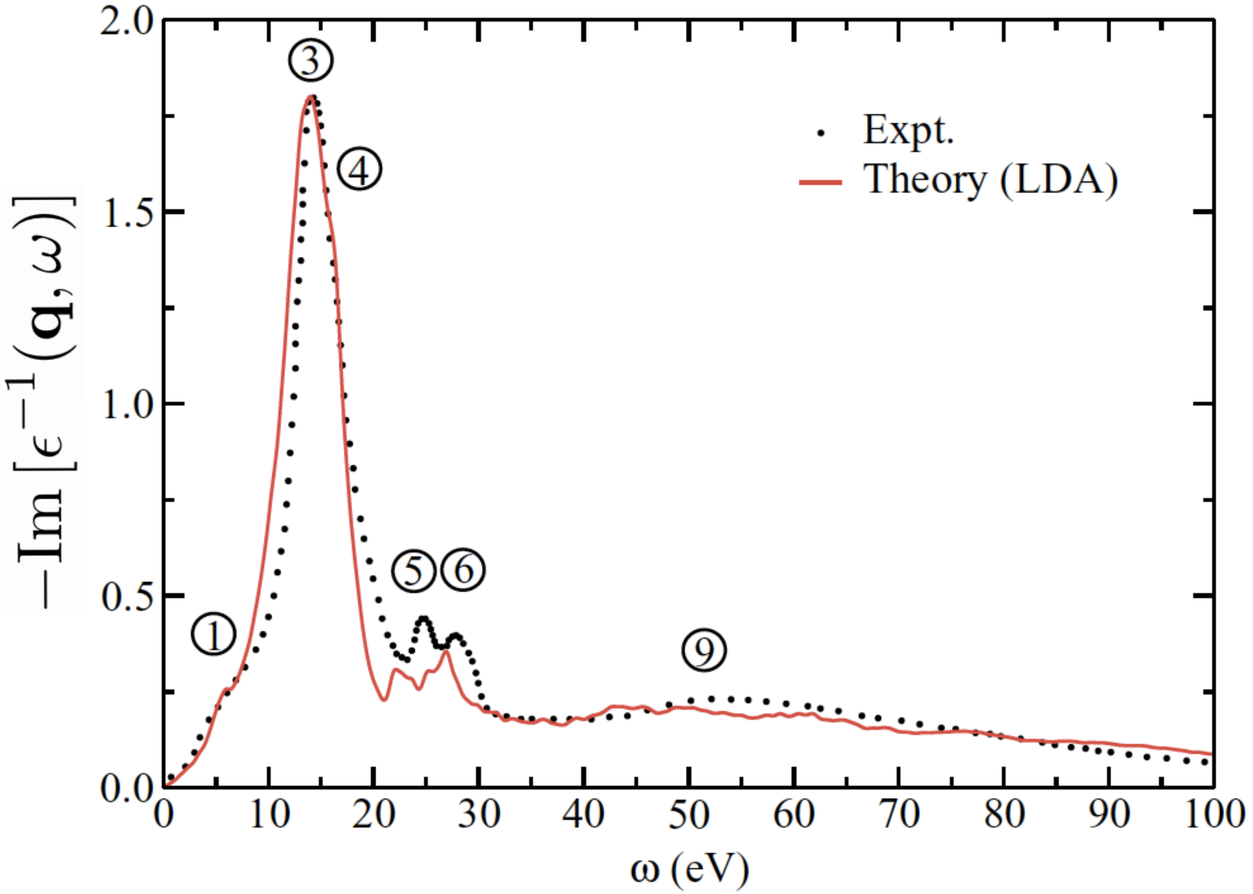

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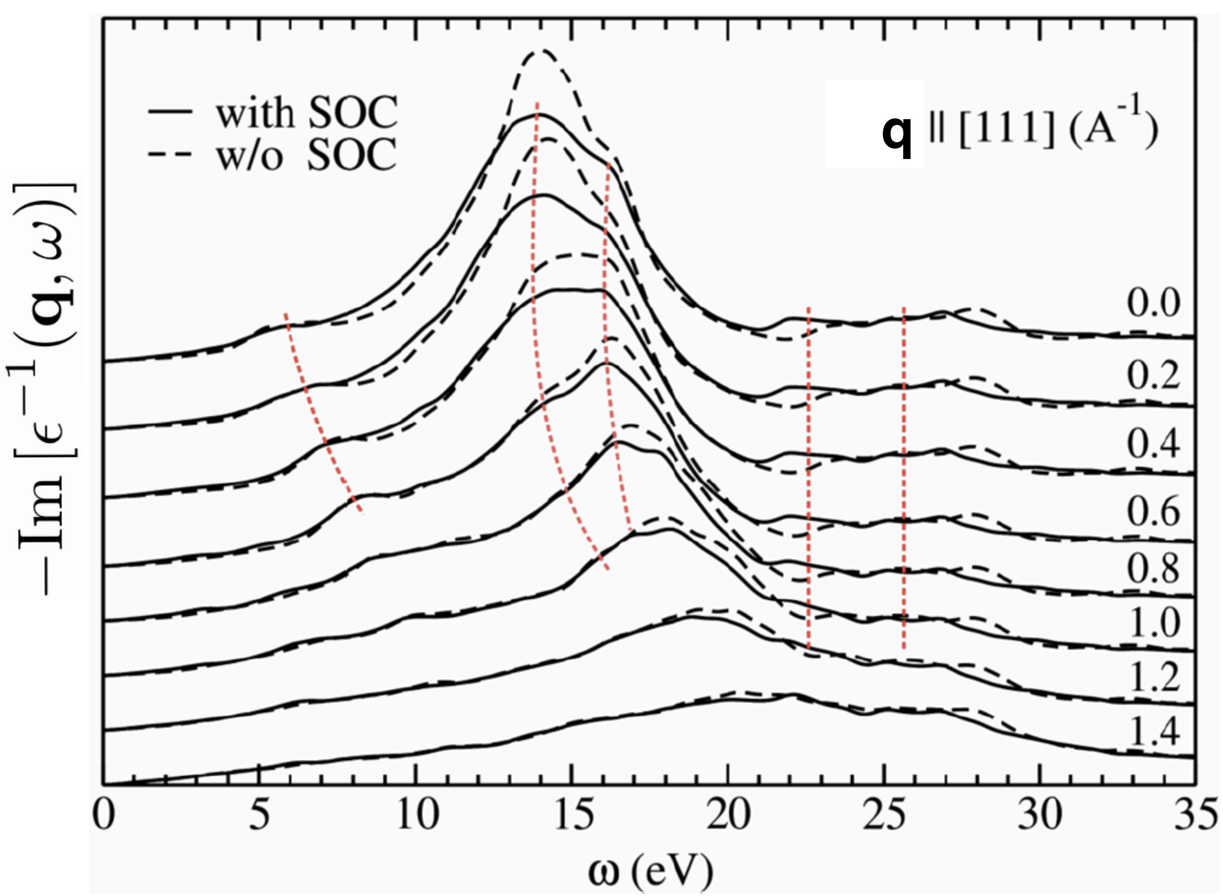


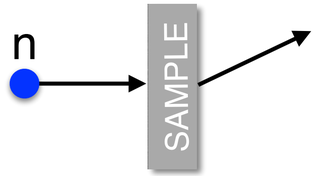
TDDFT@ALDA gives good results for EELS in solids! Limitation: excitons are not captured by ALDA.

I. Timrov, M. Markov, T. Gorni, M. Raynaud, O. Motornyi, R. Gebauer, and S. Baroni, and N. Vast, Phys. Rev. B **95**, 094301 (2017).

Inelastic neutron scattering in solids

Let us consider an external perturbation which is an incoming neutron:

$$\tilde{V}'_{ext,\mathbf{q}}(\mathbf{r},\omega) = -\mu_{\mathrm{B}}\,\boldsymbol{\sigma}\cdot\mathbf{B}(\omega)\,e^{i\mathbf{q}\cdot\mathbf{r}}$$



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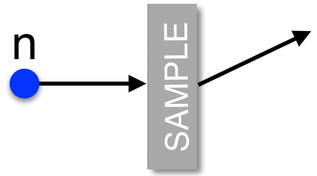

$$\tilde{V}'_{ext,\mathbf{q}}(\mathbf{r},\omega) = -\mu_{\mathrm{B}}\,\boldsymbol{\sigma}\cdot\mathbf{B}(\omega)\,e^{i\mathbf{q}\cdot\mathbf{r}}$$

The magnetization-density susceptibility (spin-spin response function) reads:

$$\boldsymbol{\chi}_{\mathrm{m}}(\mathbf{q},\omega) = \langle\hat{\mathbf{m}}_{\mathbf{q}}|(\hbar\omega - \hat{\mathcal{L}}_{\mathbf{q}})^{-1}\cdot[\hat{\mathbf{m}}_{\mathbf{q}},\hat{\rho}^{0}]\rangle$$

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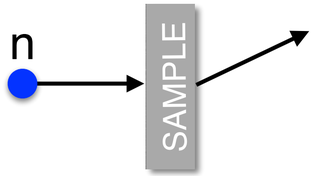

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This allows us to compute the following quantity:

$$S(\mathbf{q},\omega) = -\mathrm{Im}\,\mathrm{Tr}\,[\mathbf{P}(\mathbf{q})\,\chi(\mathbf{q},\omega)]$$

$$\mathrm{P}_{\alpha\beta}(\mathbf{q}) = \delta_{\alpha\beta} - q_\alpha q_\beta / q^2$$

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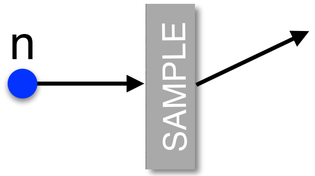

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Double-differential cross section:

$$\frac{d^2\sigma}{d\Omega d\varepsilon} \propto S(\mathbf{q},\omega)$$

The code to compute INS spectra will be available in the next official release of QE.

turboMagnon code

Computer Physics Communications 280 (2022) 108500

Contents lists available at ScienceDirect

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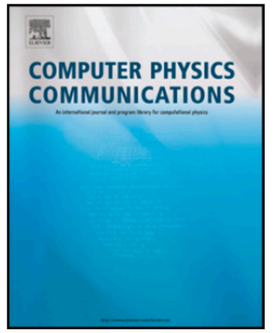
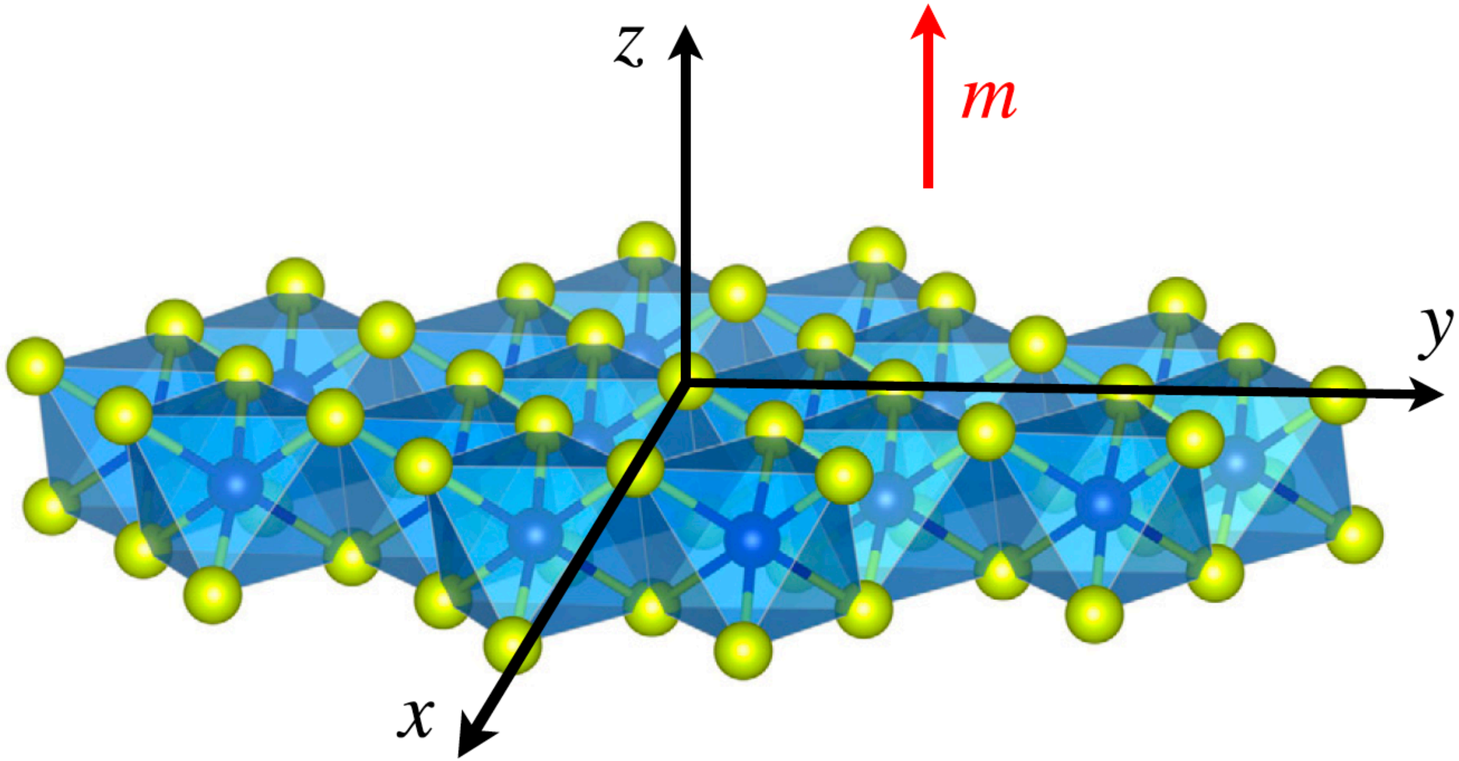
www.elsevier.com/locate/cpc



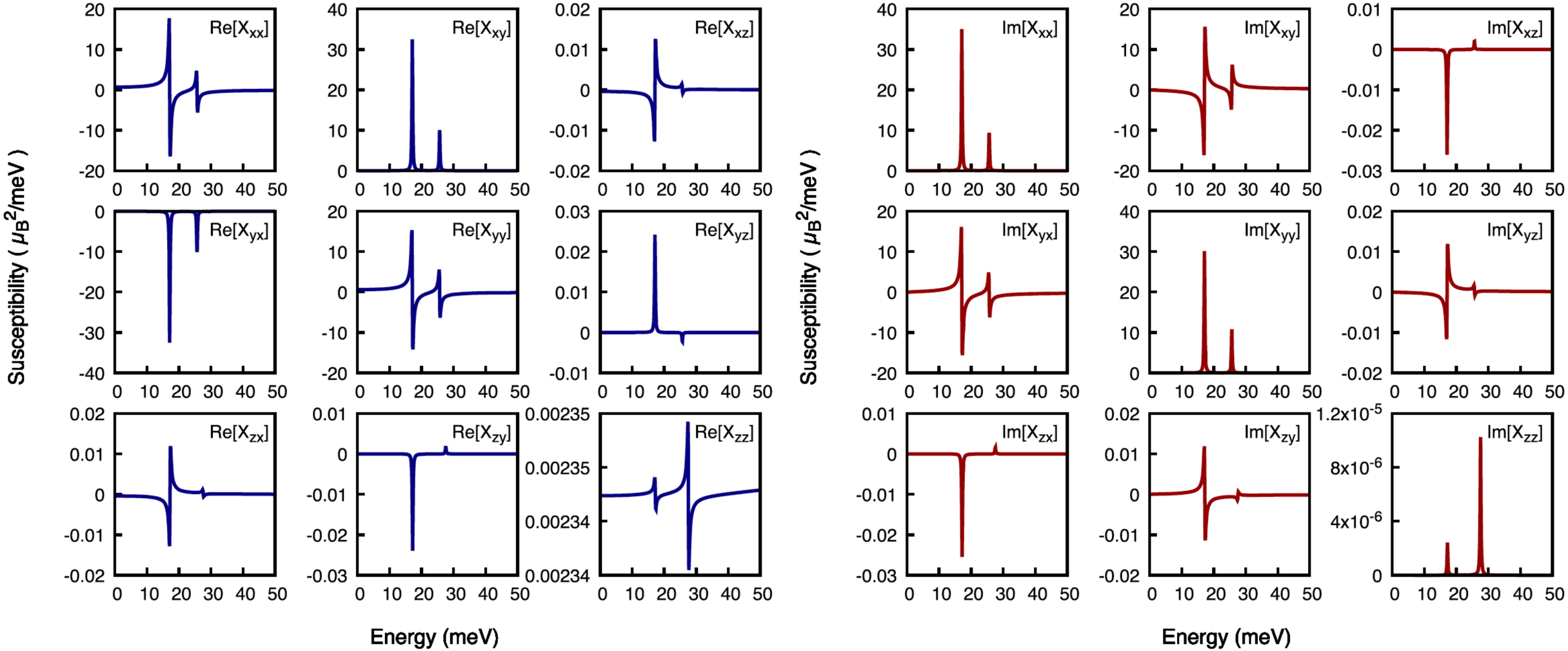
turboMagnon – A code for the simulation of spin-wave spectra using the Liouville-Lanczos approach to time-dependent density-functional perturbation theory ☆, ☆☆

Tommaso Gorni [a,*], Oscar Baseggio [b], Pietro Delugas [b], Stefano Baroni [b], Iurii Timrov [c,**]

CrI_3 monolayer

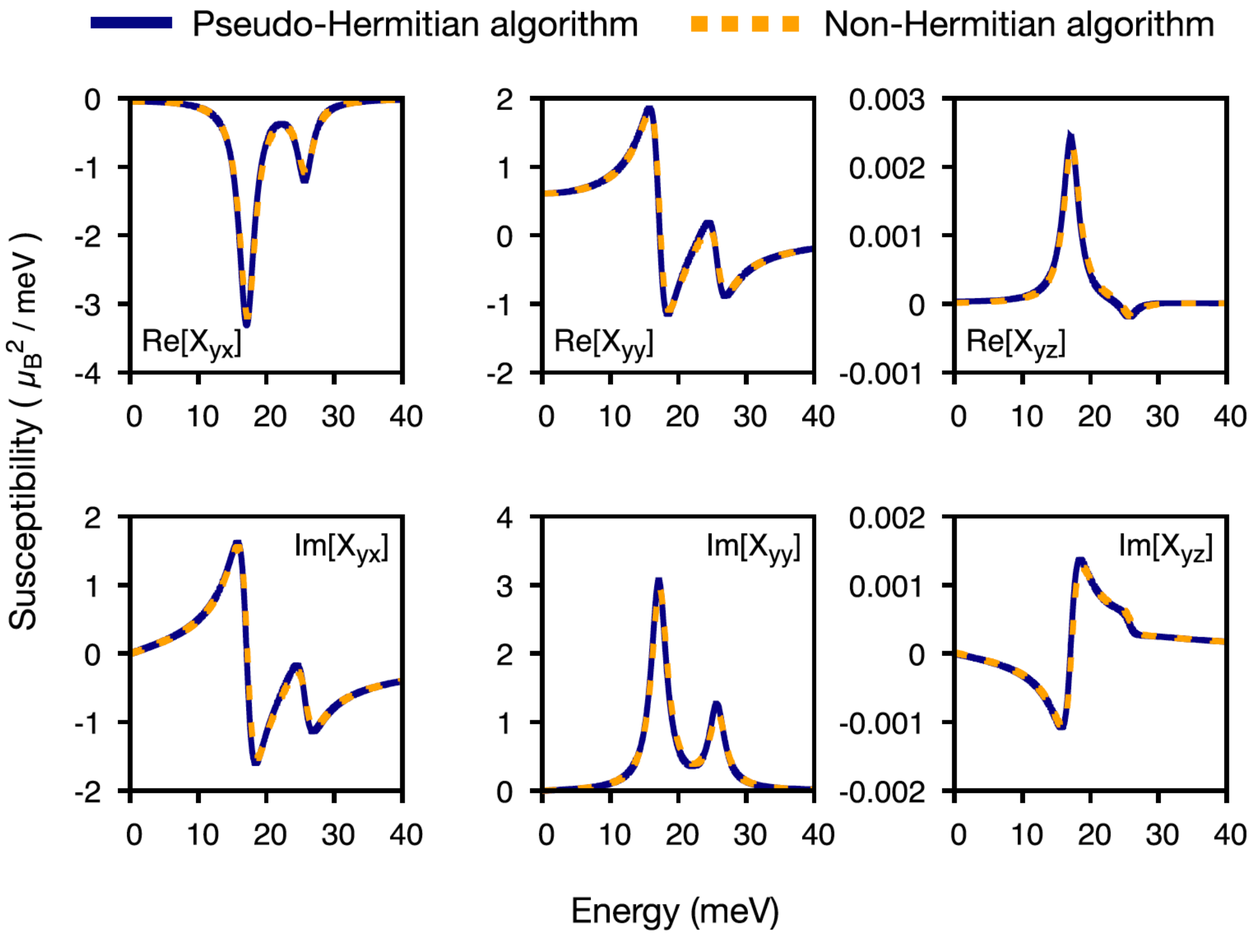


Spin susceptibility matrix of a CrI_3 monolayer



T. Gorni, O. Baseggio, P. Delugas, S. Baroni, I. Timrov, Comput. Phys. Commun. 280, 108500 (2022).

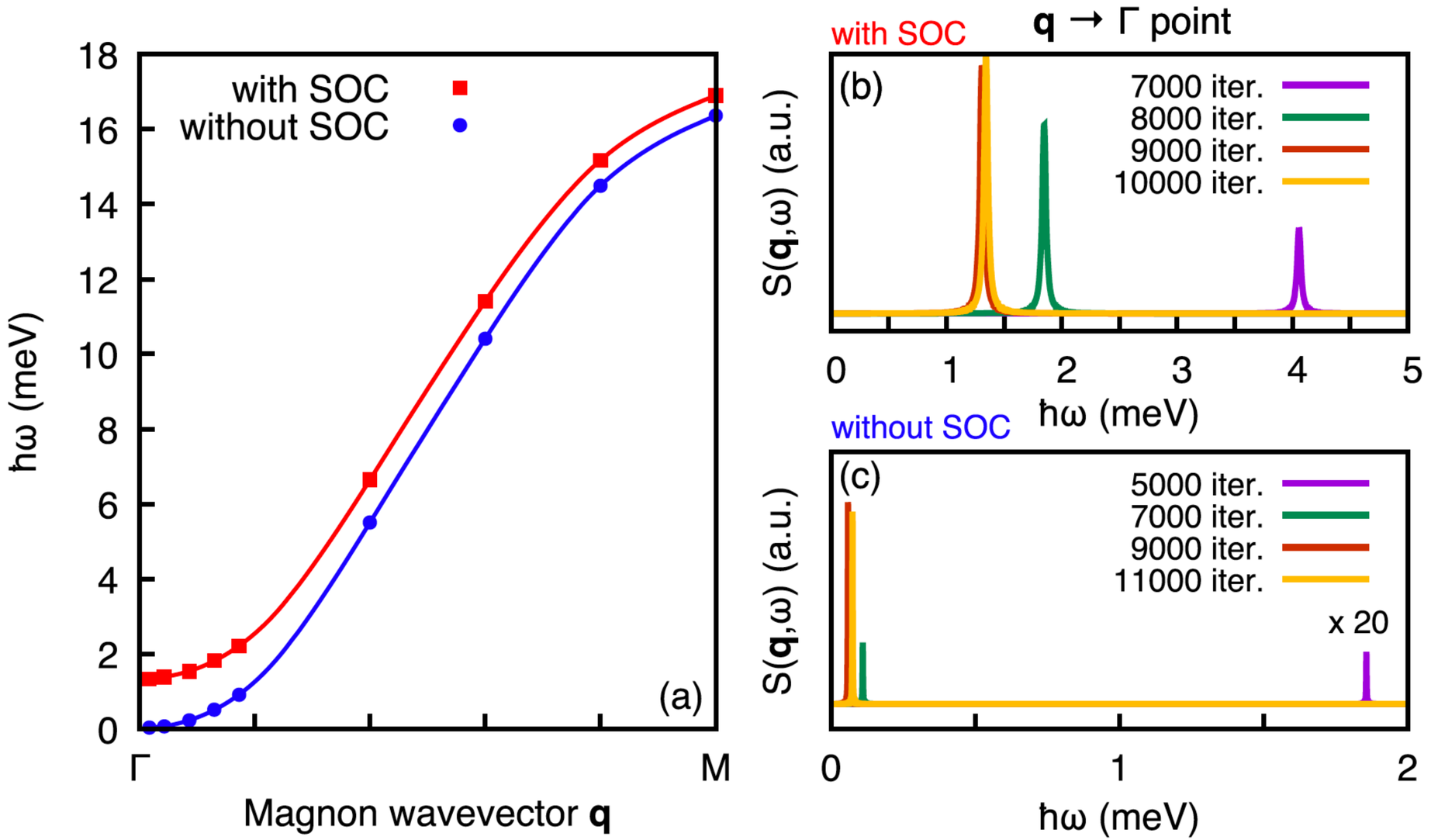
Pseudo-Hermitian vs Non-Hermitian Lanczos algorithms



Pseudo-Hermitian algorithm is 2 times faster than then Non-Hermitian algorithm

T. Gorni, O. Baseggio, P. Delugas, S. Baroni, I. Timrov, Comput. Phys. Commun. 280, 108500 (2022).

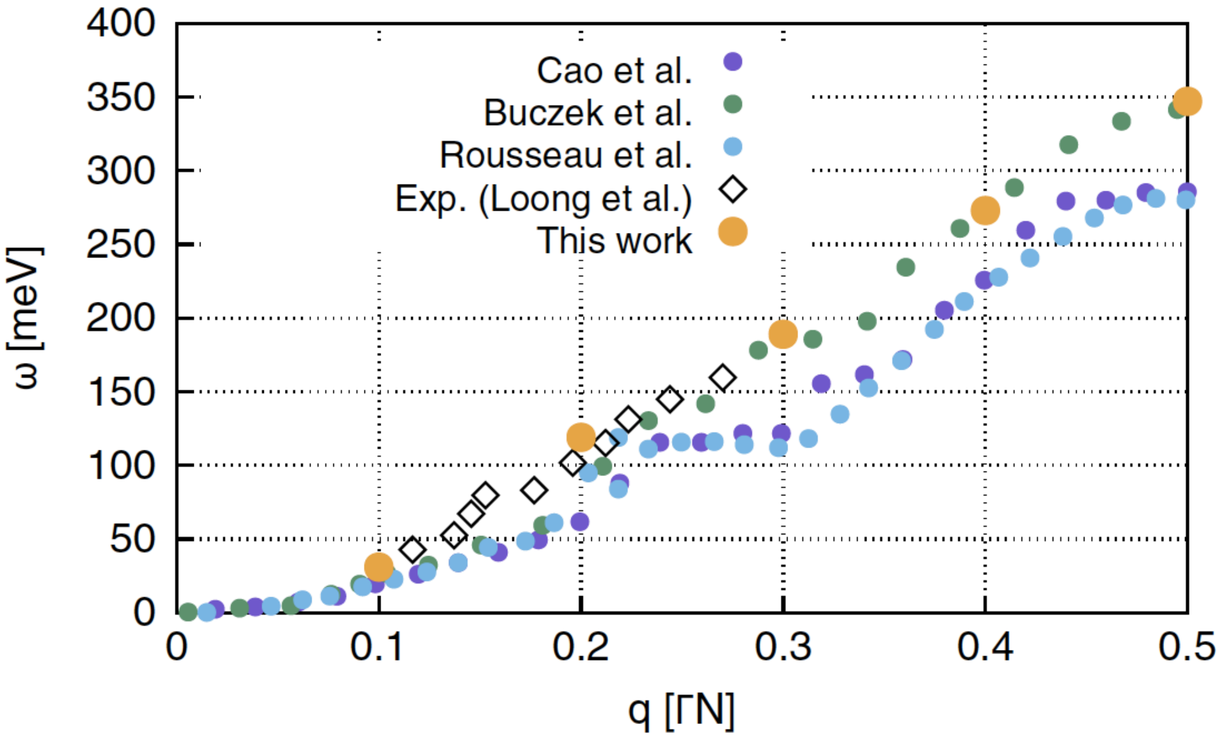
Magnon dispersion of a CrI_3 monolayer



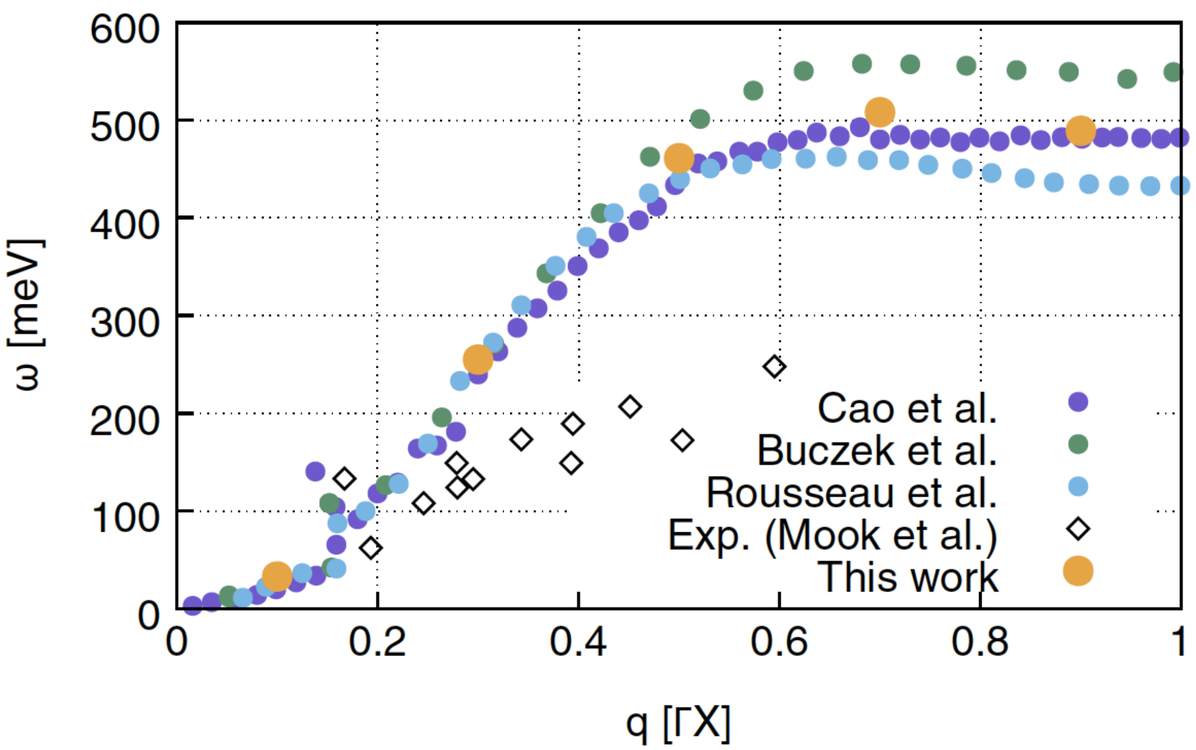
T. Gorni, O. Baseggio, P. Delugas, S. Baroni, I. Timrov, Comput. Phys. Commun. 280, 108500 (2022).

Magnon dispersion of bulk Fe and Ni

Magnon dispersion in bulk iron



Magnon dispersion in bulk nickel



TDDFT@ALDA gives excellent results for Fe but overestimates magnon energies by a factor of 2 for Ni.

T. Gorni, I. Timrov, and S. Baroni, Eur. Phys. J. B **91**, 249 (2018) - Special edition (in honor of Hardy Gross).

Summary

- Linear response TDDFT (or TDDFPT) is a well-established theory for modelling various spectroscopies. It owes its popularity to its relatively low computational cost (compared to many-body theories as e.g. BSE) when used with the adiabatic approximation.

- Adiabatic approximation gives satisfactory results for many properties (e.g. plasmons and magnons). But certain properties come out to be unsatisfactory in adiabatic approximation (e.g. no excitons). Hence, spatial non-locality and/or frequency-dependence in the exchange-correlation kernel is needed, but the cost of TDDFPT with such kernels increases very rapidly.

- The Quantum ESPRESSO distribution contains a TDDFPT module which can be used for calculations of optical absorption spectra of finite systems (molecules), electron energy loss spectra of non-magnetic solids, and inelastic neutron scattering spectra of magnetic solids.