

Introduction to time-dependent density-functional perturbation theory

Iurii Timrov

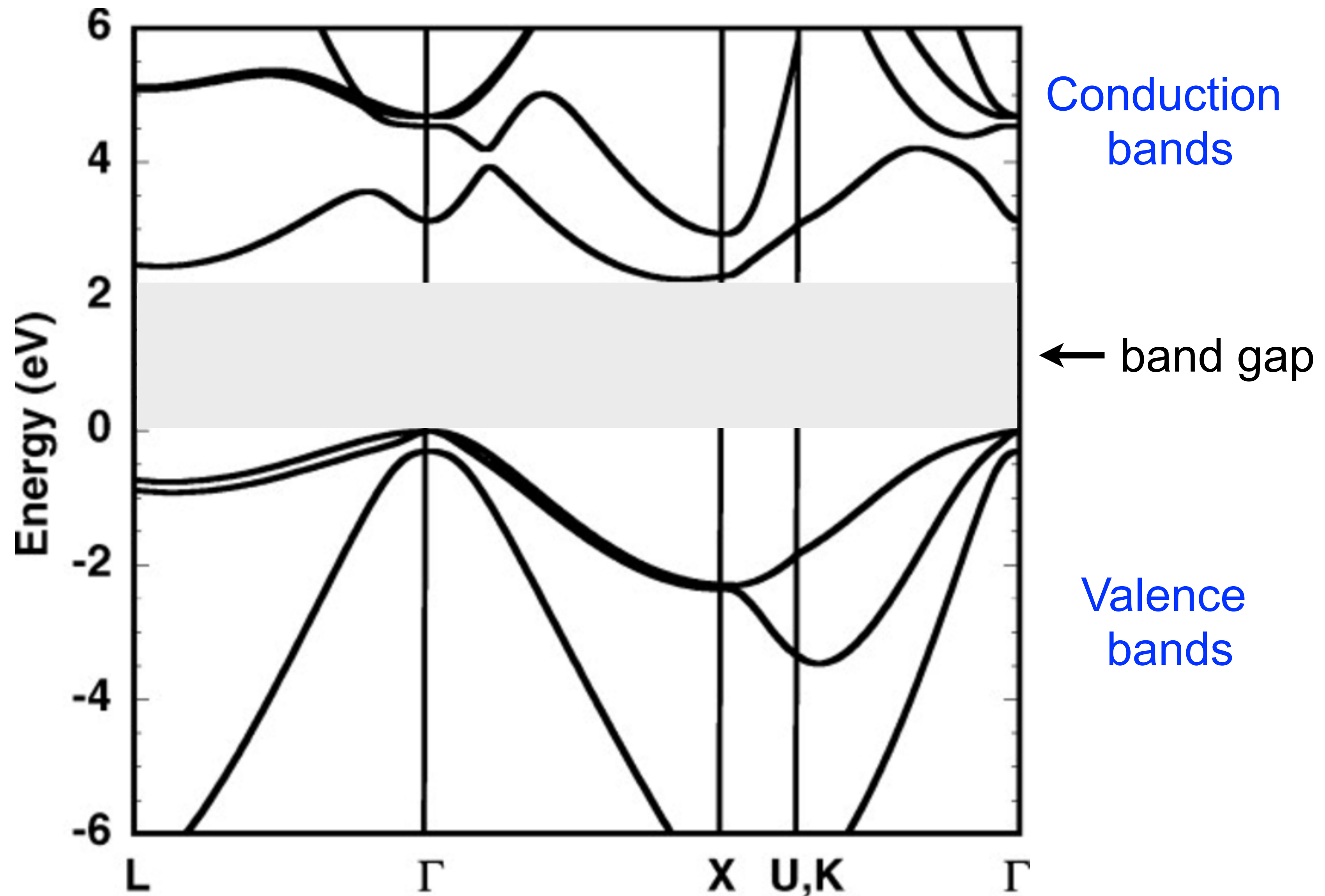
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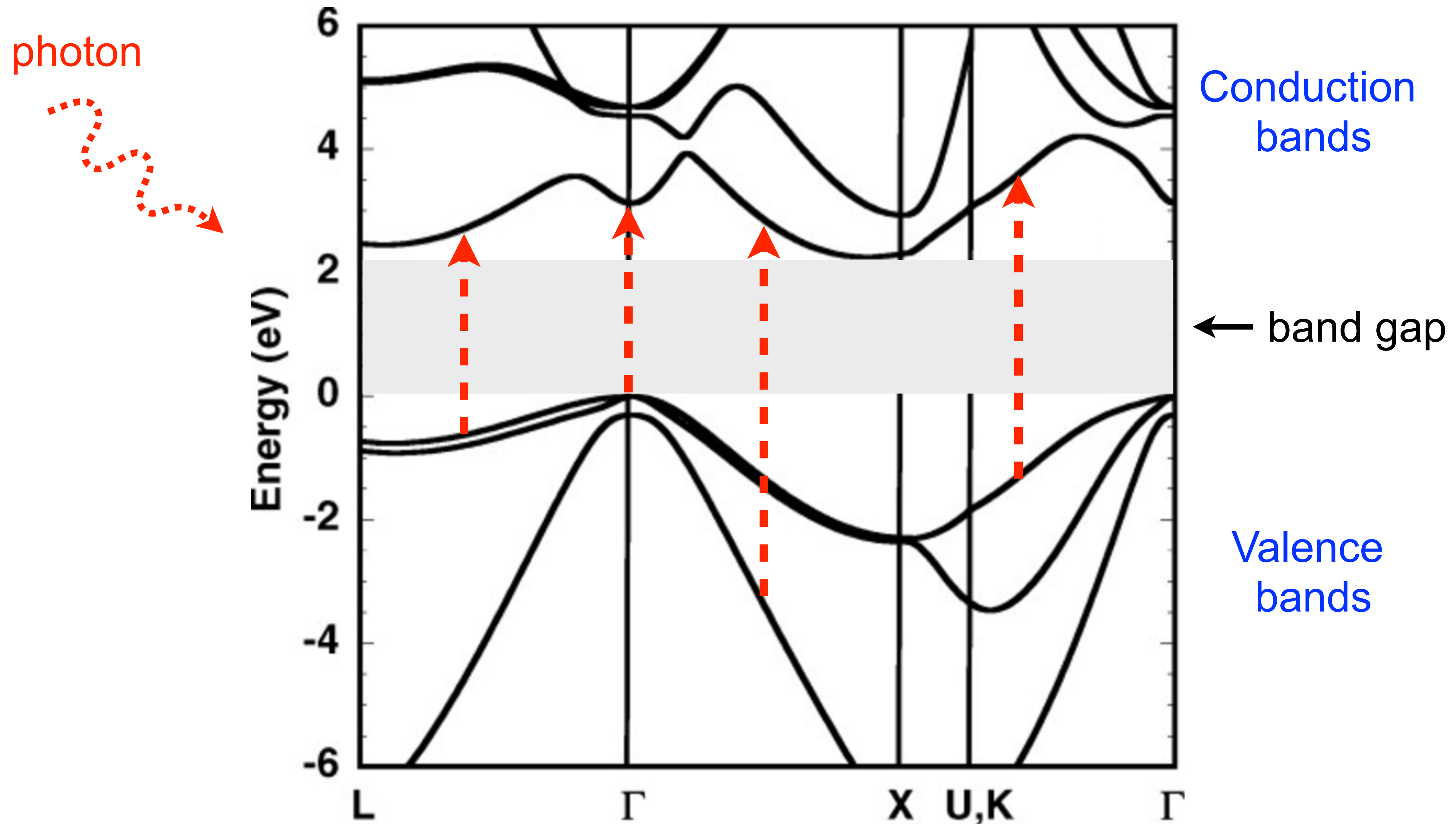


12 March 2024

Computational spectroscopy: from ground state to excited state



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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

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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:

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

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

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

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

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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

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

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

Time-dependent Kohn-Sham equations:

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

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

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

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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:

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

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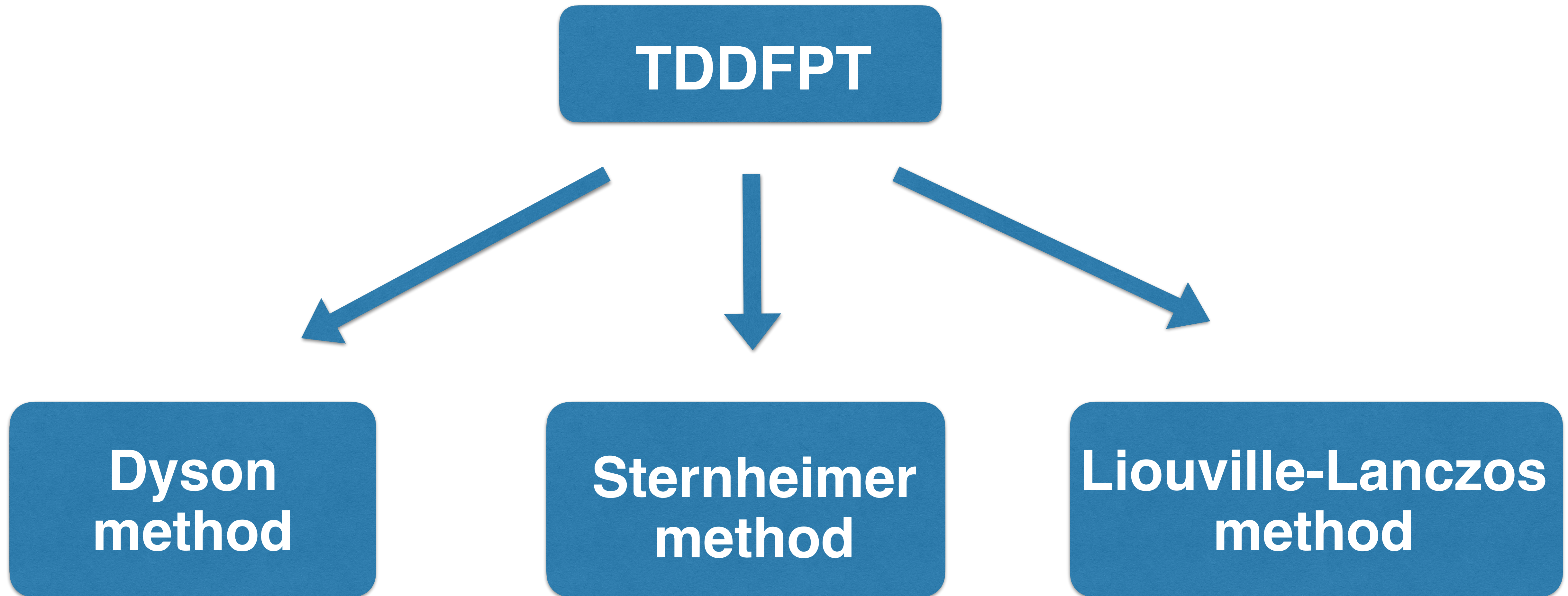
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Time-dependent density functional perturbation theory (TDDFPT) is TDDFT in conjunction with perturbation theory. If we keep only the first-order term in the Taylor expansion, then this is linear-response TDDFT.

Different ways how to compute the susceptibility from TDDFPT



Dyson method

The **Dyson-like matrix equation** in the reciprocal space:

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

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

$f_{\mathbf{G},\mathbf{G}'}^{\text{xc}}(\mathbf{q},\omega)$ is the Fourier transform of the exchange-correlation kernel (RPA: $f_{\text{xc}} = 0$)

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$$\chi_{\mathbf{G},\mathbf{G}'}^0(\mathbf{q},\omega) = \frac{1}{\Omega} \sum_{\mathbf{k}} \sum_{n,n'}^{\text{BZ}} \frac{f_{n,\mathbf{k}} - f_{n',\mathbf{k}+\mathbf{q}}}{\hbar\omega + \varepsilon_{n,\mathbf{k}} - \varepsilon_{n',\mathbf{k}+\mathbf{q}} + i\eta} \langle \varphi_{n,\mathbf{k}}^0 | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | \varphi_{n',\mathbf{k}+\mathbf{q}}^0 \rangle \langle \varphi_{n',\mathbf{k}+\mathbf{q}}^0 | e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'} | \varphi_{n,\mathbf{k}}^0 \rangle$$

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

Sternheimer method

The time-dependent Kohn-Sham equations:

$$i\hbar \frac{\partial \varphi_v(\mathbf{r}, t)}{\partial t} = H_{KS}(\mathbf{r}, t) \varphi_v(\mathbf{r}, t)$$

The Kohn-Sham Hamiltonian:

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

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

$$\begin{aligned} i\hbar \frac{\partial \varphi'_v(\mathbf{r}, t)}{\partial t} &= (\hat{H}^0 - \varepsilon_v) \varphi'_v(\mathbf{r}, t) + [V'_{ext}(\mathbf{r}, t) + V'_{Hxc}(\mathbf{r}, t)] \varphi_v^0(\mathbf{r}) \\ -i\hbar \frac{\partial \varphi'^*_v(\mathbf{r}, t)}{\partial t} &= (\hat{H}^0 - \varepsilon_v) \varphi'^*_v(\mathbf{r}, t) + [V'_{ext}(\mathbf{r}, t) + V'_{Hxc}(\mathbf{r}, t)] \varphi_v^{0*}(\mathbf{r}) \end{aligned}$$

Sternheimer method

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

$$\begin{aligned}(\hat{H}^0 - \varepsilon_v - \hbar\omega)\tilde{\varphi}'_v(\mathbf{r}, \omega) + \hat{P}_c\tilde{V}'_{Hxc}(\mathbf{r}, \omega)\varphi_v^0(\mathbf{r}) &= -\hat{P}_c\tilde{V}'_{ext}(\mathbf{r}, \omega)\varphi_v^0(\mathbf{r}), \\(\hat{H}^0 - \varepsilon_v + \hbar\omega)\tilde{\varphi}'_v^*(\mathbf{r}, -\omega) + \hat{P}_c\tilde{V}'_{Hxc}(\mathbf{r}, \omega)\varphi_v^0(\mathbf{r}) &= -\hat{P}_c\tilde{V}'_{ext}(\mathbf{r}, \omega)\varphi_v^0(\mathbf{r})\end{aligned}$$

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

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

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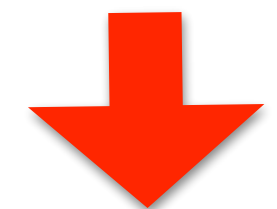
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**SELF-CONSISTENT
PROBLEM**



Solved iteratively

Sternheimer method

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

$$\begin{aligned}
 (\hat{H}^0 - \varepsilon_v - \hbar\omega) \tilde{\varphi}'_v(\mathbf{r}, \omega) + \hat{P}_c \tilde{V}'_{Hxc}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r}) &= -\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r}), \\
 (\hat{H}^0 - \varepsilon_v + \hbar\omega) \tilde{\varphi}'_v{}^*(\mathbf{r}, -\omega) + \hat{P}_c \tilde{V}'_{Hxc}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r}) &= -\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r})
 \end{aligned}$$

Projector on empty states:

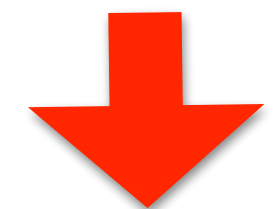
$$\hat{P}_c = \sum_c |\varphi_c^0\rangle \langle \varphi_c^0|$$

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

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

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

SELF-CONSISTENT PROBLEM



Solved iteratively

Sternheimer method

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

$$\begin{aligned}
 (\hat{H}^0 - \varepsilon_v - \hbar\omega) \tilde{\varphi}'_v(\mathbf{r}, \omega) + \hat{P}_c \tilde{V}'_{Hxc}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r}) &= -\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r}), \\
 (\hat{H}^0 - \varepsilon_v + \hbar\omega) \tilde{\varphi}'_v{}^*(\mathbf{r}, -\omega) + \hat{P}_c \tilde{V}'_{Hxc}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r}) &= -\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r})
 \end{aligned}$$

Projector on empty states:

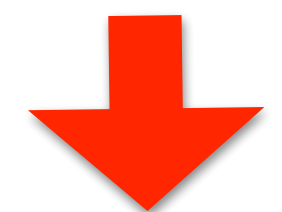
$$\hat{P}_c = \sum_c |\varphi_c^0\rangle \langle \varphi_c^0|$$

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

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

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

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:

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

Liouville-Lanczos method

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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:

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

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

B. Walker, A.M. Saitta, R. Gebauer, and S. Baroni, Phys. Rev. Lett. **96**, 113001 (2006).

D. Rocca, R. Gebauer, Y. Saad, and S. Baroni, J. Chem. Phys. **128**, 154105 (2008).

Liouville-Lanczos method

Let us rewrite the linear-response quantum Liouville equation by defining the [Liouville superoperator](#):

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

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

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

$$(\hbar\omega - \hat{\mathcal{L}}) \cdot \hat{\rho}'(\omega) = [\hat{V}'_{ext}(\omega), \hat{\rho}^0]$$

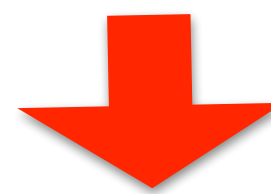
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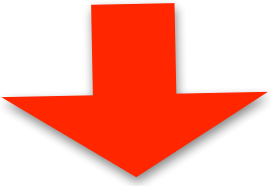
$$\hat{\rho}'(\omega) = (\hbar\omega - \hat{\mathcal{L}})^{-1} \cdot [\hat{V}'_{ext}(\omega), \hat{\rho}^0]$$

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

Liouville-Lanczos method

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

Liouville-Lanczos method

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We define the **standard batch representation**:

$$q_v(\mathbf{r}) = \frac{1}{2} [\tilde{\varphi}'_v(\mathbf{r}, \omega) + \tilde{\varphi}'_v{}^*(\mathbf{r}, -\omega)]$$

$$\mathbf{q} = \{q_v(\mathbf{r})\}$$

$$p_v(\mathbf{r}) = \frac{1}{2} [\tilde{\varphi}'_v(\mathbf{r}, \omega) - \tilde{\varphi}'_v{}^*(\mathbf{r}, -\omega)]$$

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$$\left(\hbar\omega - \hat{\mathcal{L}}\right) \cdot \hat{\rho}'(\omega) = [\hat{V}'_{ext}(\omega), \hat{\rho}^0] \quad \rightarrow \quad \left(\begin{array}{cc} \hbar\omega & -\hat{\mathcal{D}} \\ -\hat{\mathcal{D}} - 2\hat{\mathcal{K}} & \hbar\omega \end{array} \right) \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix} = \begin{pmatrix} 0 \\ \{\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r})\} \end{pmatrix}$$

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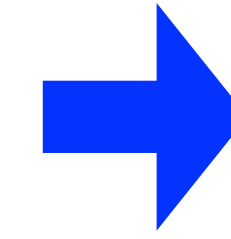
$$\mathbf{q} = \{q_v(\mathbf{r})\} \quad \mathbf{p} = \{p_v(\mathbf{r})\}$$

$$\left(\hbar\omega - \hat{\mathcal{L}}\right) \cdot \hat{\rho}'(\omega) = [\hat{V}'_{ext}(\omega), \hat{\rho}^0] \quad \rightarrow \quad \begin{pmatrix} \hbar\omega & -\hat{\mathcal{D}} \\ -\hat{\mathcal{D}} & \hbar\omega \end{pmatrix} \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix} = \begin{pmatrix} 0 \\ \{\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r})\} \end{pmatrix}$$

$$\hat{\mathcal{D}} \cdot q_v(\mathbf{r}) = \left(\hat{H}^0 - \varepsilon_v\right) q_v(\mathbf{r}) \quad \hat{\mathcal{K}} \cdot q_v(\mathbf{r}) = 2\hat{P}_c \sum_{v'} \int \left[\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}') \right] \varphi_v^0(\mathbf{r}) \varphi_{v'}^{0*}(\mathbf{r}') q_{v'}(\mathbf{r}') d\mathbf{r}'$$

Liouville-Lanczos method

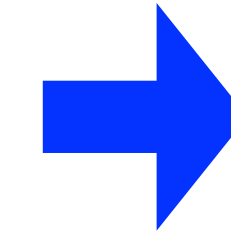
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Lanczos recursion
algorithm

Liouville-Lanczos method

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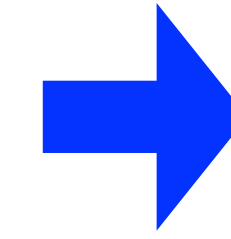
Lanczos recursion
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Let us define two two-component Lanczos vectors:

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

Liouville-Lanczos method

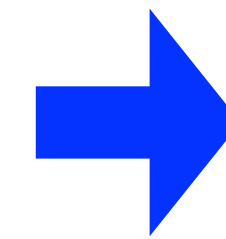
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Lanczos recursion algorithm

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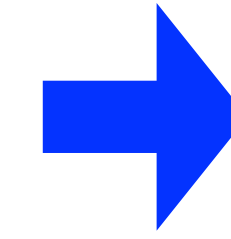


Lanczos recursion chain:

$$\begin{aligned} \beta_{i+1} \mathbf{V}_{i+1} &= \hat{\mathcal{L}} \mathbf{V}_i - \gamma_i \mathbf{V}_{i-1} \\ \gamma_{i+1} \mathbf{U}_{i+1} &= \hat{\mathcal{L}}^T \mathbf{U}_i - \beta_i \mathbf{U}_{i-1} \end{aligned}$$

Liouville-Lanczos method

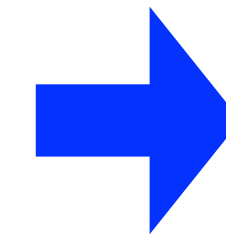
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Lanczos recursion algorithm

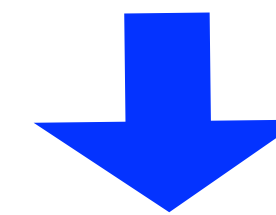
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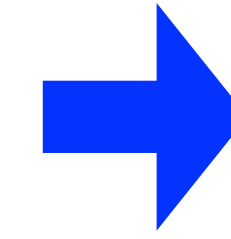


Tridiagonal matrix:

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

Liouville-Lanczos method

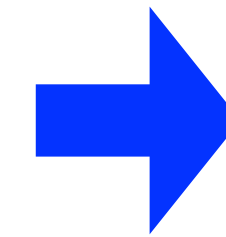
$$\begin{pmatrix} \hbar\omega & -\hat{D} \\ -\hat{D} - 2\hat{K} & \hbar\omega \end{pmatrix} \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix} = \begin{pmatrix} 0 \\ \{\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r})\} \end{pmatrix}$$



Lanczos recursion algorithm

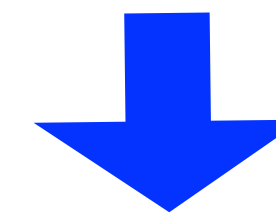
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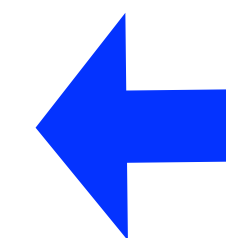


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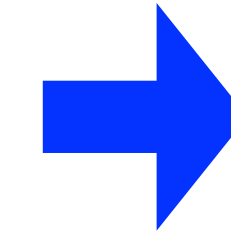
Susceptibility is computed in a postprocessing step:

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



Liouville-Lanczos method

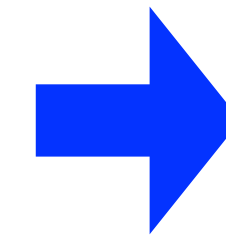
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Lanczos recursion algorithm

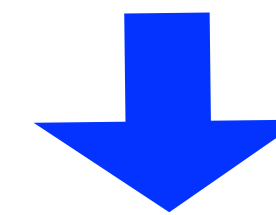
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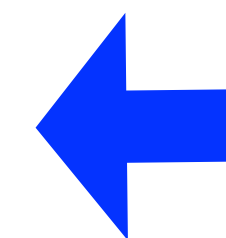
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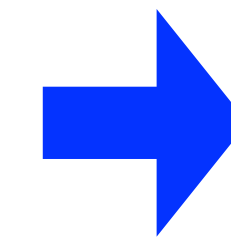
$$\chi_A(\omega) = \langle \zeta^N | \left(\hbar\omega \hat{I}^N - \hat{T}^N \right)^{-1} \cdot e_1^N \rangle$$

$$\zeta^N = \{ \langle (\hat{P}_c \hat{A} \varphi_v^0(\mathbf{r}), 0) | \mathbf{V}_i \rangle \}_N$$



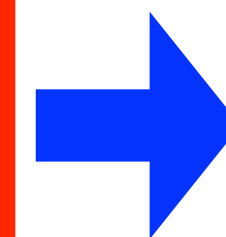
Liouville-Lanczos method

$$\begin{pmatrix} \hbar\omega & -\hat{D} \\ -\hat{D} - 2\hat{K} & \hbar\omega \end{pmatrix} \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix} = \begin{pmatrix} 0 \\ \{\hat{P}_c \tilde{V}'_{ext}(\mathbf{r}, \omega) \varphi_v^0(\mathbf{r})\} \end{pmatrix}$$



Lanczos recursion algorithm

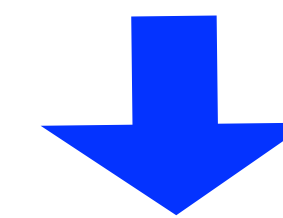
- 😊 No need in empty states
- 😊 The tridiagonal matrix \hat{T}^N must be computed only once (independently of frequency)
- 😊 The postprocessing is inexpensive; extrapolation of Lanczos coefficients allows us to speed up the convergence enormously



Lanczos recursion chain:

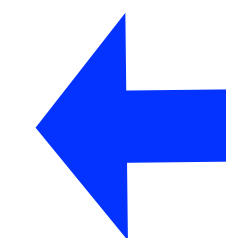
$$\beta_{i+1} \mathbf{V}_{i+1} = \hat{\mathcal{L}} \mathbf{V}_i - \gamma_i \mathbf{V}_{i-1}$$

$$\gamma_{i+1} \mathbf{U}_{i+1} = \hat{\mathcal{L}}^T \mathbf{U}_i - \beta_i \mathbf{U}_{i-1}$$



Tridiagonal matrix:

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



Susceptibility is computed in a postprocessing step:

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

$$\zeta^N = \{ \langle (\hat{P}_c \hat{A} \varphi_v^0(\mathbf{r}), 0) | \mathbf{V}_i \rangle \}_N$$

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

TDDFPT

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graph TD; A[TDDFPT] --> B[Electron energy loss spectroscopy]; A --> C[Inelastic neutron scattering spectroscopy];
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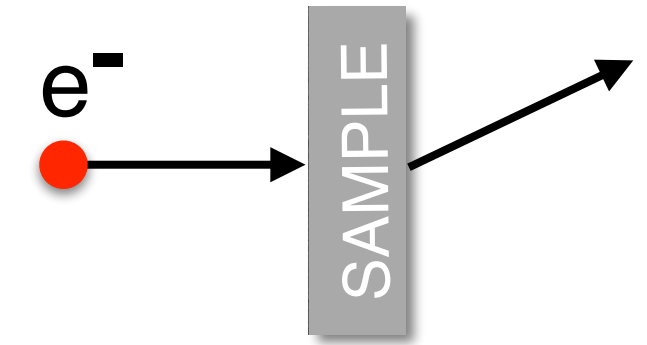
**Electron energy loss
spectroscopy**

**Inelastic neutron scattering
spectroscopy**

Electron energy loss in solids

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

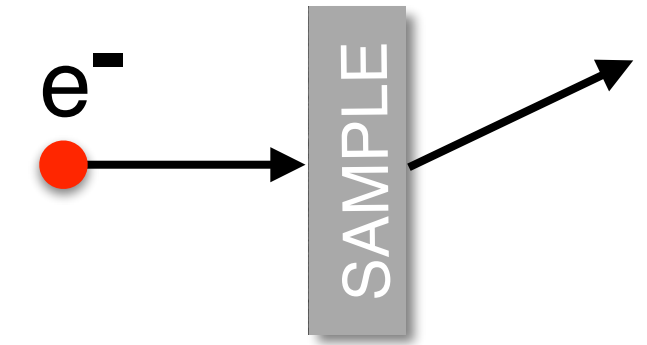
$$\tilde{V}'_{ext,\mathbf{q}}(\mathbf{r}, \omega) = e^{i\mathbf{q}\cdot\mathbf{r}}$$



Electron energy loss in solids

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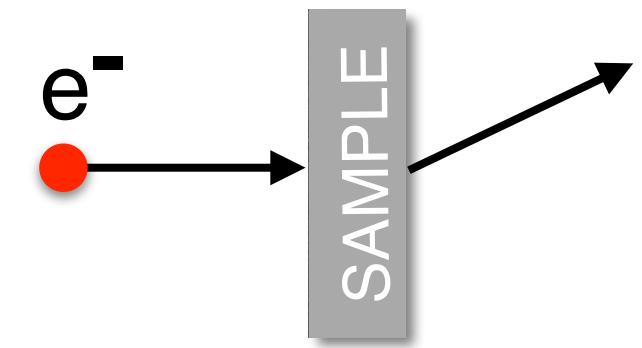
The charge-density susceptibility (density-density response function) reads:

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

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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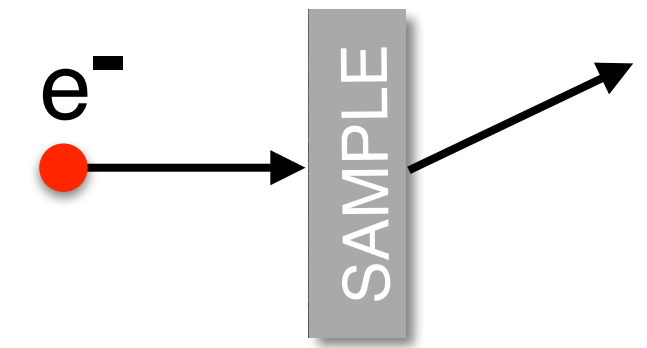
This allows us to compute the inverse dielectric function:

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

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Double-differential cross section:

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

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

turboEELS code

Computer Physics Communications 196 (2015) 460–469

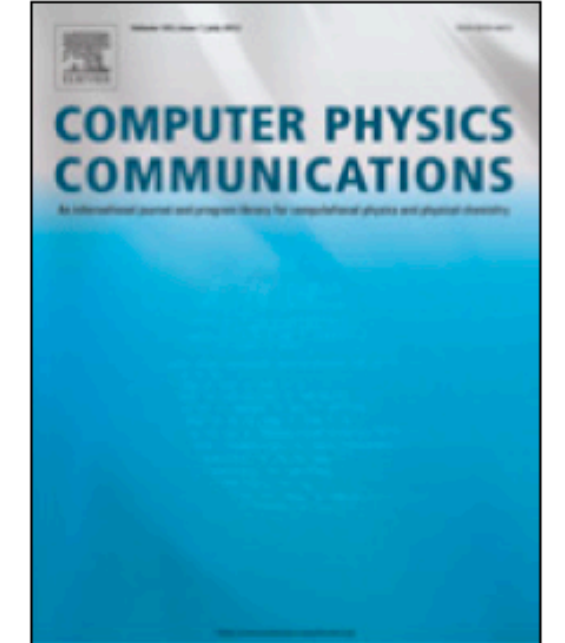


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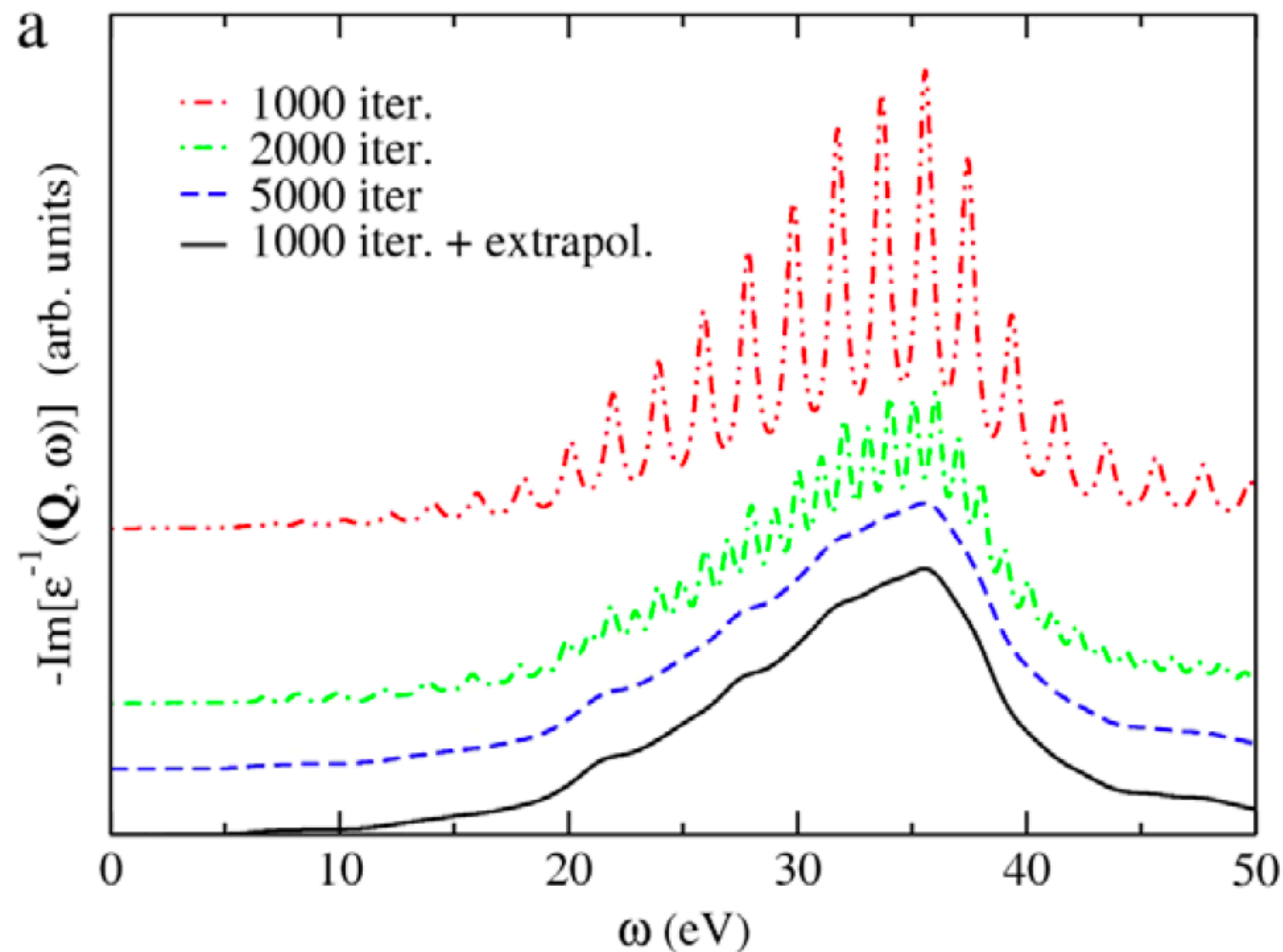
turboEELS—A code for the simulation of the electron energy loss and inelastic X-ray scattering spectra using the Liouville–Lanczos approach to time-dependent density-functional perturbation theory[☆]

Iurii Timrov^{a,b,1}, Nathalie Vast^a, Ralph Gebauer^c, Stefano Baroni^{b,*}

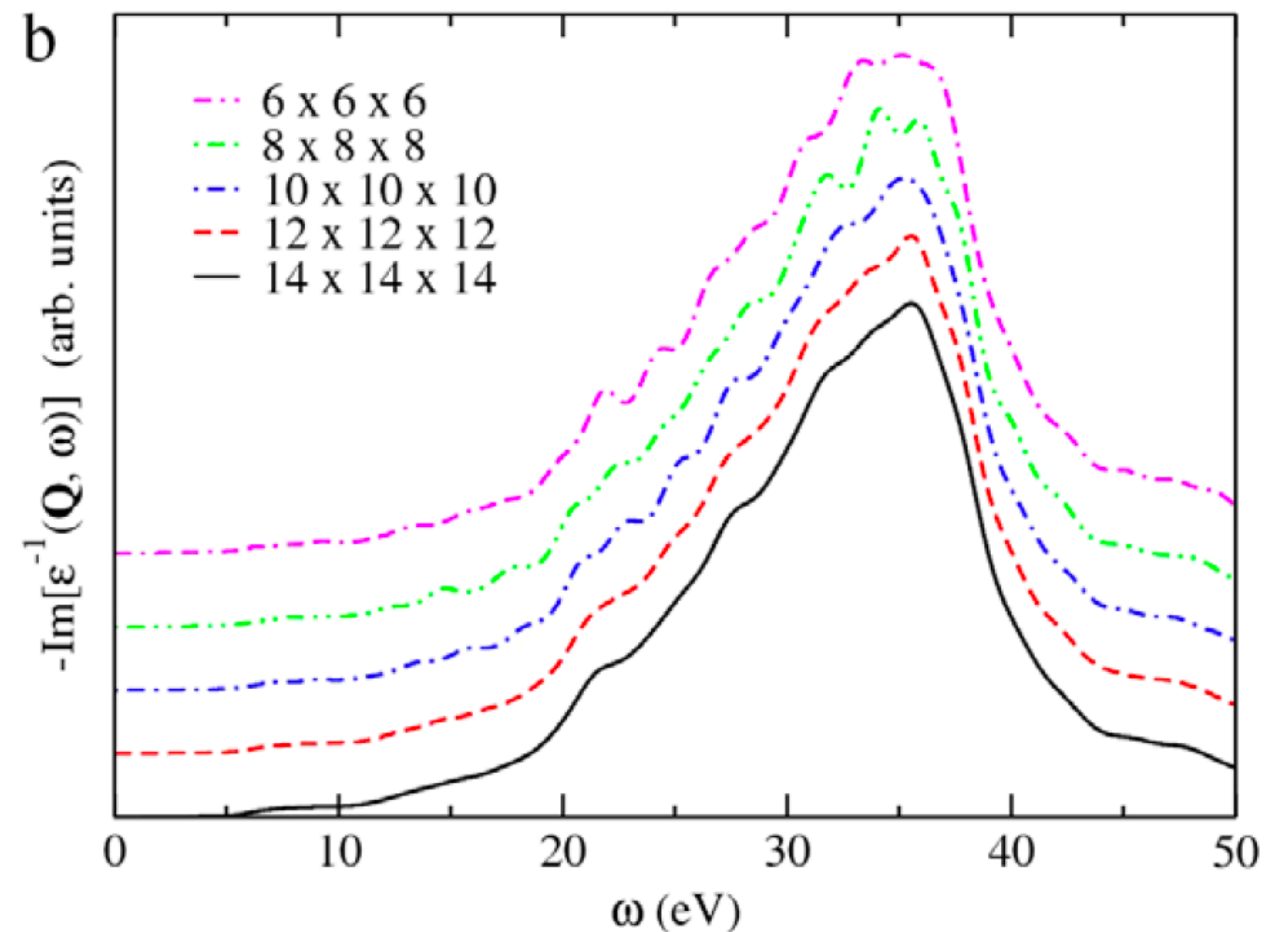


Loss function of bulk diamond

Convergence w.r.t. Lanczos iterations



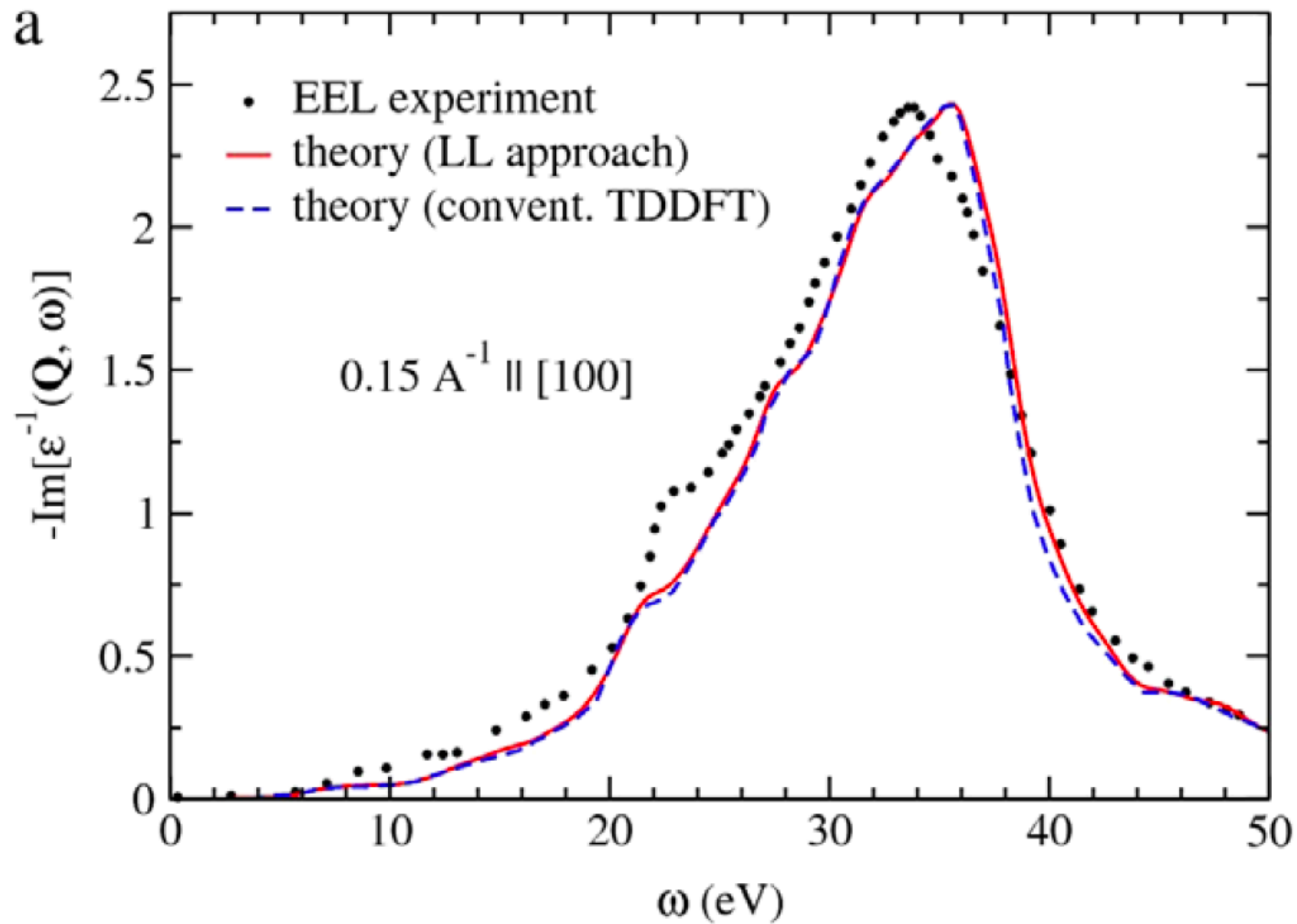
Convergence w.r.t. **k** points mesh



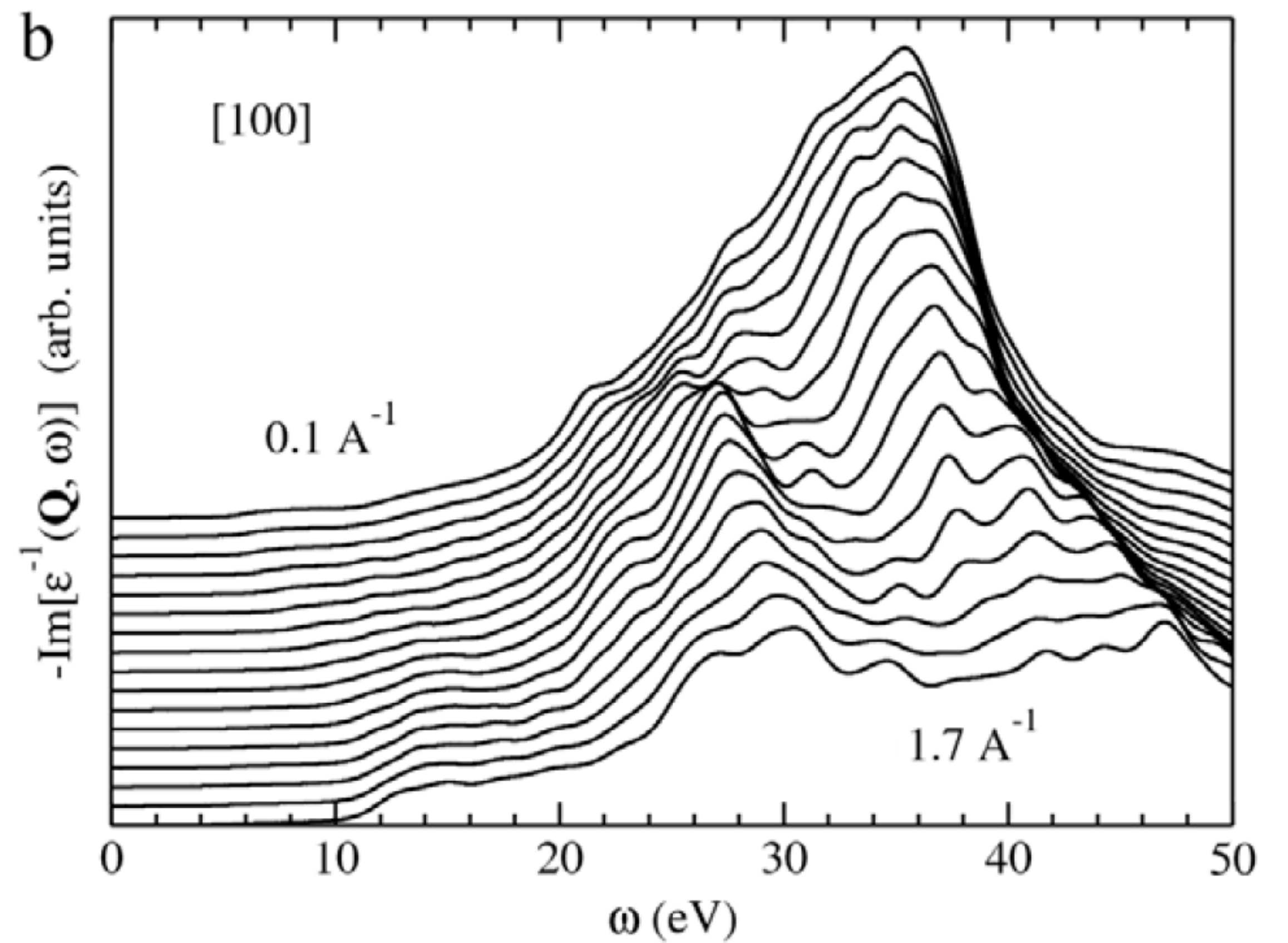
The loss function is computed for $q = 0.15 \text{ (\text{Å}^{-1})}$ along the $[100]$ direction

Loss function of bulk diamond

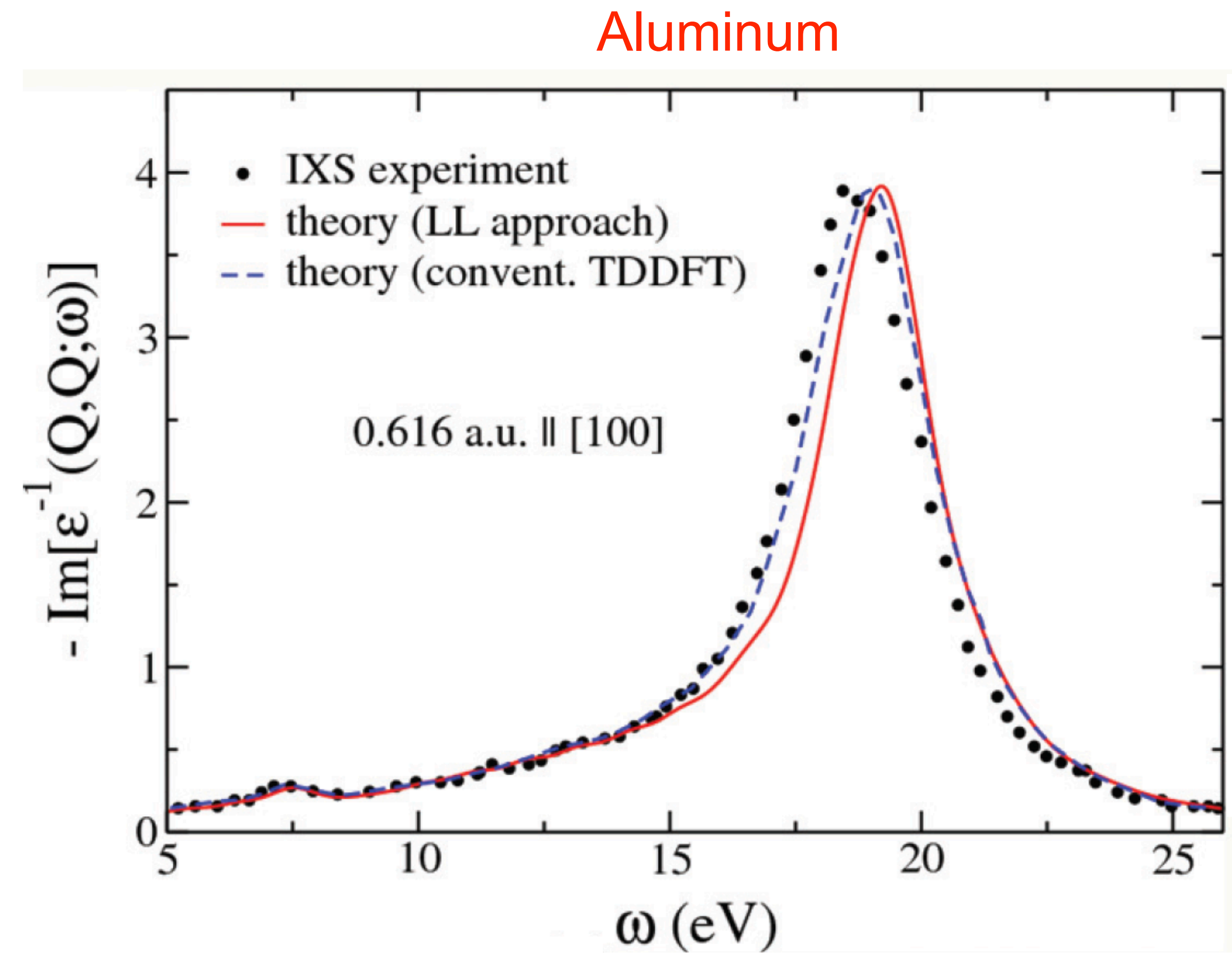
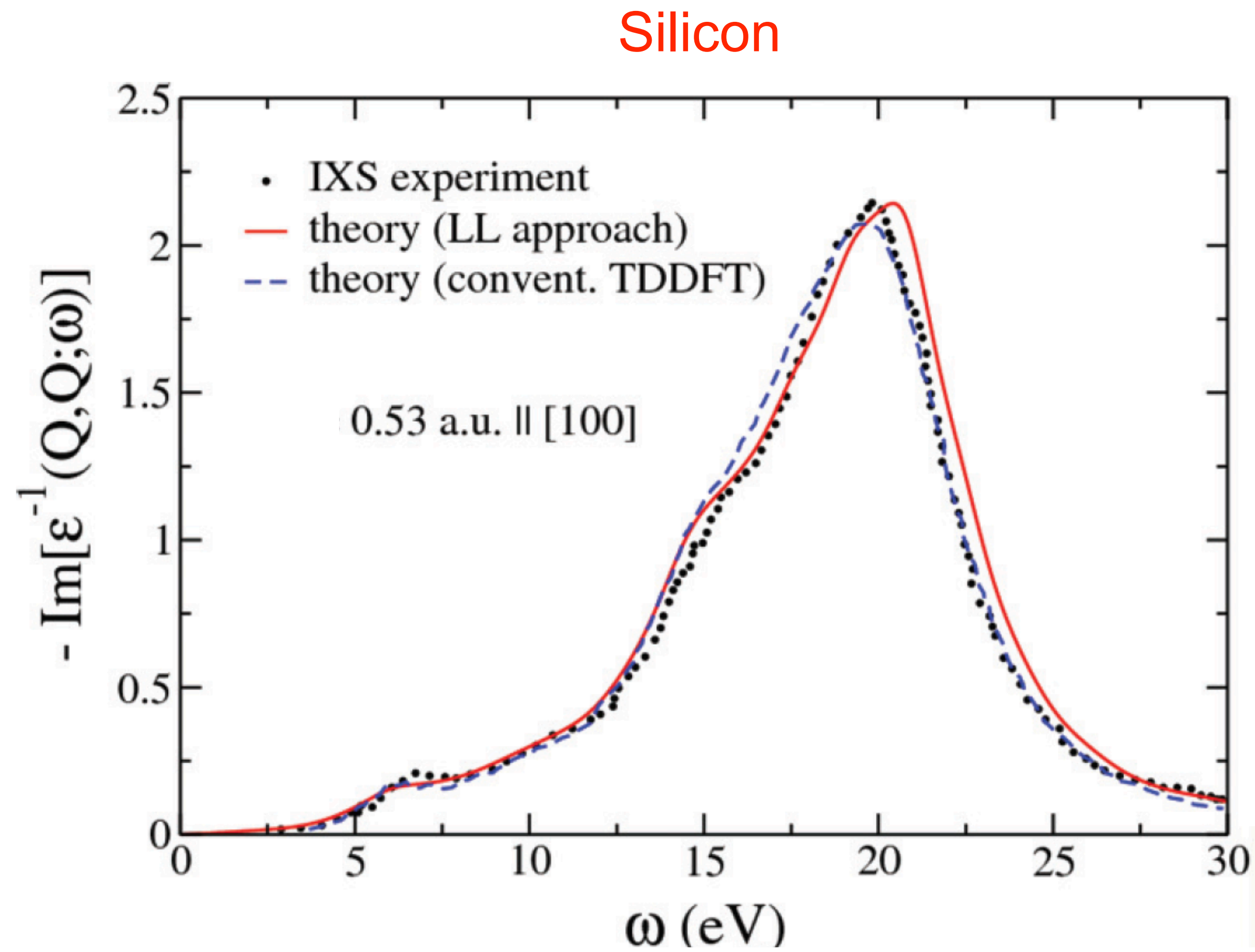
Comparison with experiment



Evolution as a function of \mathbf{q}

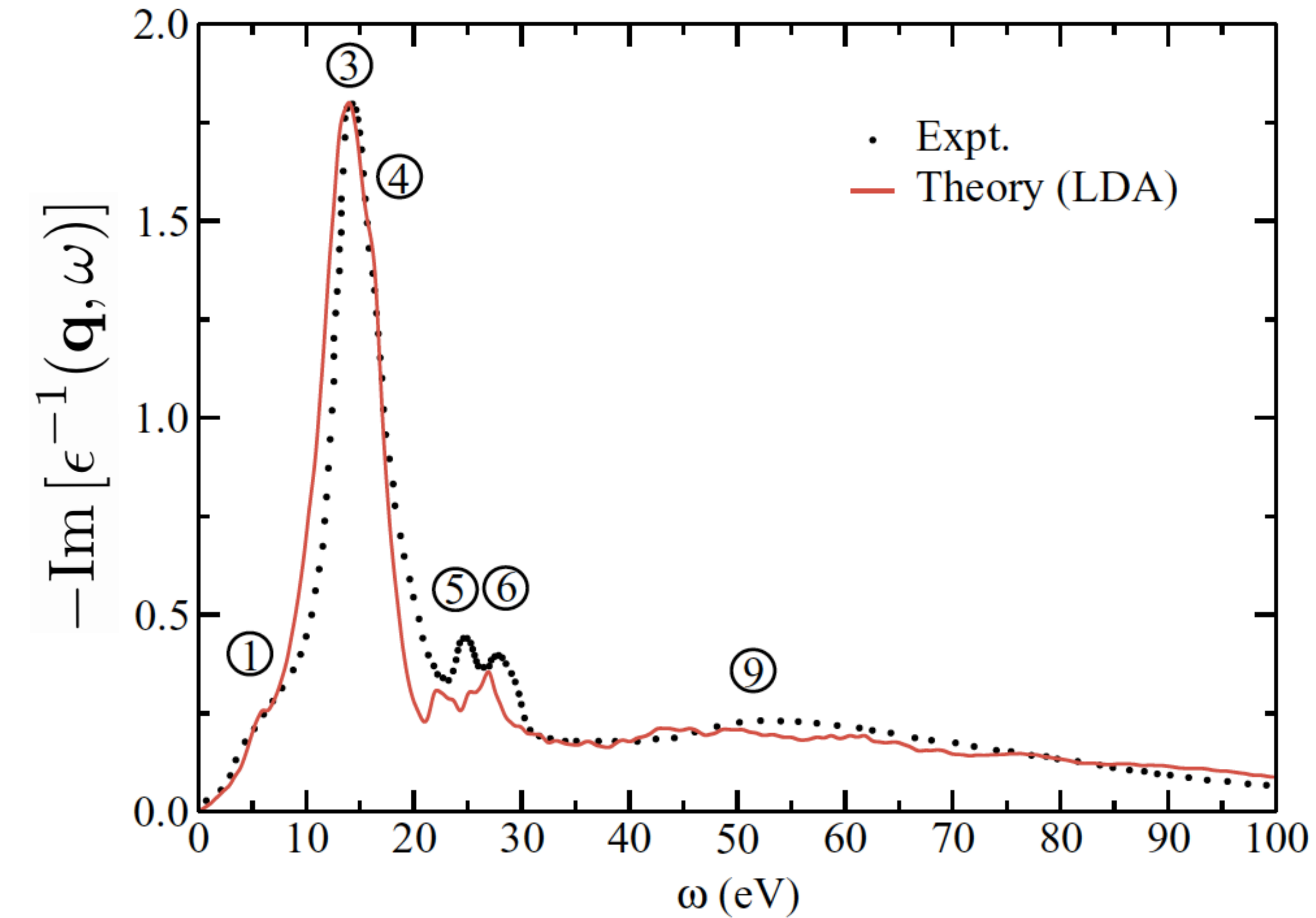


Loss function of bulk silicon and aluminum



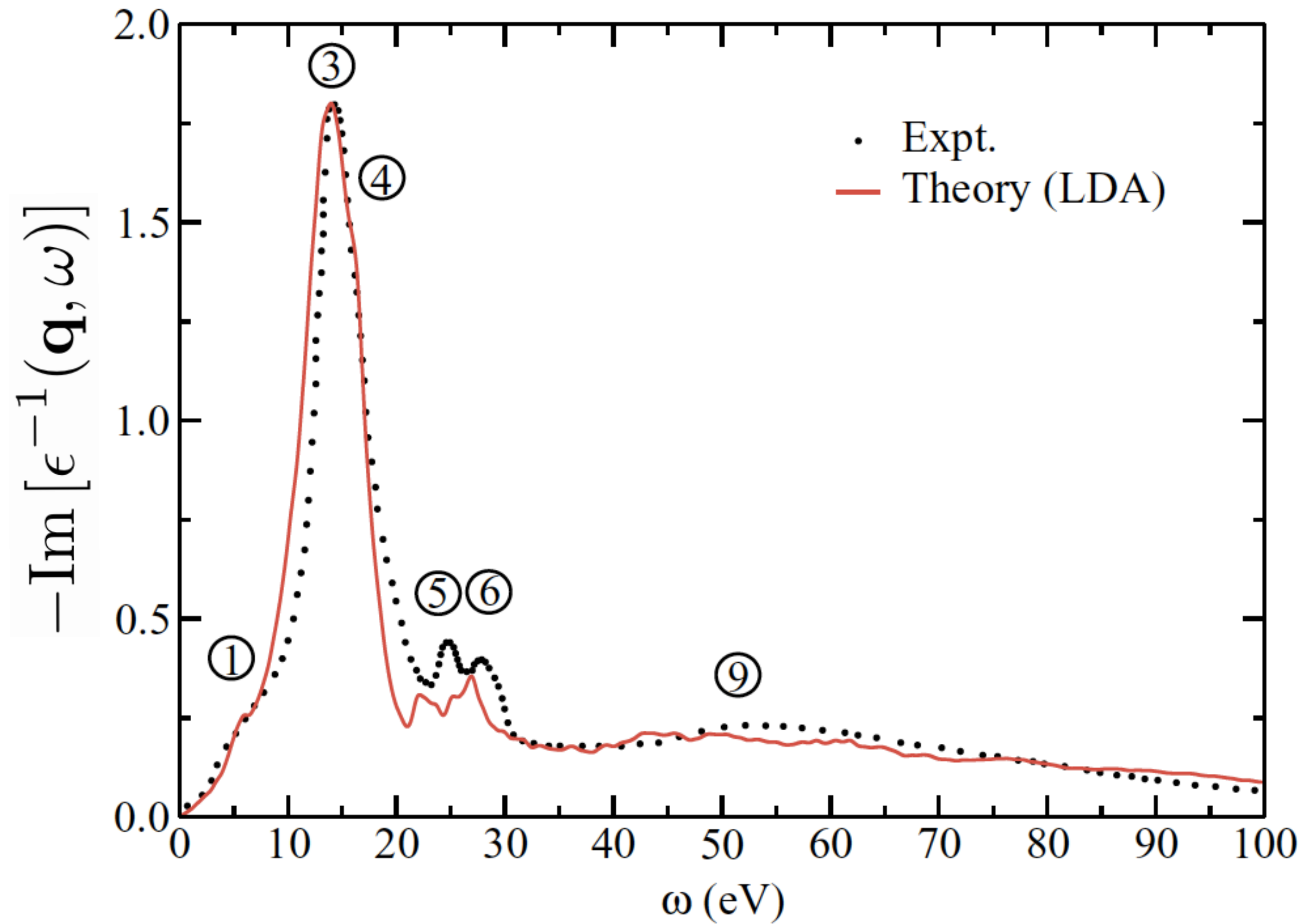
Loss function of bulk bismuth

EELS spectrum of bulk bismuth

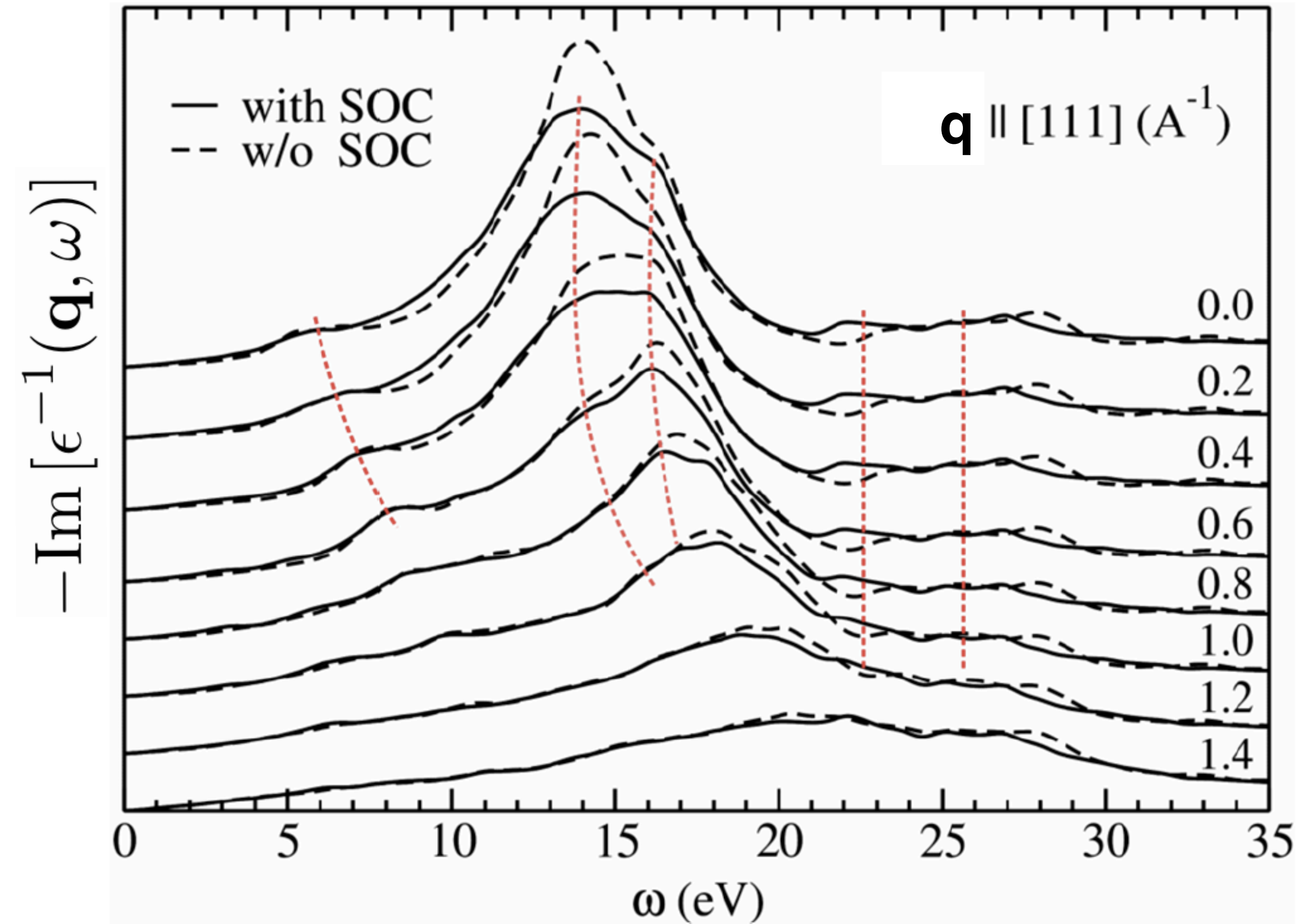


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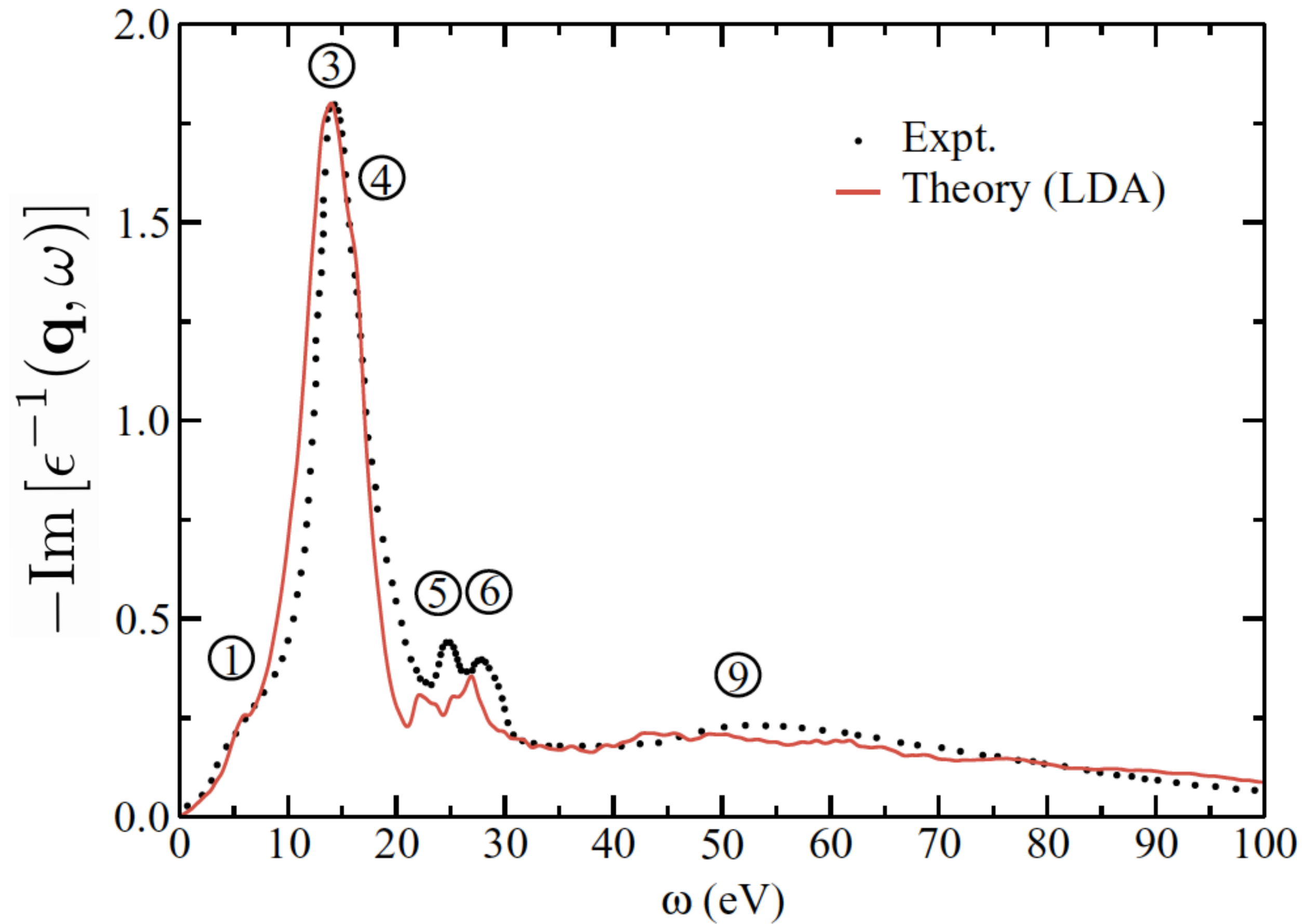


Peaks dispersion as a function of \mathbf{q}

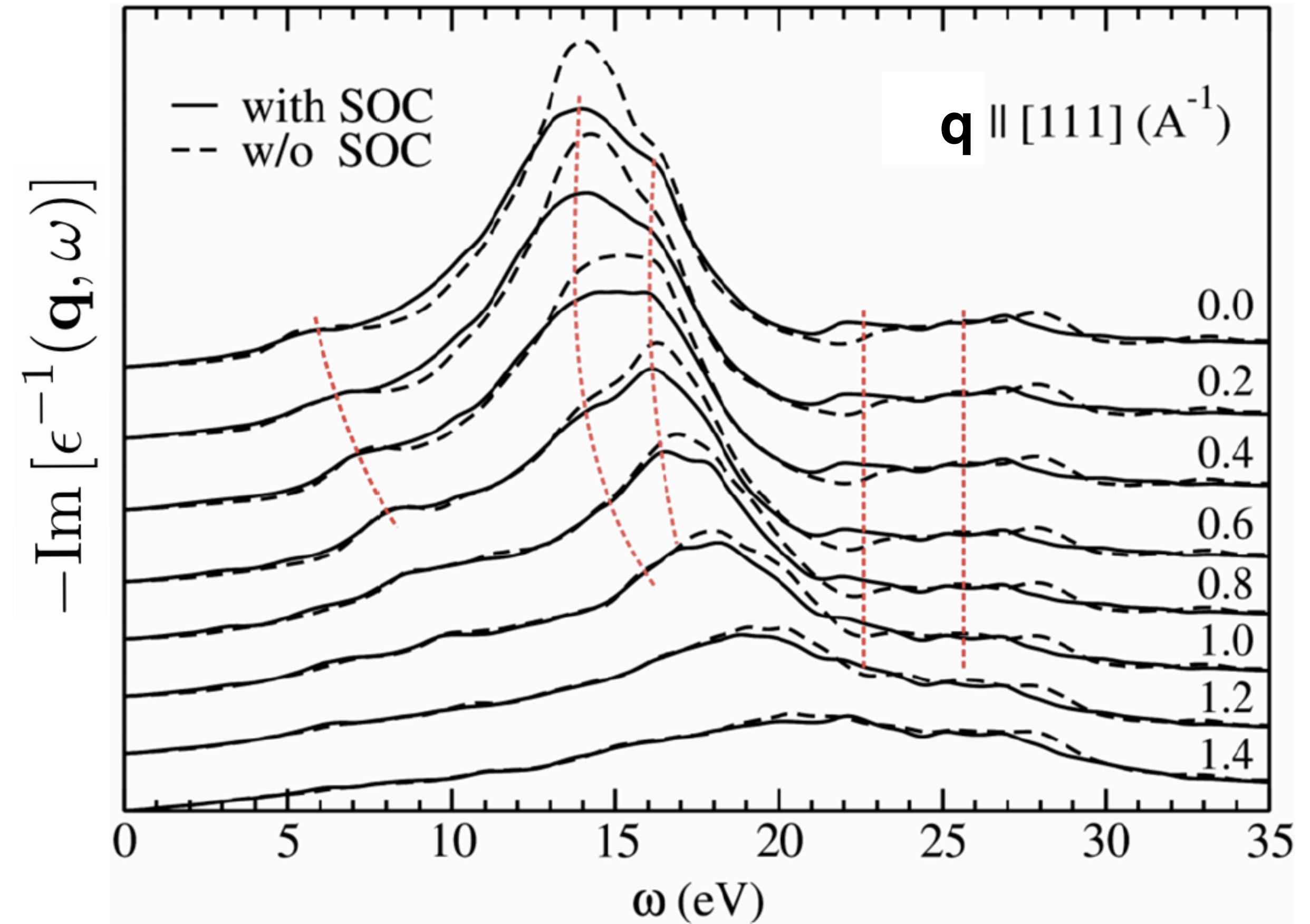


Loss function of bulk bismuth

EELS spectrum of bulk bismuth



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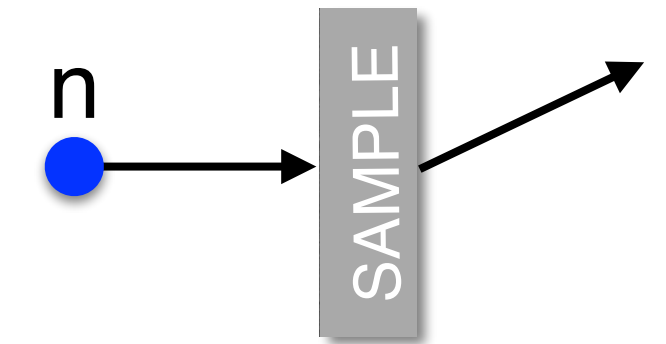


TDDFT@ALDA gives good results for EELS in solids! Limitation: excitons are not captured by ALDA.

Inelastic neutron scattering in solids

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

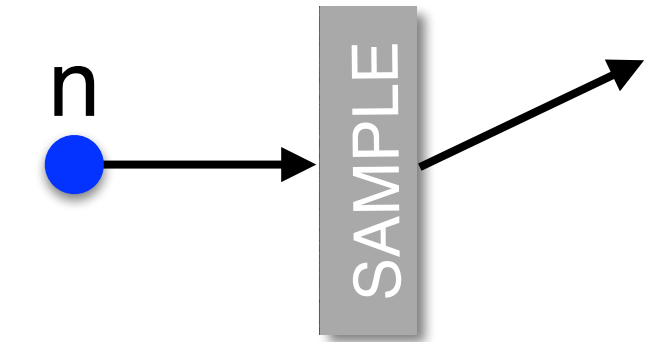
$$\tilde{V}'_{ext,\mathbf{q}}(\mathbf{r}, \omega) = -\mu_B \boldsymbol{\sigma} \cdot \mathbf{B}(\omega) e^{i\mathbf{q}\cdot\mathbf{r}}$$



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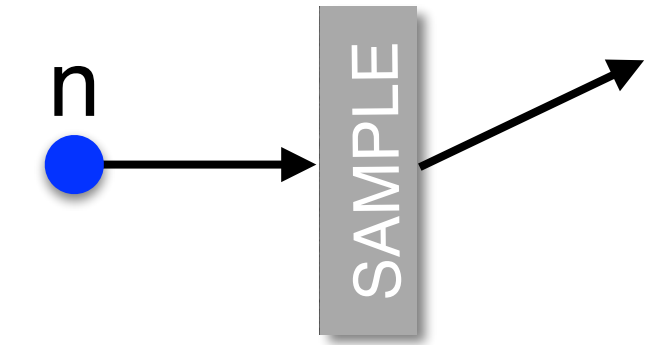
The magnetization-density susceptibility (spin-spin response function) reads:

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

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This allows us to compute the following quantity:

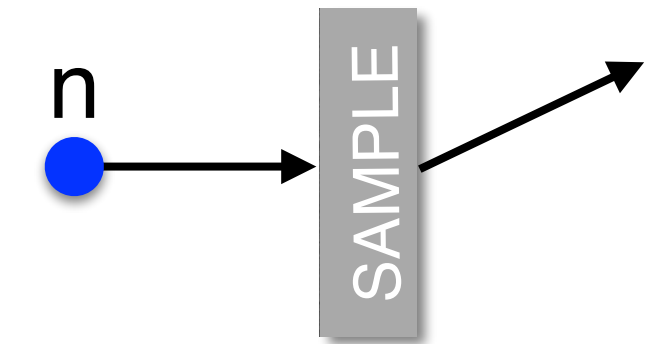
$$S(\mathbf{q}, \omega) = -\text{Im Tr} [\mathbf{P}(\mathbf{q}) \chi(\mathbf{q}, \omega)]$$

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

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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 is called turboMagnon.

turboMagnon code

Computer Physics Communications 280 (2022) 108500

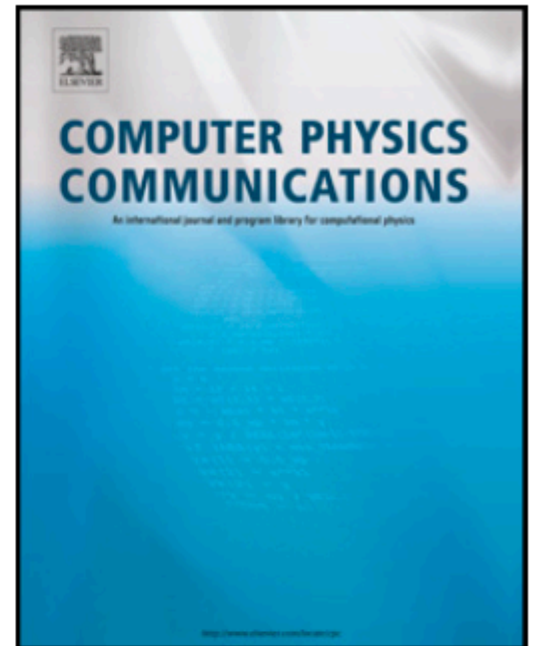


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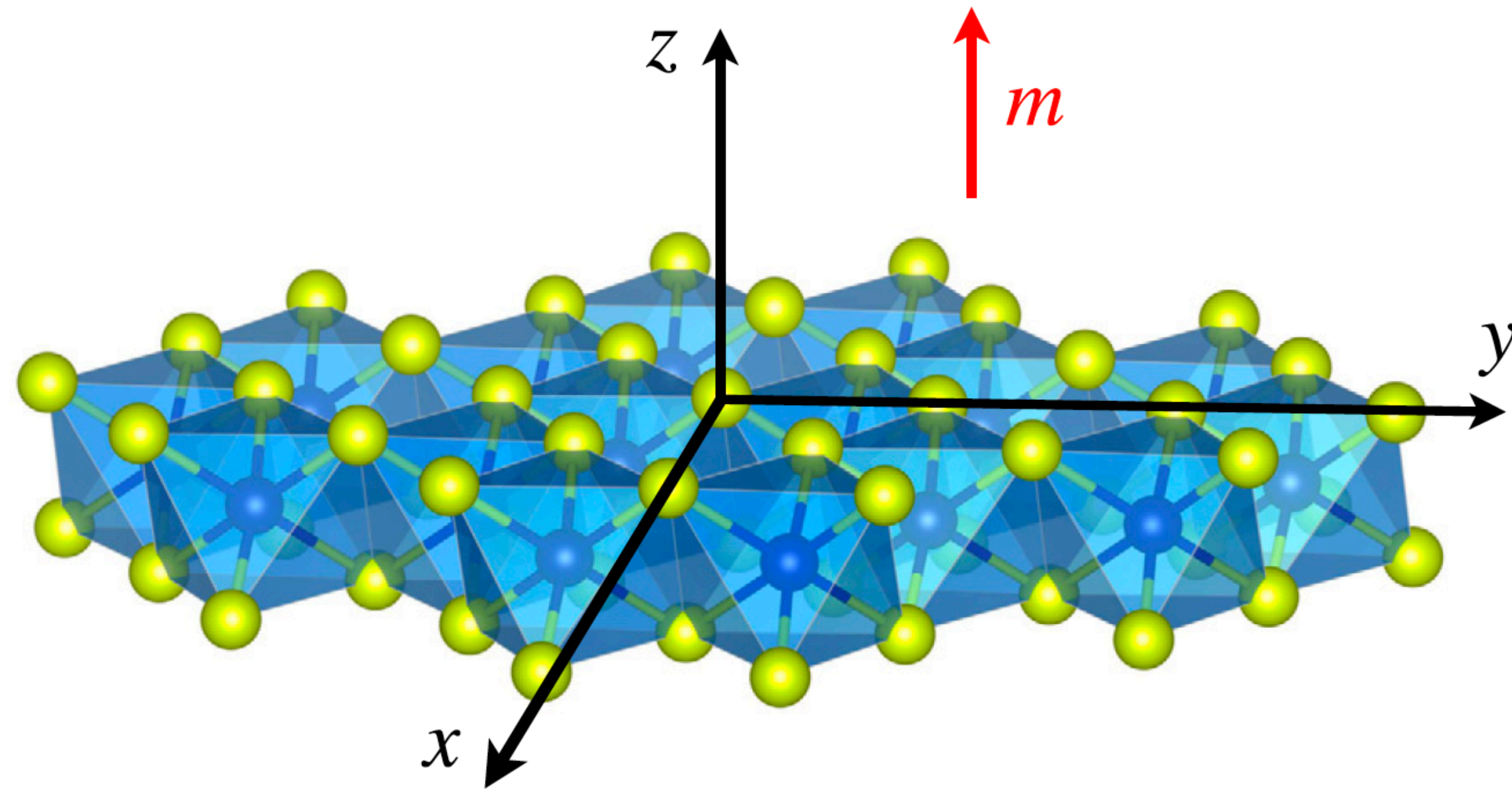


turboMagnon – A code for the simulation of spin-wave spectra using the Liouville-Lanczos approach to time-dependent density-functional perturbation theory ☆,☆☆

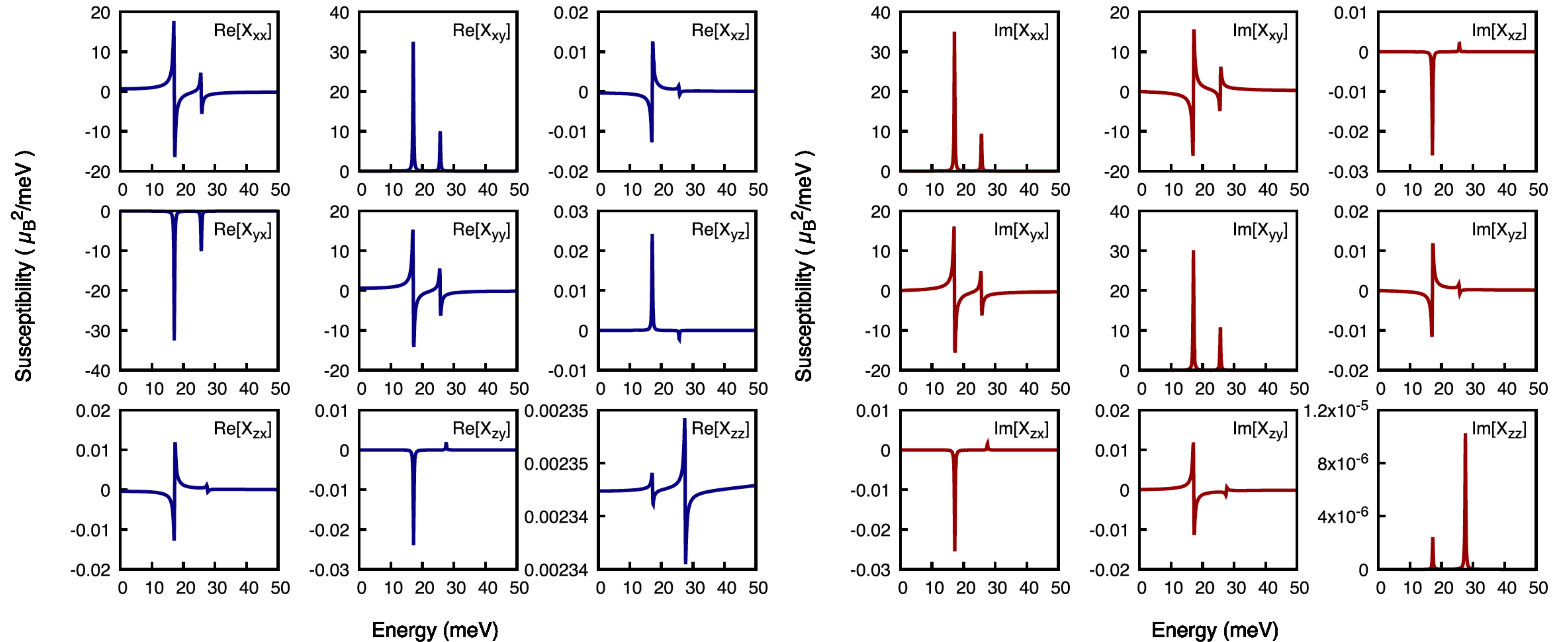


Tommaso Gorni^{a,*}, Oscar Baseggio^b, Pietro Delugas^b, Stefano Baroni^b, Iurii Timrov^{c,**}

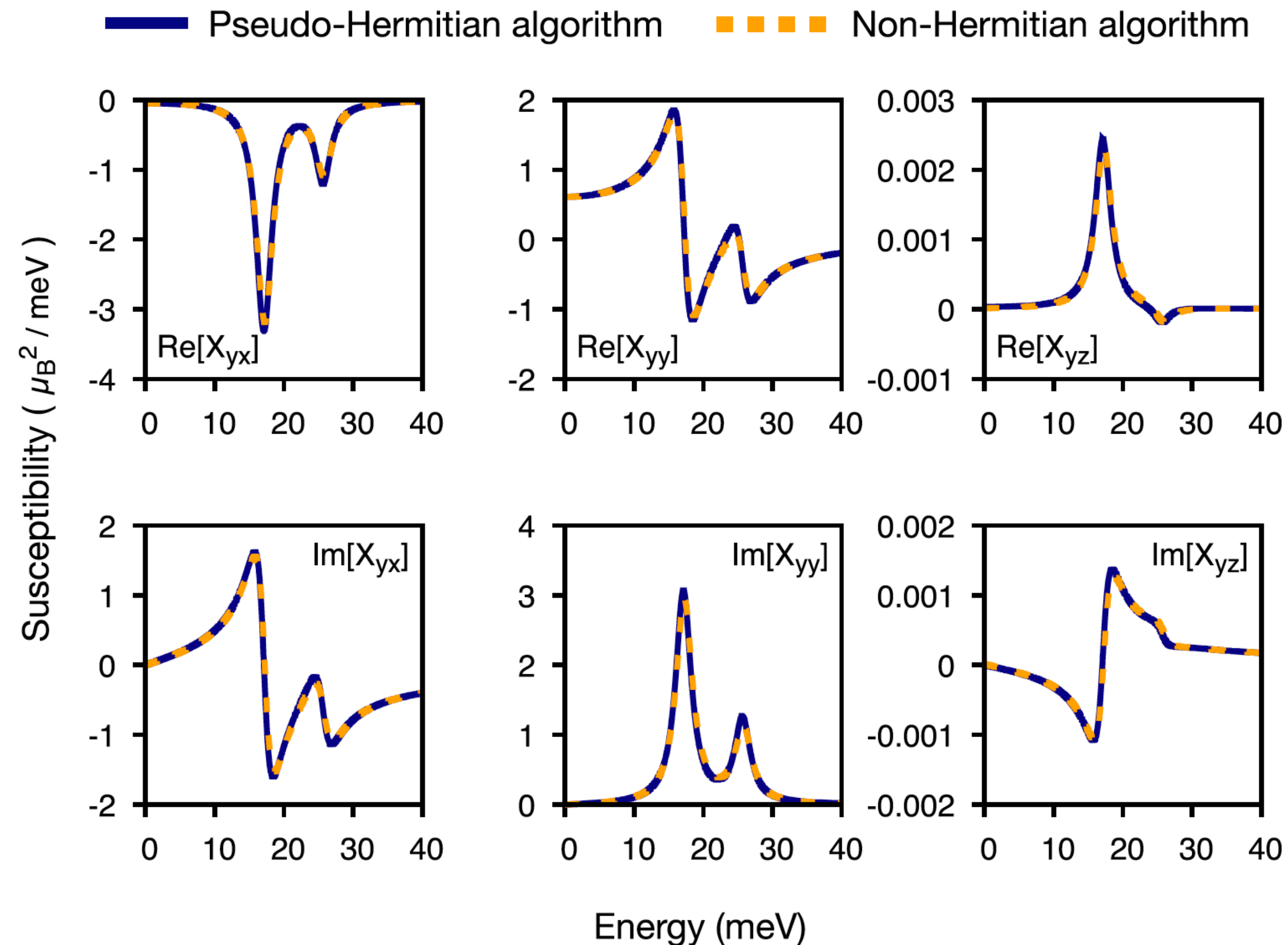
CrI_3 monolayer



Spin susceptibility matrix of a CrI₃ monolayer

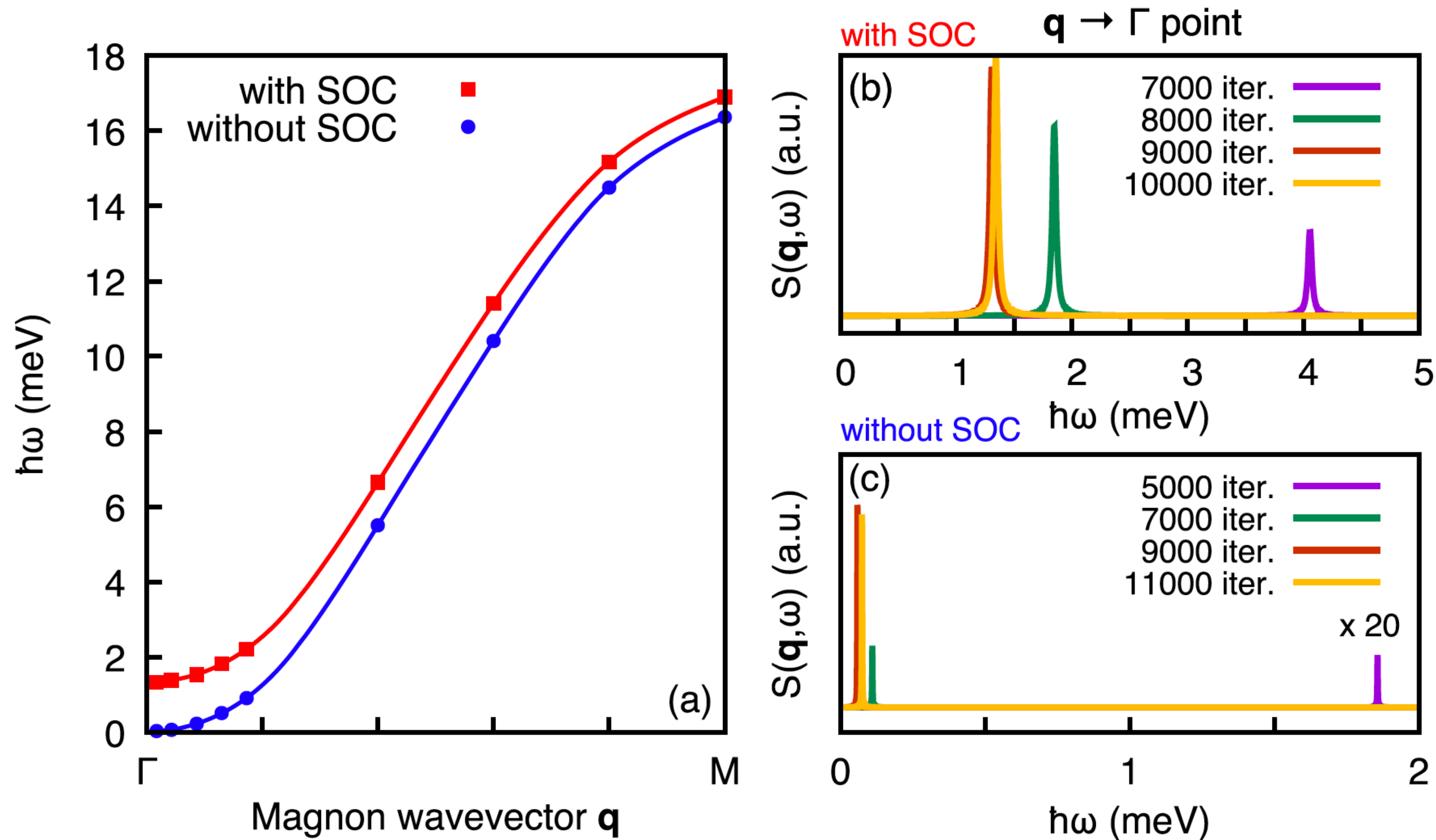


Pseudo-Hermitian vs Non-Hermitian Lanczos algorithms

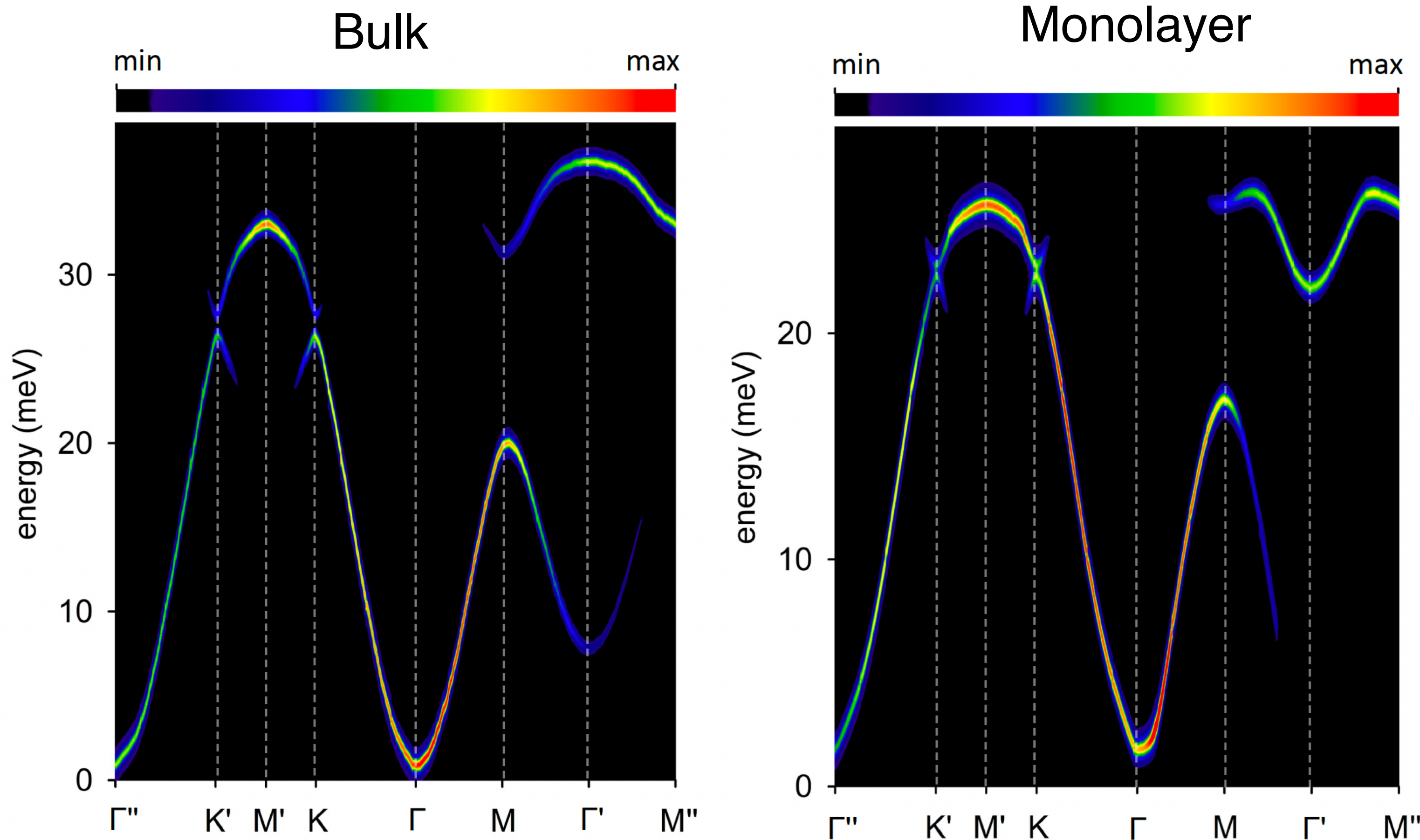


Pseudo-Hermitian algorithm is 2 times faster than then Non-Hermitian algorithm

Magnon dispersion of a CrI₃ monolayer



Magnon dispersion of CrI₃



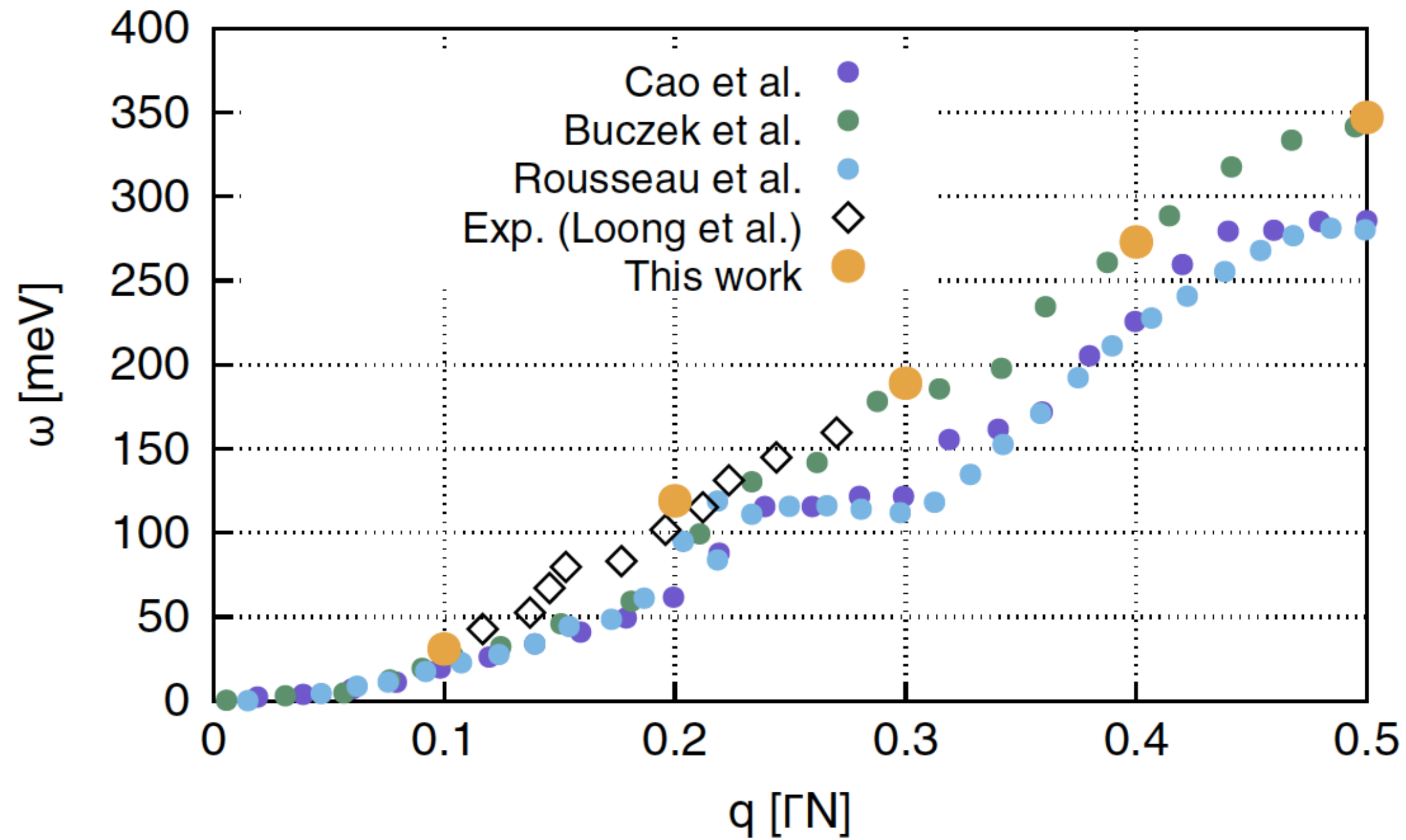
- Fully first-principles TDDFT calculations including spin-orbit coupling (no assumptions about Dzyaloshinskii–Moriya and Kitaev interactions)
- Explains the microscopic origin and shift of the magnon gap around the Dirac point K (it is due to spin-orbit coupling and interlayer exchange interactions)

T. Gorni, O. Baseggio, P. Delugas, I. Timrov, S. Baroni, PRB **107**, L220410 (2023).

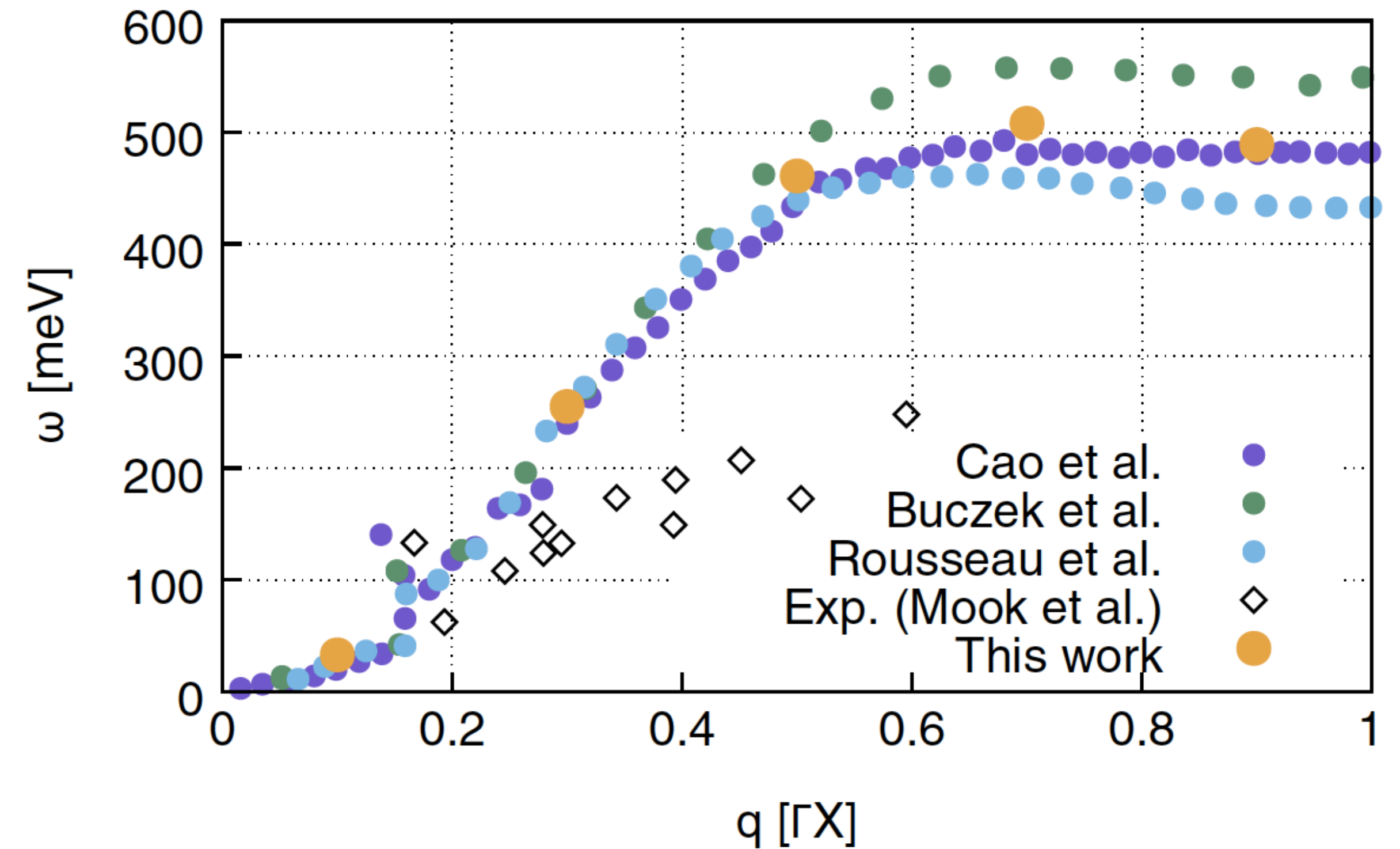
P. Delugas, O. Baseggio, I. Timrov, S. Baroni, T. Gorni, PRB **107**, 214452 (2023).

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.

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.