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THEOS

THEORY AND SIMULATION
OF MATERIALS

Time-dependent density functional (perturbation) theory:

optical absorption, electron energy loss, and inelastic neutron scattering spectroscopies

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Outline

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

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Time-dependent Schrödinger equation

As in the static case, let us consider the Born-Oppenheimer approximation, which assumes that the motion of electrons and nuclei can be separated.

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

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

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

The solution of the time-dependent Schrödinger equation for the many-electron system is even more complex than the solution of the static (time-independent) Schrödinger equation!

From wavefunction to charge density

By analogy to the static case, instead of considering the electronic wavefunction of $3N$+1 variables one 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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After the great success of static density-functional theory in the description of the many-body systems, Runge and Gross extended DFT to the time domain (i.e. TDDFT).

E. Runge and E.K.U Gross, “Density-functional theory for time-dependent systems”,
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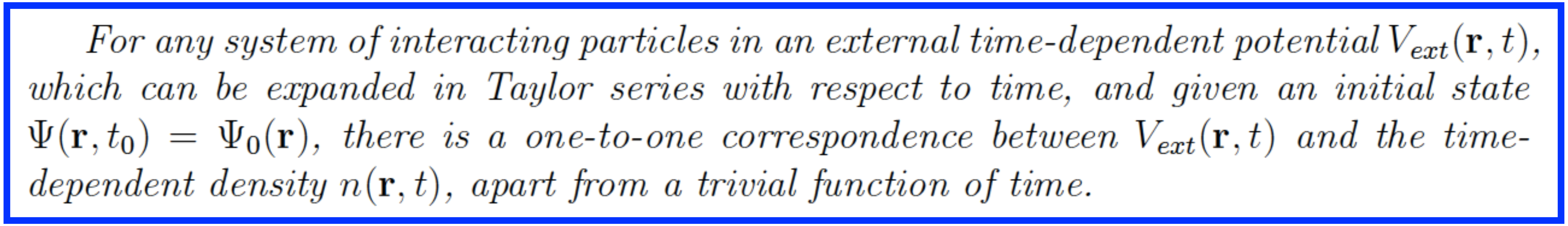
DFT: one-to-one mapping between static charge density and static external potential (minimization principle of the total energy).

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 Theorem I



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.*

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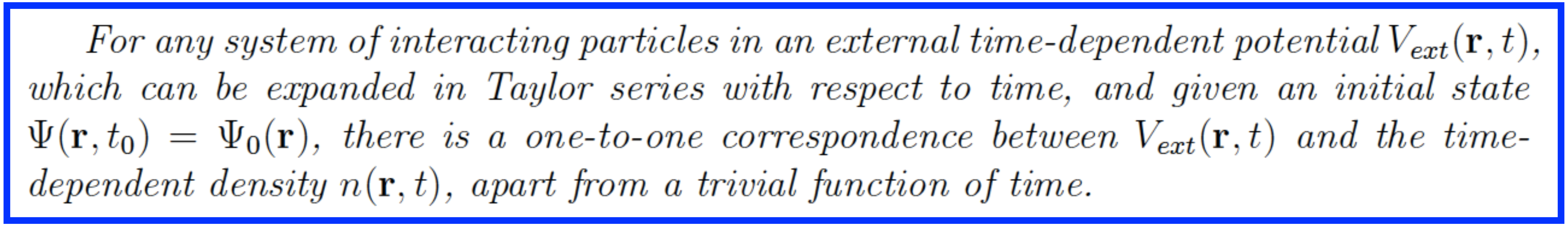

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Therefore, all observables can be regarded as functionals of the time-dependent charge density.

In contrast to static DFT, in TDDFT we need to set an initial condition, since the system follows an evolution in time and we need to know the starting point.

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In contrast to static DFT, in TDDFT we need to set an initial condition, since the system follows an evolution in time and we need to know the starting point.

In TDDFT the variational principle cannot be formulated in terms of the energy. Alternatively, there exists a quantity analogous to the energy - the quantum-mechanical action functional - which is dened in Theorem II.

Runge-Gross Theorem II

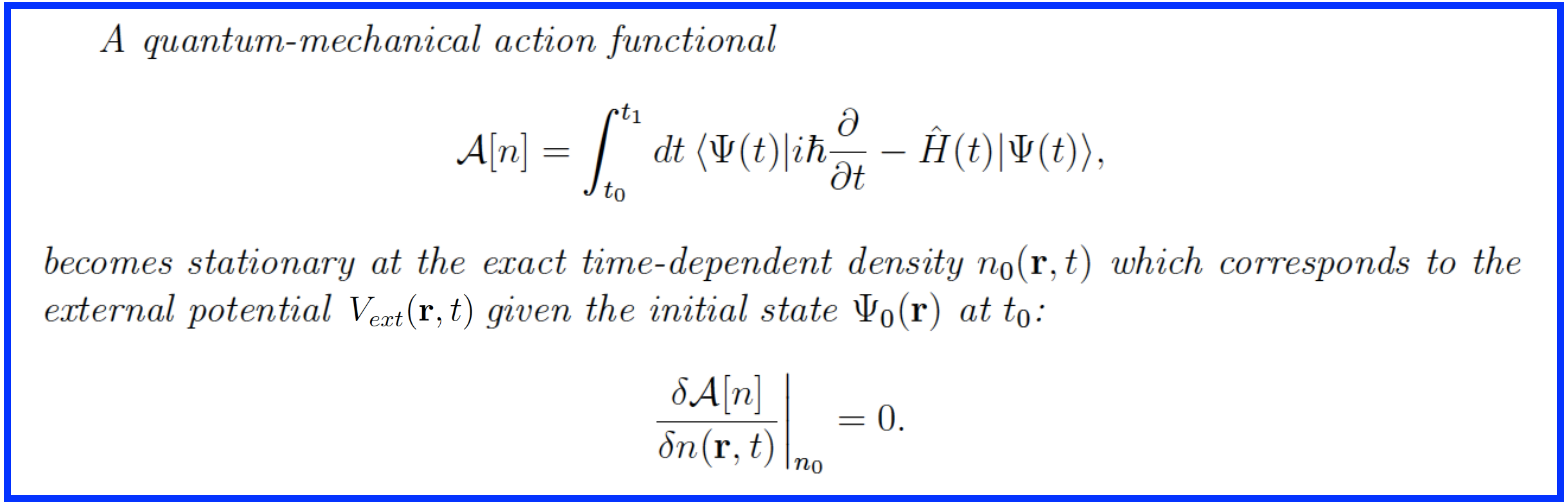
A quantum-mechanical action functional

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

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*:*

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

Runge-Gross Theorem II



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Theorem II means that it is possible to solve the time-dependent problem by searching for the stationary point of the action $\mathcal{A}$.

In contrast to the energy in the static case, the stationary point is not necessarily a minimum.

The value of the action itself does not provide any relevant additional information, since for the true density $\mathcal{A}[n_0] = 0$.

Quantum-mechanical action functional

In TDDFT the action functional $\mathcal{A}$ can be decomposed on the components, much in the same way as it is done for the energy functional of DFT:

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

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

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In order to approximate the unknown action functional $\mathcal{A}$, Gross and Kohn have introduced an auxiliary fictitious system of non-interacting particles that satisfy the time-dependent Kohn-Sham equations.

E.K.U Gross and W. Kohn, “Local density-functional theory of frequency-dependent linear response”, Phys. Rev. Lett. 55, 2850 (1985).

Time-dependent Kohn-Sham equations

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

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

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

The effective time-dependent Kohn-Sham potential $V_{KS}(\mathbf{r},t)$ has such a form that the time-dependent charge density of the non-interacting system equals to the time-dependent charge density of the real system of interacting electrons.

Adiabatic approximation

As in the static DFT, the time-dependent Kohn-Sham equations require a suitable approximation for the exchange-correlation (xc) potential in order to be applied in practice.

In the time-dependent case, the xc potential is time-dependent and depends on density $n(\mathbf{r}, t)$ at all past times, and thus it is absolutely nontrivial and even more difficult than in the static case to find an expression for it.

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The most popular choice is the adiabatic local-density approximation (ALDA) which is obtained by evaluating the standard LDA potential with the time-dependent density $n(\mathbf{r}, t)$:

$$V_{\mathrm{xc}}^{\mathrm{ALDA}}[n](\mathbf{r}, t) = V_{\mathrm{xc}}^{\mathrm{LDA}}(n(\mathbf{r}, t))$$

Limitations of ALDA: optical properties of solids, double excitations, charge-transfer excitations, ...

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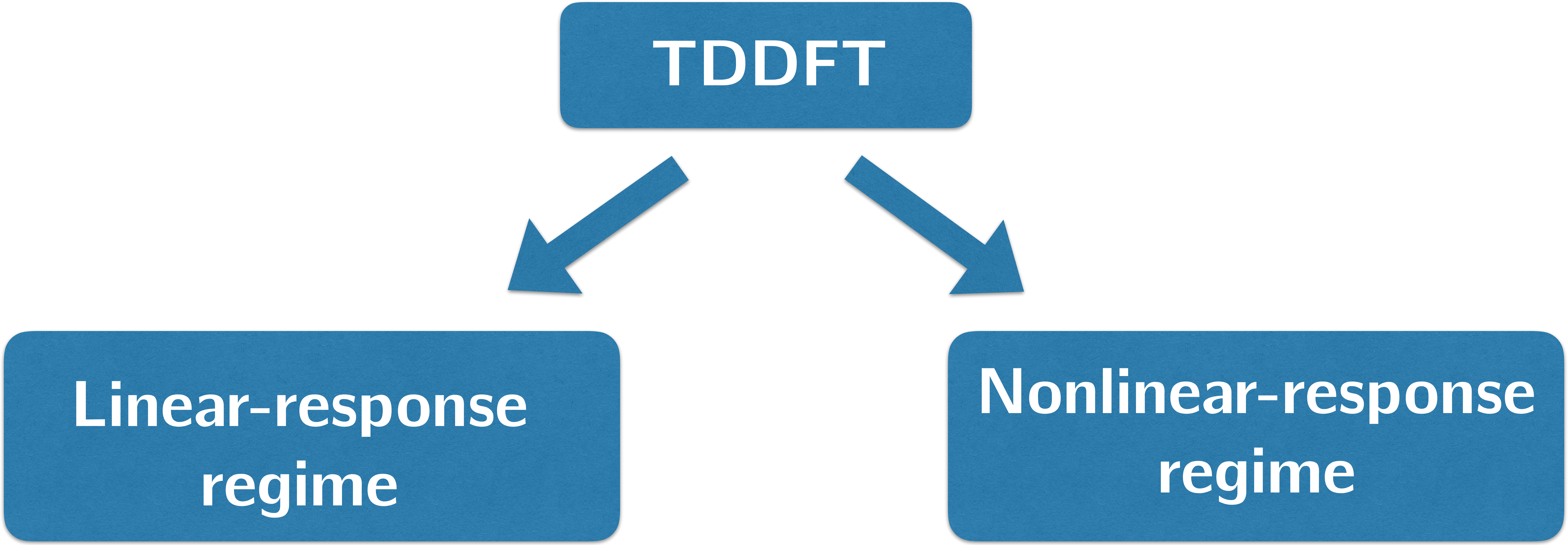
Linear vs nonlinear response regimes



TDDFT

Linear-response regime

Nonlinear-response regime

External perturbation is **weak**

(solve TDDFT equations in
the time or frequency domain)

External perturbation is **strong**

(solve TDDFT equations
in the time domain)

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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Susceptibility

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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 terms in the Taylor expansion, then this is linear-response TDDFT.

Different ways how to compute the susceptibility from TDDFPT

TDDFPT

Dyson method

Sternheimer method

Liouville-Lanczos method

Casida-Davidson method

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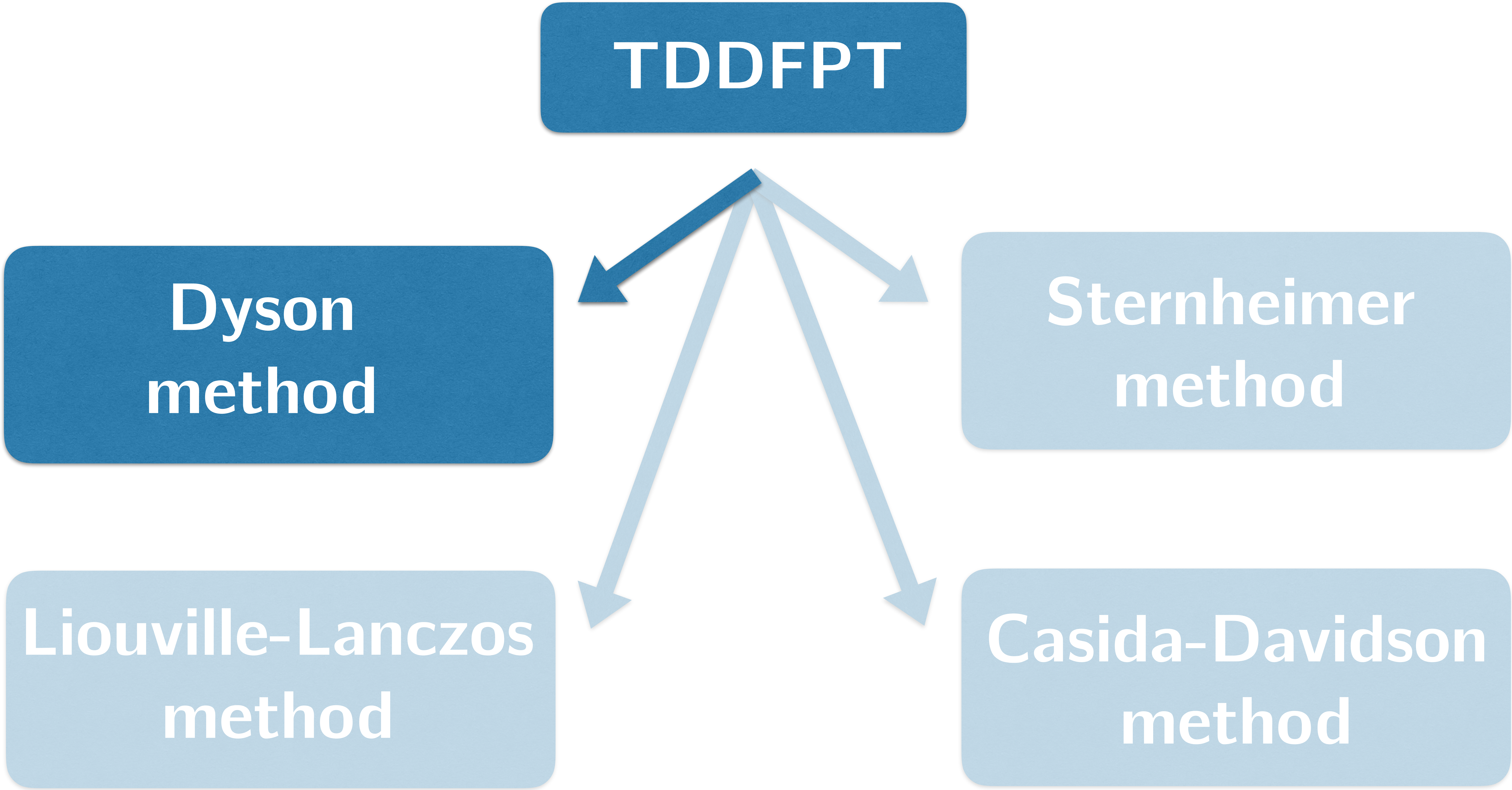

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Charge-density susceptibility: $\chi(\mathbf{r},\mathbf{r}',t-t') = \left.\dfrac{\delta n(\mathbf{r},t)}{\delta V_{ext}(\mathbf{r}',t')}\right|_{V_{ext}(\mathbf{r}',t')=V^0_{ext}(\mathbf{r}')}$

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Let us use the chain rule for functional derivatives:

$$\chi(\mathbf{r},\mathbf{r}',t-t') = \int_{-\infty}^{\infty} dt' \int d\mathbf{r}'' \, \frac{\delta n(\mathbf{r},t)}{\delta V_{KS}(\mathbf{r}'',t'')} \frac{\delta V_{KS}(\mathbf{r}'',t'')}{\delta V_{ext}(\mathbf{r}',t')}$$

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Exchange-correlation kernel: $$f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',t-t') \equiv \left.\frac{\delta V_{\mathrm{xc}}(\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\right|_{n(\mathbf{r}',t')=n^0(\mathbf{r}')}$$

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Dyson method

After gathering all terms together, and performing a Fourier transformation to the frequency domain, one obtains the final integral equation, which is called the Dyson-like screening equation:

$$\boxed{\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) + \int d\mathbf{r}'' \int d\mathbf{r}''' \, \chi^0(\mathbf{r},\mathbf{r}'',\omega) \left(\frac{e^2}{|\mathbf{r}''-\mathbf{r}'''|} + f_{\mathrm{xc}}(\mathbf{r}'',\mathbf{r}''',\omega) \right) \chi(\mathbf{r}''',\mathbf{r}',\omega)}$$

G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

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Independent-particle polarizability: $$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{i,j} (f_j - f_i) \frac{\varphi_i^0(\mathbf{r})\varphi_j^{0\,*}(\mathbf{r})\varphi_j^0(\mathbf{r}')\varphi_i^{0\,*}(\mathbf{r}')}{\hbar\omega - (\varepsilon_i - \varepsilon_j) + i\eta}$$

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Dyson method

After gathering all terms together, and performing a Fourier transformation to the frequency domain, one obtains the final integral equation, which is called the Dyson-like screening equation:

$$\boxed{\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) + \int d\mathbf{r}'' \int d\mathbf{r}''' \, \chi^0(\mathbf{r},\mathbf{r}'',\omega) \left(\frac{e^2}{|\mathbf{r}''-\mathbf{r}'''|} + f_{\text{xc}}(\mathbf{r}'',\mathbf{r}''',\omega) \right) \chi(\mathbf{r}''',\mathbf{r}',\omega)}$$

Independent-particle polarizability: $\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{i,j} (f_j - f_i) \frac{\varphi_i^0(\mathbf{r}) \varphi_j^{0\,*}(\mathbf{r}) \varphi_j^0(\mathbf{r}') \varphi_i^{0\,*}(\mathbf{r}')}{\hbar\omega - (\varepsilon_i - \varepsilon_j) + i\eta}$

Let us rewrite the Dyson-like equation in the reciprocal space. To this end, let us make use of the Fourier transformation from real space to reciprocal space:

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{\Omega} \sum_{\mathbf{q}}^{\text{BZ}} \sum_{\mathbf{G},\mathbf{G}'} e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} \, \chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) \, e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}$$

G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

Dyson method

The Dyson-like matrix equation in the reciprocal space:

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

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

$f^{\mathrm{xc}}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ is the Fourier transform of the exchange-correlation kernel

Dyson method

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Dyson method

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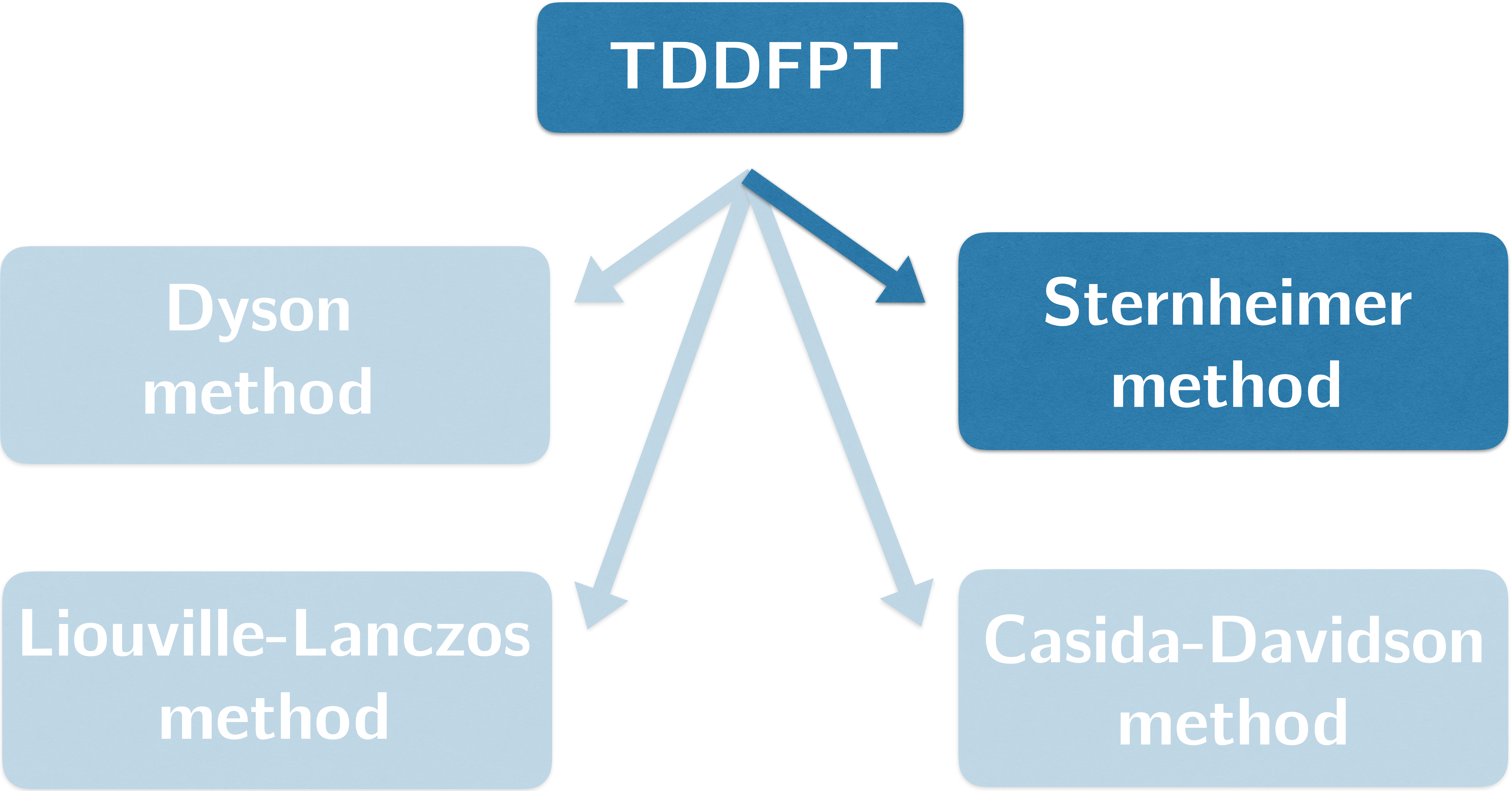
🙁 Sum over numerous empty states n' in the calculation of $\chi^0_{\mathbf{G},\mathbf{G}'}$

🙁 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

Different ways how to compute the susceptibility from TDDFPT



TDDFPT

Dyson method

Sternheimer method

Liouville-Lanczos method

Casida-Davidson method

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:

Sternheimer method

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$$H_{KS}(\mathbf{r},t) = -\frac{\hbar^2}{2m_0}\nabla^2 + V_{ext}(\mathbf{r},t) + V_{H\mathrm{xc}}(\mathbf{r},t)$$

Sternheimer method

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Sternheimer method

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

Sternheimer method

Therefore, we can rewrite the Kohn-Sham Hamiltonian as:

$$H_{KS}(\mathbf{r},t) = H^0(\mathbf{r}) + V'(\mathbf{r},t)$$

Sternheimer method

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$$V'(\mathbf{r},t) = V'_{ext}(\mathbf{r},t) + V'_{H\mathrm{xc}}(\mathbf{r},t)$$

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

Sternheimer method

Therefore, we can rewrite the Kohn-Sham Hamiltonian as:

$$H_{KS}(\mathbf{r},t) = H^0(\mathbf{r}) + V'(\mathbf{r},t)$$

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

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

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

Sternheimer method

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

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

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

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

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

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

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

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Sternheimer method

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

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

$$
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$$

SELF-CONSISTENT PROBLEM

⬇

Solved iteratively

Sternheimer method

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

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

Projector on empty states:

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

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

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

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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:

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SELF-CONSISTENT PROBLEM

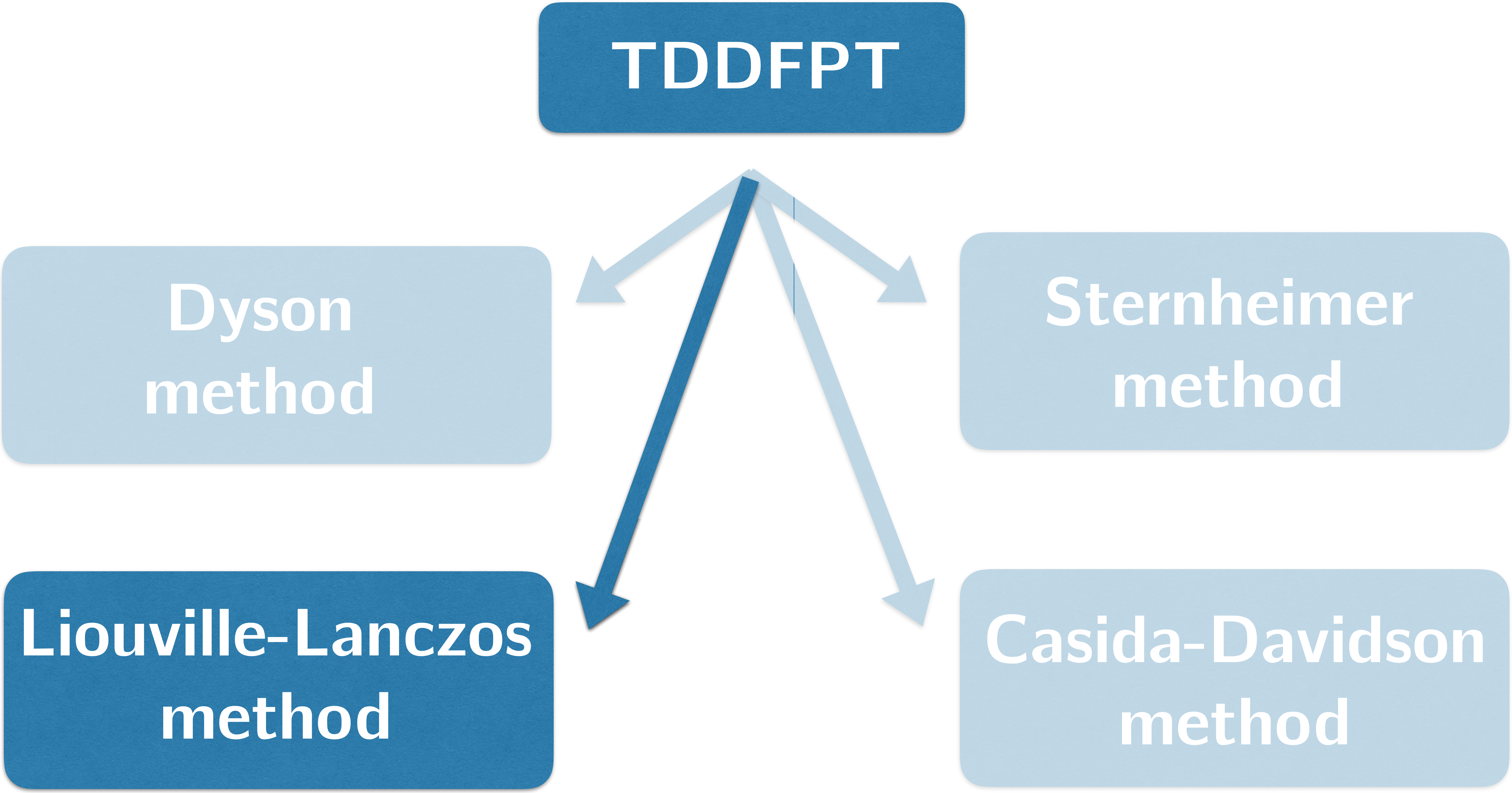
↓

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

Different ways how to compute the susceptibility from TDDFPT



TDDFPT

Dyson method

Sternheimer method

Liouville-Lanczos method

Casida-Davidson method

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).

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

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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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$$\rho(\mathbf{r},\mathbf{r}';t) = 2\sum_v \varphi_v(\mathbf{r},t)\,\varphi_v^*(\mathbf{r}',t)$$

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

Liouville-Lanczos method

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

$$\boxed{\begin{aligned} i\hbar\frac{\partial\hat{\rho}'(t)}{\partial t} &= \hat{\mathcal{L}}\cdot\hat{\rho}'(t) + [\hat{V}'_{ext}(t), \hat{\rho}^0] \\ \hat{\mathcal{L}}\cdot\hat{\rho}' &= [\hat{H}^0, \hat{\rho}'] + \left[V'_{Hxc}[\hat{\rho}'], \hat{\rho}^0\right] \end{aligned}}$$

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

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

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

$$\Downarrow$$

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

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

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

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

$$\Downarrow$$

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

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

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).

X. Ge, S.J. Binnie, D. Rocca, R. Gebauer, and S. Baroni, Comput. Phys. Comun. **185**, 2080 (2014).

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

O.B. Malcioglu, R. Gebauer, D. Rocca, and S. Baroni, Comput. Phys. Comun. **182**, 1744 (2011).
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Liouville-Lanczos method

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➡ Lanczos recursion
algorithm

Liouville-Lanczos method

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Let us define two two-component Lanczos vectors:

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Liouville-Lanczos method

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➡

Lanczos recursion chain:

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

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Liouville-Lanczos method

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Tridiagonal matrix:

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

Liouville-Lanczos method

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Susceptibility is computed in a postprocessing step:

$$\chi_A(\omega) = \langle \zeta^N | \left(\hbar\omega \hat{I}^N - \hat{T}^N \right)^{-1} \cdot e^N_1 \rangle$$

Liouville-Lanczos method

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

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

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 to speed up the convergence

Lanczos recursion chain:

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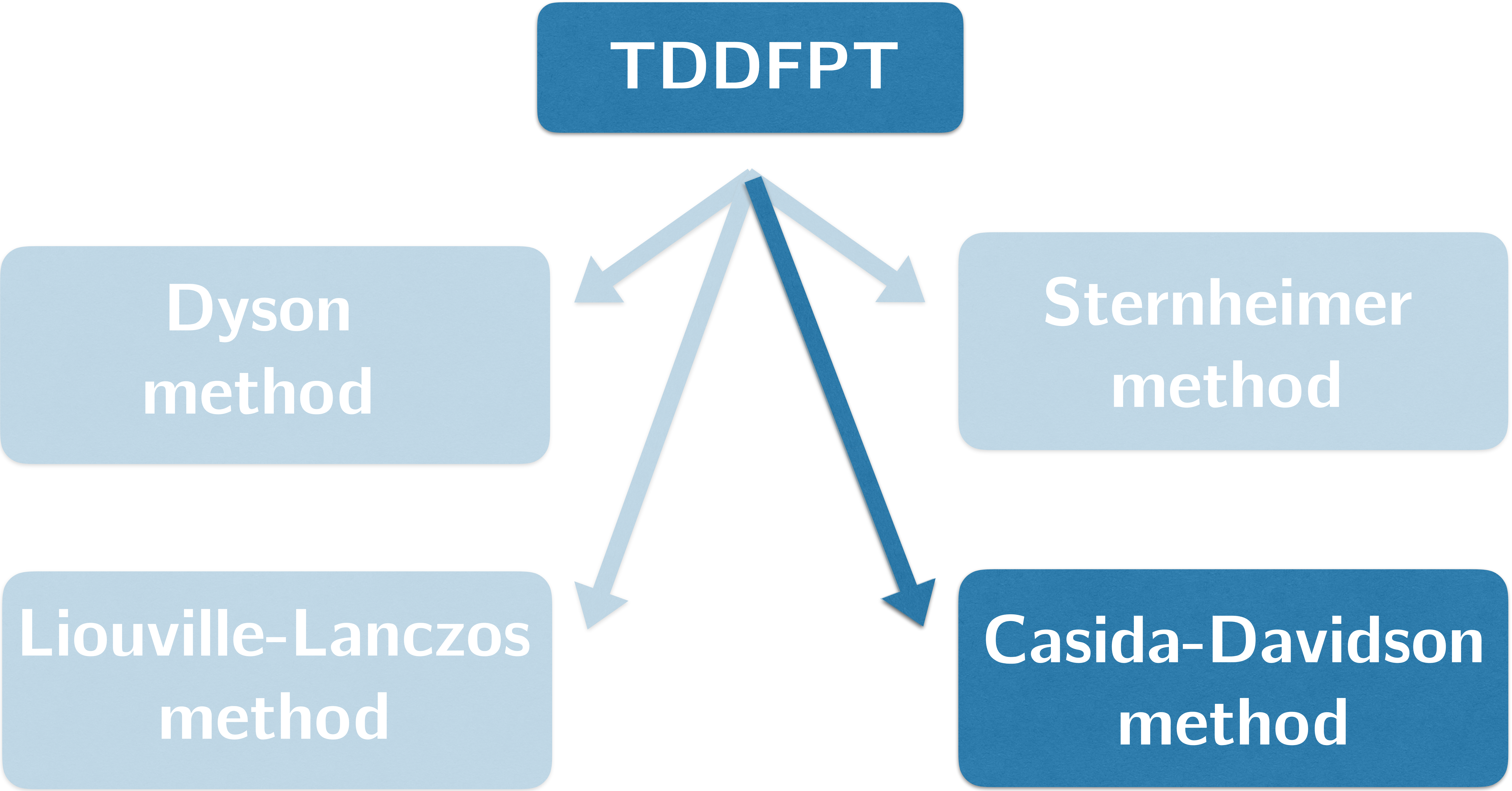
Different ways how to compute the susceptibility from TDDFPT



TDDFPT

Dyson method

Sternheimer method

Liouville-Lanczos method

Casida-Davidson method

Casida-Davidson method

Let us recall the equations from the Sternheimer method:

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

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

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Casida-Davidson method

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

Now let us rewrite these equations in the matrix form (Casida equations), and determine the eigenvalues of the matrix on the left-hand side (Liouvillian) using the Davidson-like diagonalization algorithm:

$$\boxed{\begin{pmatrix} 0 & \hat{\mathcal{D}} \\ \hat{\mathcal{D}} + 2\hat{\mathcal{K}} & 0 \end{pmatrix} \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{q} \\ \mathbf{p} \end{pmatrix}}$$

The eigenvalues of the Liouvillian correspond to the poles of the susceptibility.

🙂 This is the method of choise if one is interested in a few lowest-energy excitations in the system.

X. Ge, S.J. Binnie, D. Rocca, R. Gebauer, and S. Baroni, Comput. Phys. Comun. **185**, 2080 (2014).

Outline

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

Various spectroscopies from TDDFPT

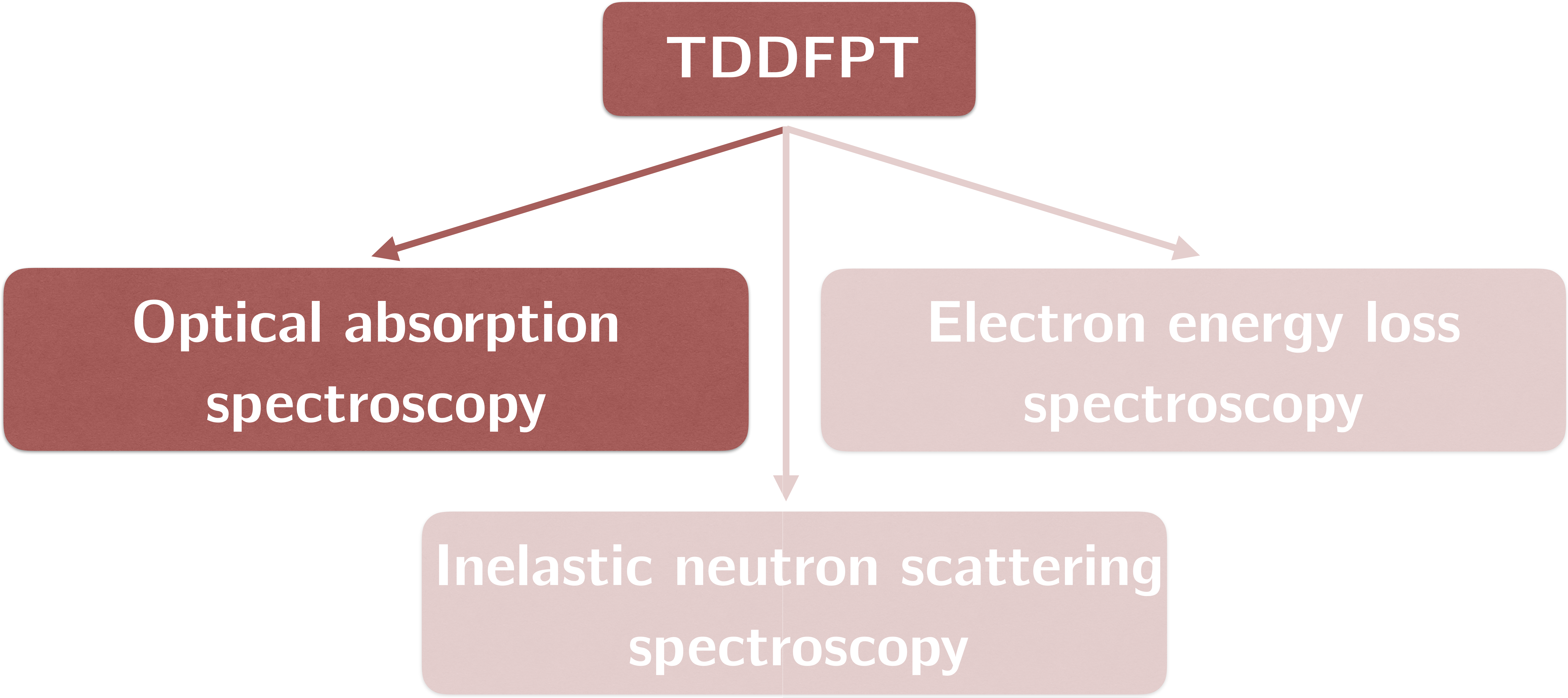
TDDFPT

Optical absorption spectroscopy

Electron energy loss spectroscopy

Inelastic neutron scattering spectroscopy

Various spectroscopies from TDDFPT



TDDFPT

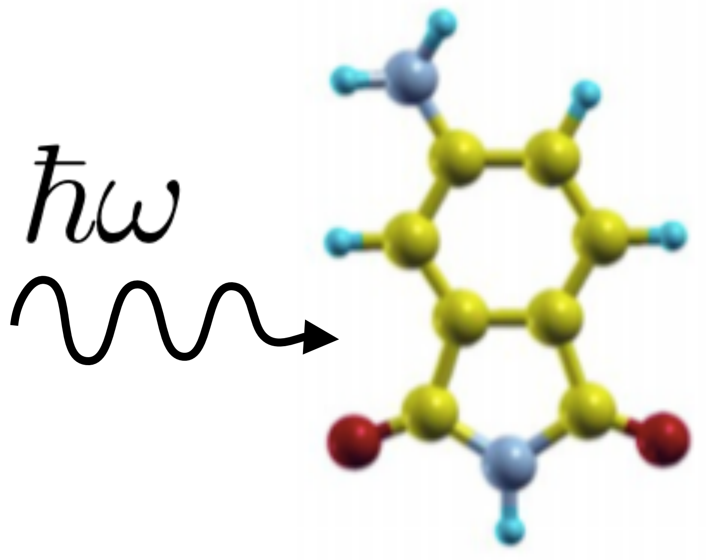
Optical absorption spectroscopy

Electron energy loss spectroscopy

Inelastic neutron scattering spectroscopy

Optical absorption in molecules

Let us consider an external perturbation which is a homogeneous electric field:



$$\tilde{V}'_{ext}(\mathbf{r},\omega) = -e\,\mathbf{E}(\omega)\cdot\mathbf{r}$$

Optical absorption in molecules

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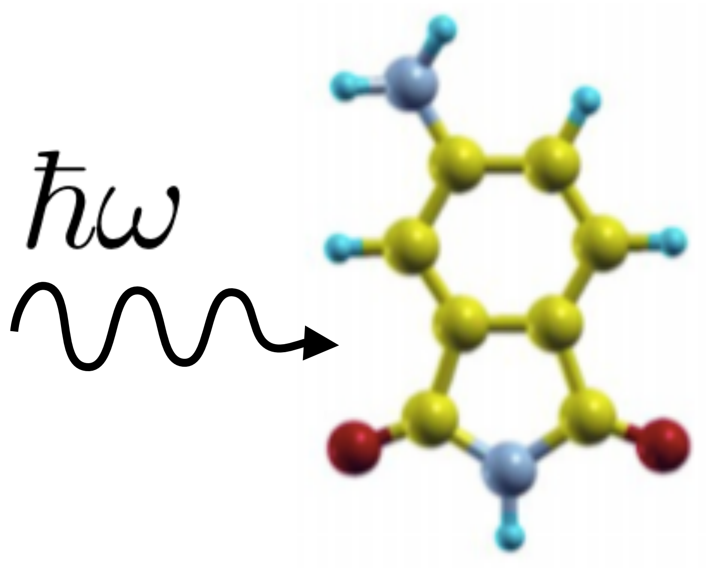
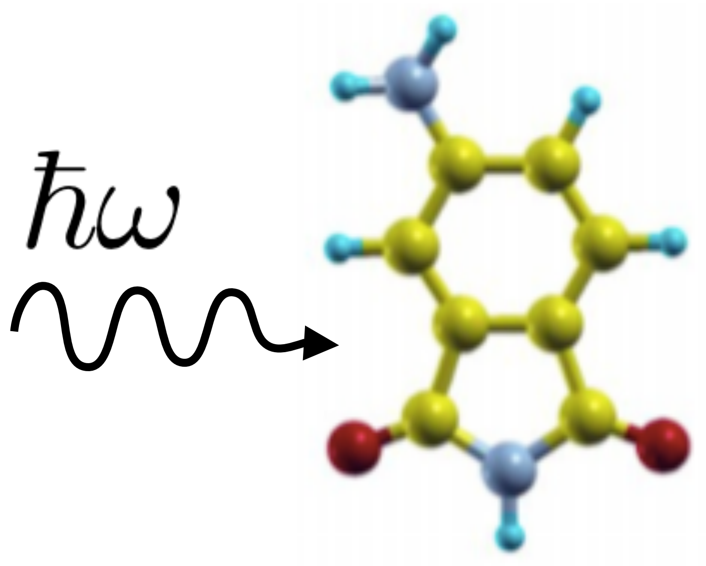


$$\tilde{V}'_{ext}(\mathbf{r},\omega) = -e\,\mathbf{E}(\omega)\cdot\mathbf{r}$$

This external perturbation linearly induces a dipole:

$$\mathbf{d}(\omega) = \mathrm{Tr}\,[\hat{\mathbf{r}}\,\hat{\rho}'(\omega)] = \langle\,\hat{\mathbf{r}}|(\hbar\omega - \hat{\mathcal{L}})^{-1}\cdot[\hat{\tilde{V}}'_{ext}(\omega),\hat{\rho}^0]\rangle$$

Optical absorption in molecules



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We can rewrite the expression above by defining the dynamical polarizability tensor of the dipole:

$$d_i(\omega) = \sum_j \alpha_{ij}(\omega)E_j(\omega)$$

$$\boxed{\alpha_{ij}(\omega) = -e\,\langle\hat{r}_i|(\hbar\omega - \hat{\mathcal{L}})^{-1}\cdot[\hat{r}_j,\hat{\rho}^0]\rangle}$$

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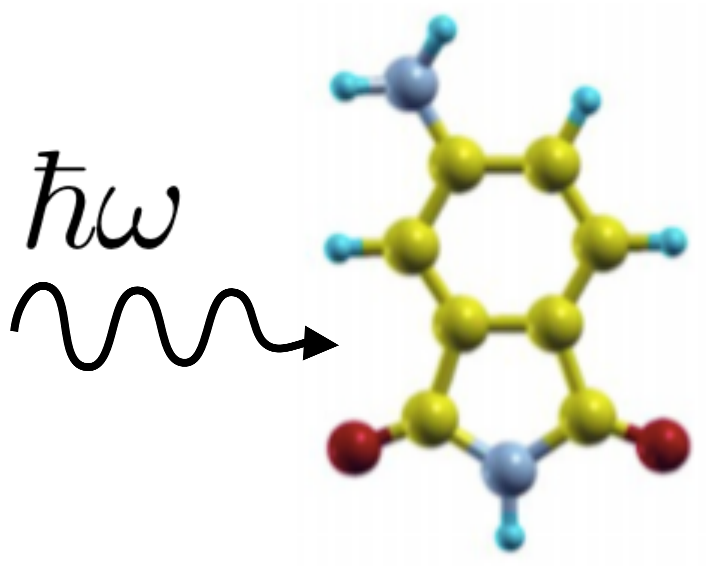

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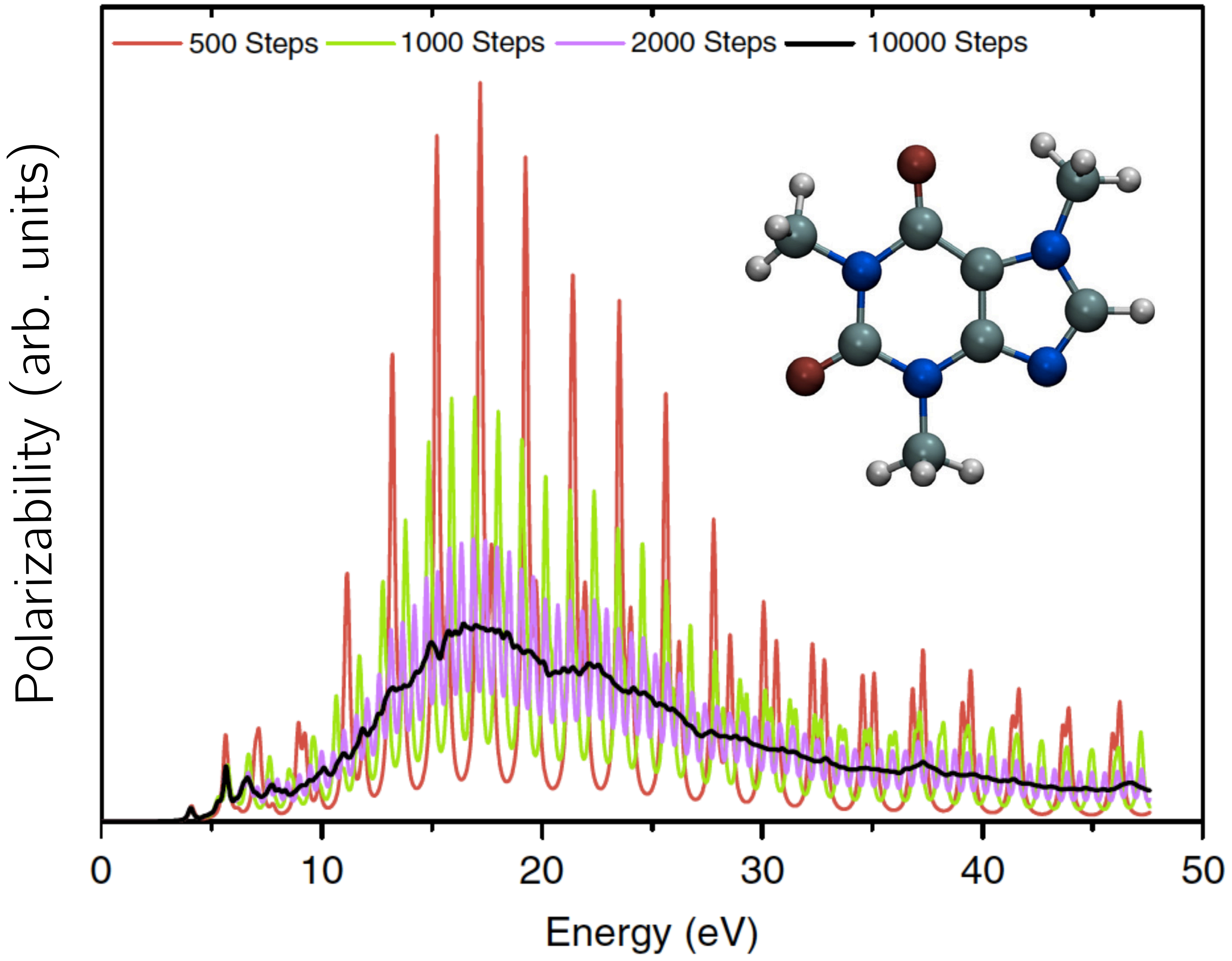
Polarizability tensor: **Liouville-Lanczos** (turbo_lanczos.x) or **Casida-Davidson** (turbo_davidson.x)

Absorption spectra of molecules in vacuum (ALDA)

Absorption in a caffeine molecule
from Liouville-Lanczos



S. Baroni *et al.*, J. Phys.: Condens. Matter **22**, 074204 (2010).

Absorption spectra of molecules in vacuum (ALDA)

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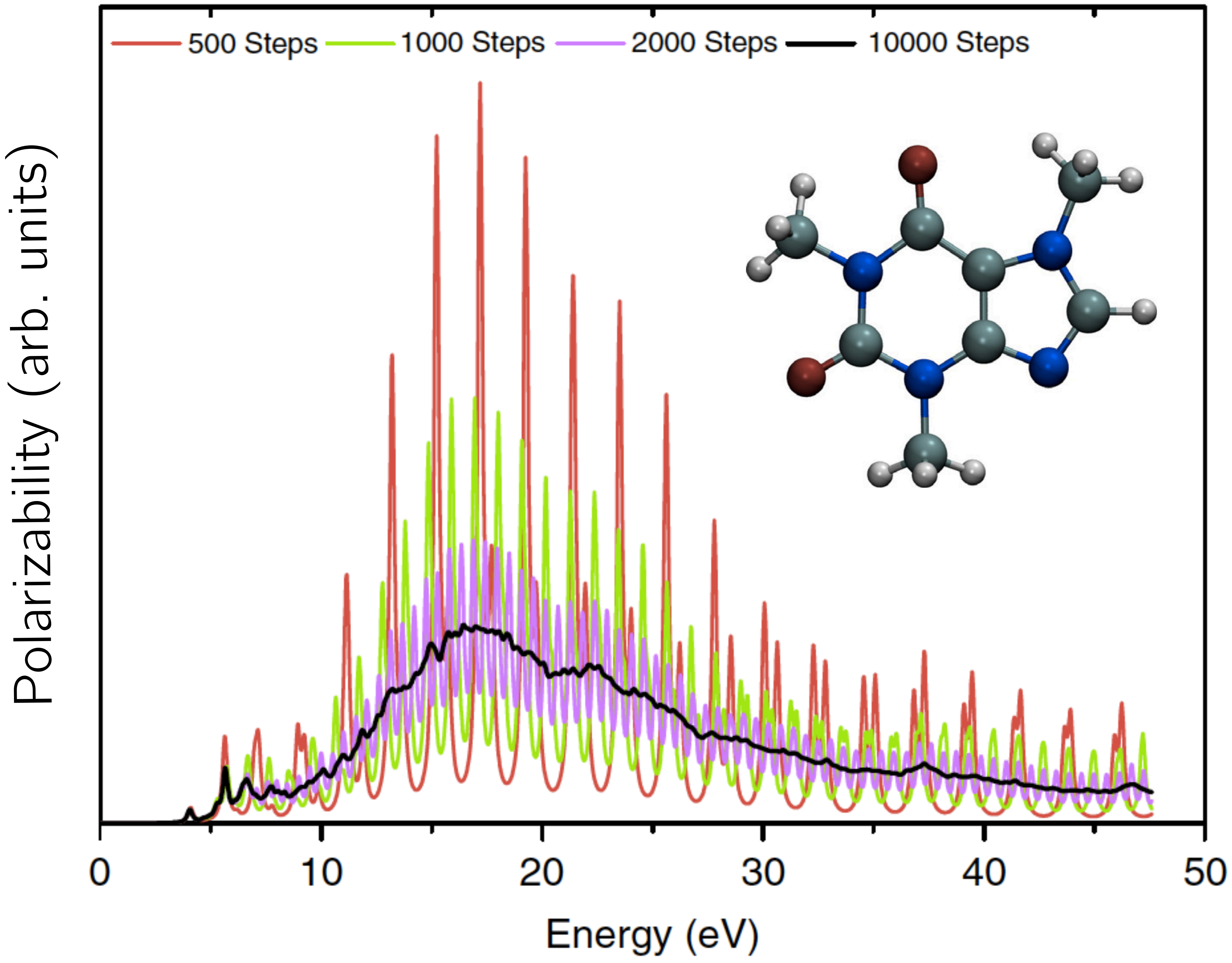
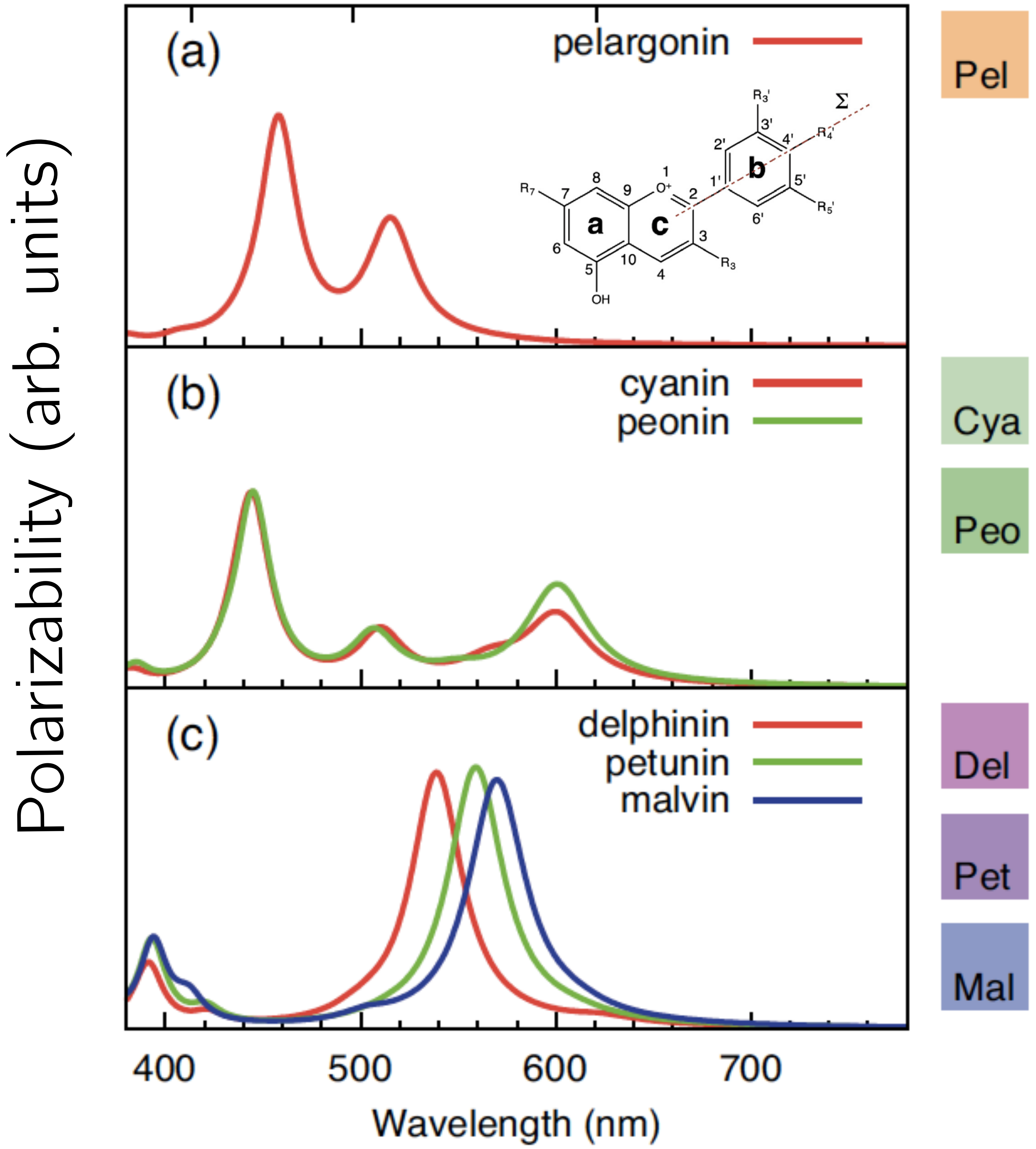


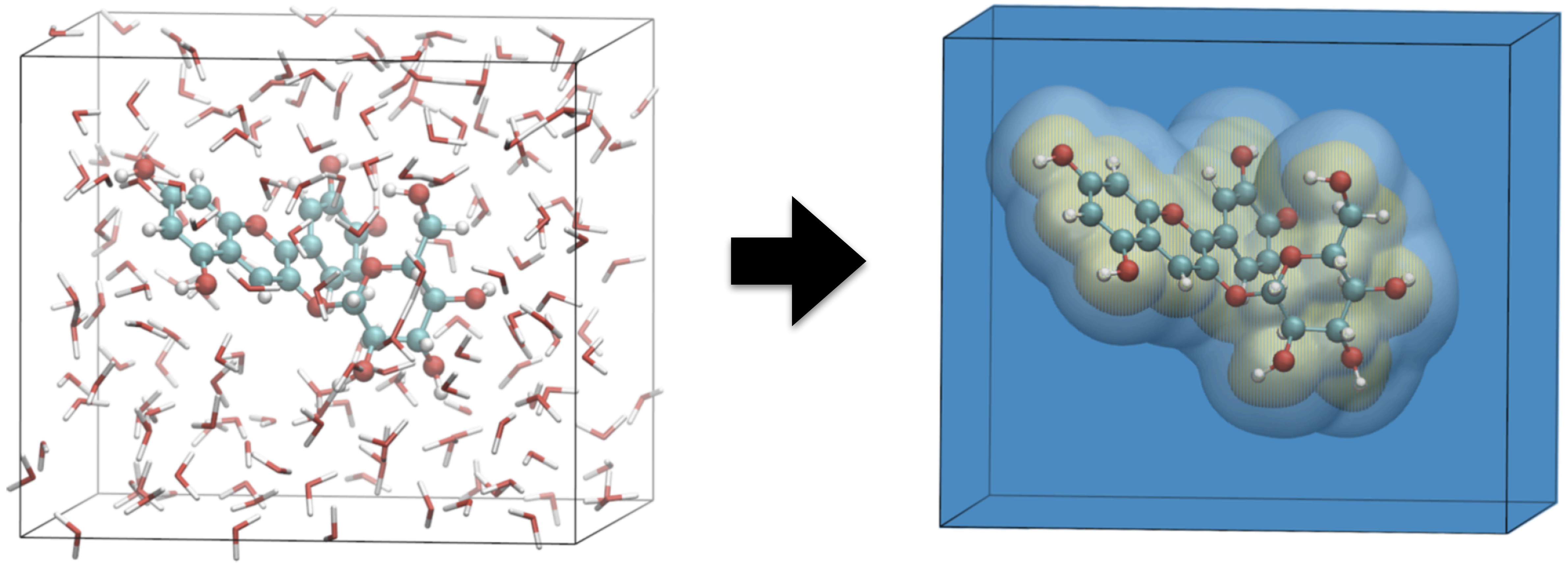
Absorption in anthocyanins from Casida-Davidson



S. Baroni *et al.*, J. Phys.: Condens. Matter **22**, 074204 (2010).

X. Ge *et al.*, Chem. Phys. Lett. **618**, 24 (2015).

Absorption spectra of molecules (with hybrids and solvent)



Replace an explicit solvent (expensive)
by an implicit solvent (inexpensive)

Self-consistent continuum solvation model
A. Andreussi et al., JCP 136, 064102 (2012)

I. Timrov, O. Andreussi, A. Biancardi, N. Marzari, and S. Baroni, J. Chem. Phys. **142**, 034111 (2015).
I. Timrov, M. Micciarelli, M. Rosa, A. Calzolari, and S. Baroni, J. Chem. Theor. Comput. **12**, 4423 (2016).

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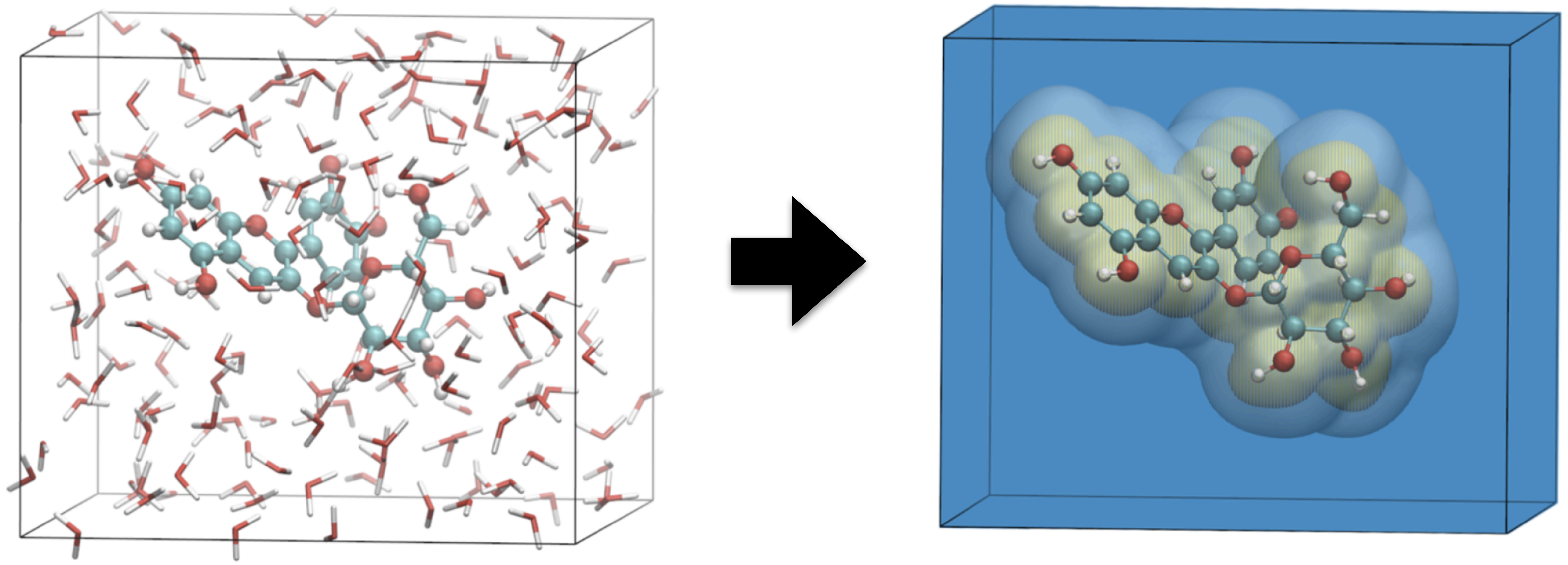

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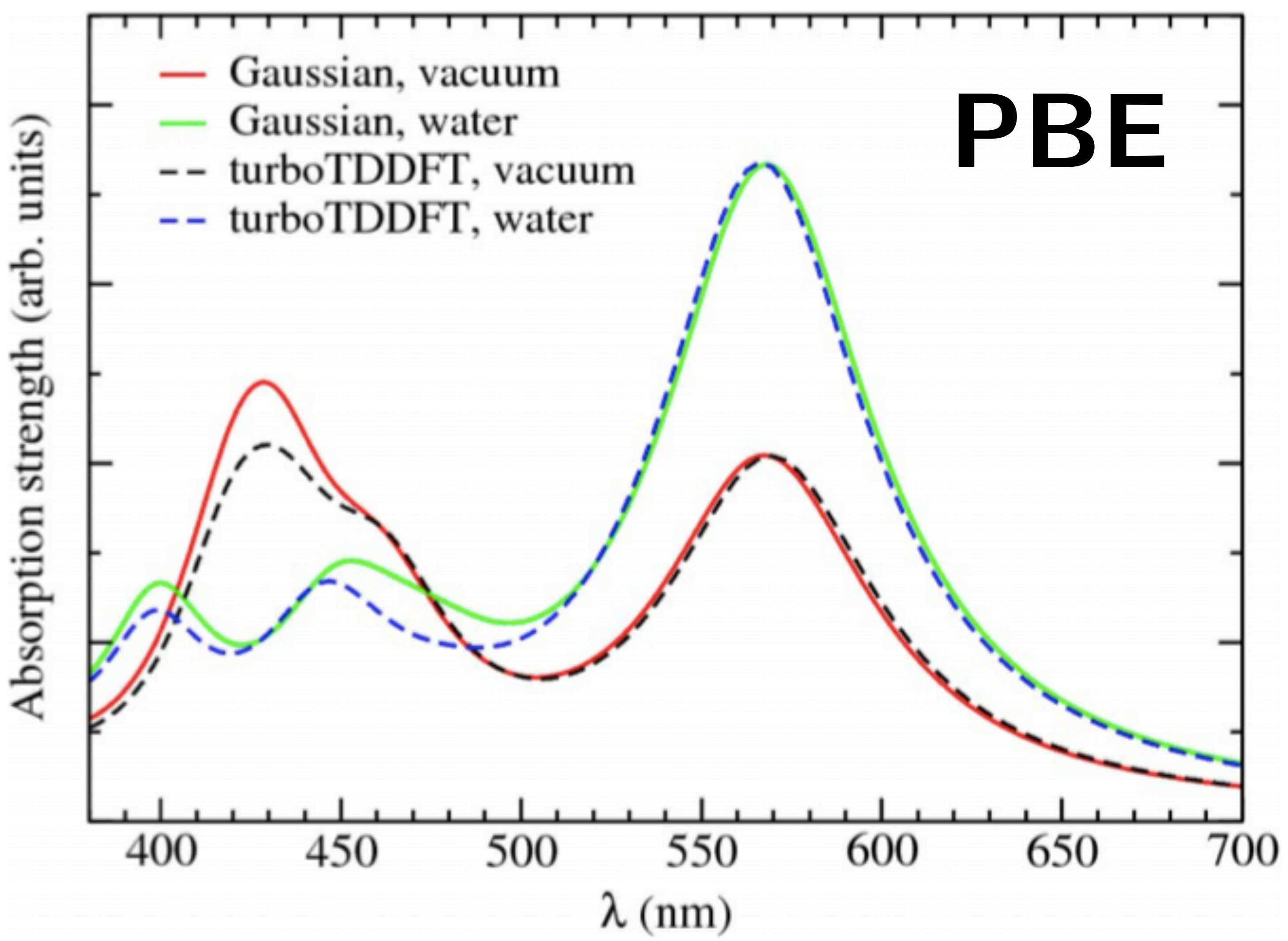

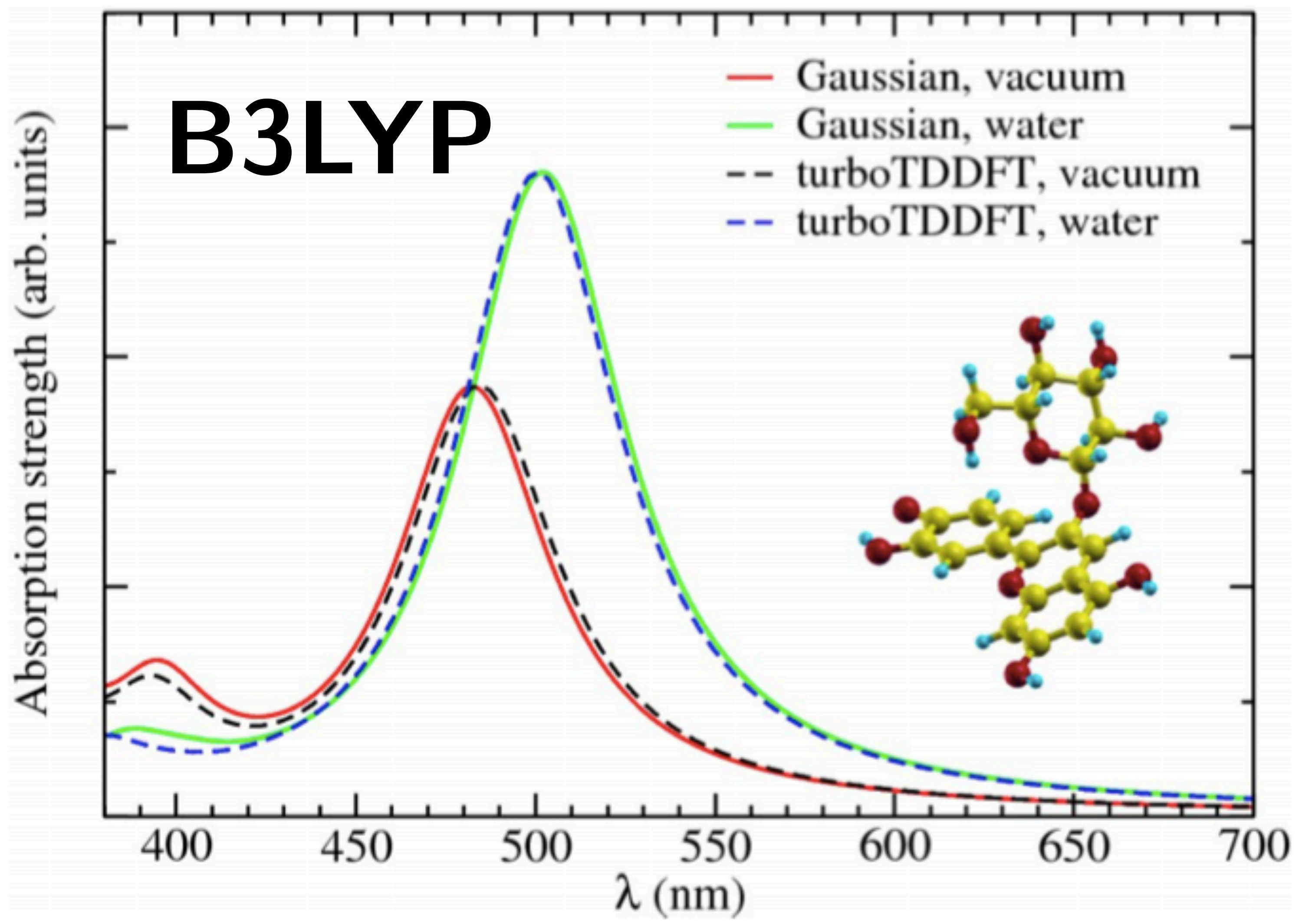

PBE → B3LYP: blue-shift of peaks

Solvatochromic effects are observed (i.e. the dependence of the optical absorption spectra on the solvation)

I. Timrov, O. Andreussi, A. Biancardi, N. Marzari, and S. Baroni, J. Chem. Phys. **142**, 034111 (2015).
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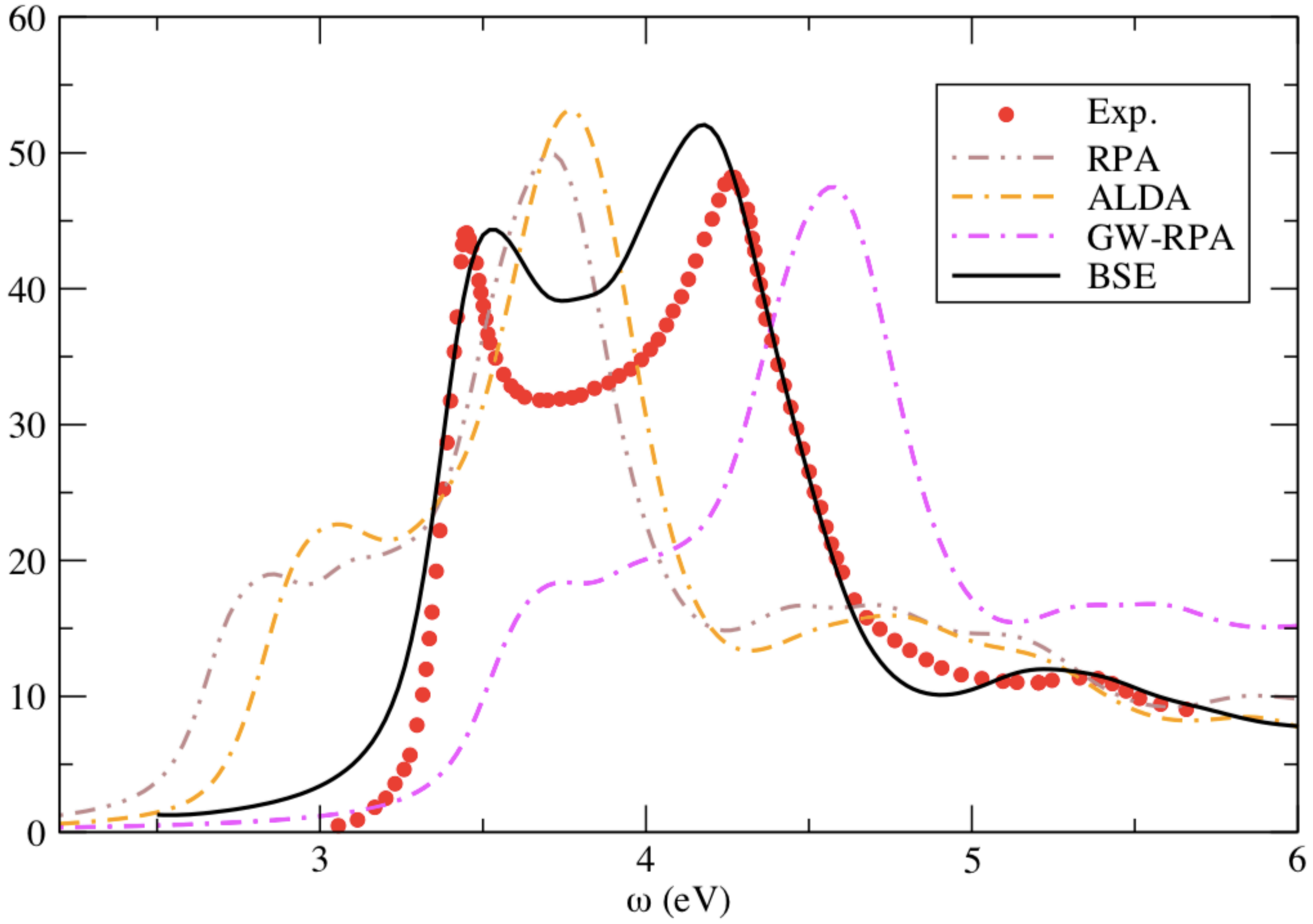
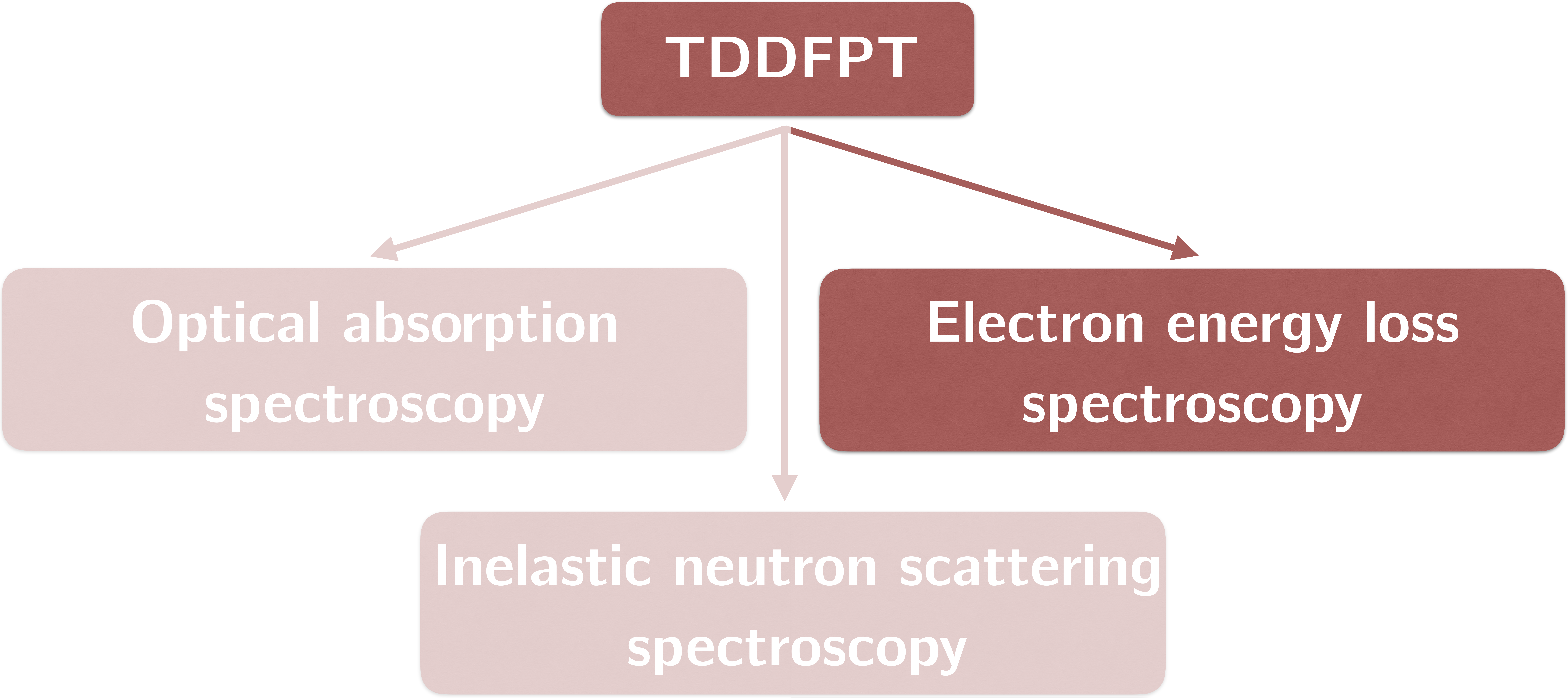
Absorption spectra of solids

Bulk silicon



Francesco Sottile, PhD thesis, École Polytechnique (France) 2003.

Various spectroscopies from TDDFPT



TDDFPT

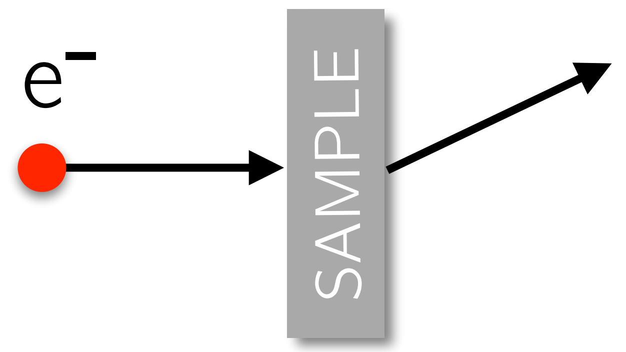
Optical absorption spectroscopy

Electron energy loss spectroscopy

Inelastic neutron scattering spectroscopy

Electron energy loss in solids

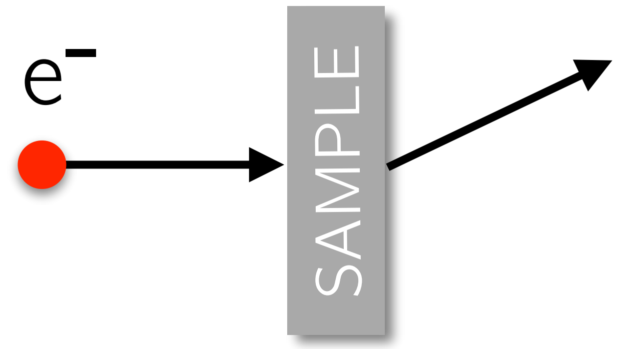
Let us consider an external perturbation which is an incoming electron (i.e. a plane wave):



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

Electron energy loss in solids

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



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

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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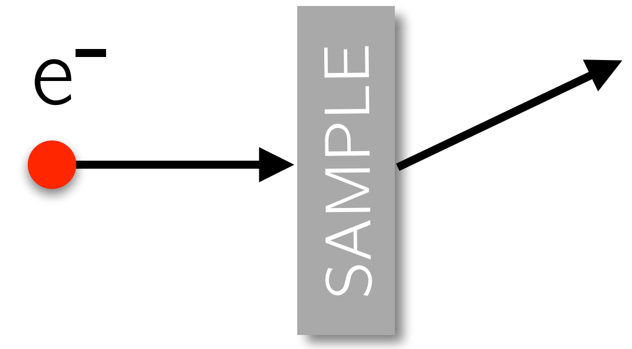

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This allows us to compute the inverse dielectric function:

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

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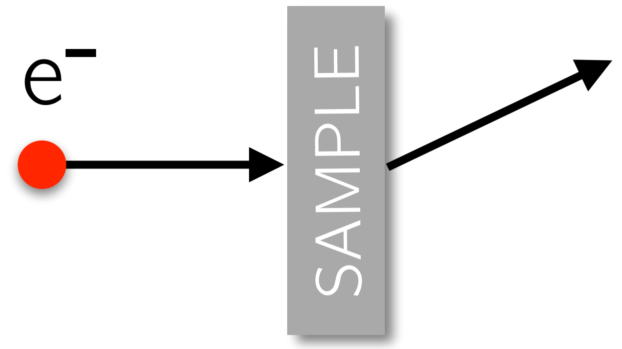

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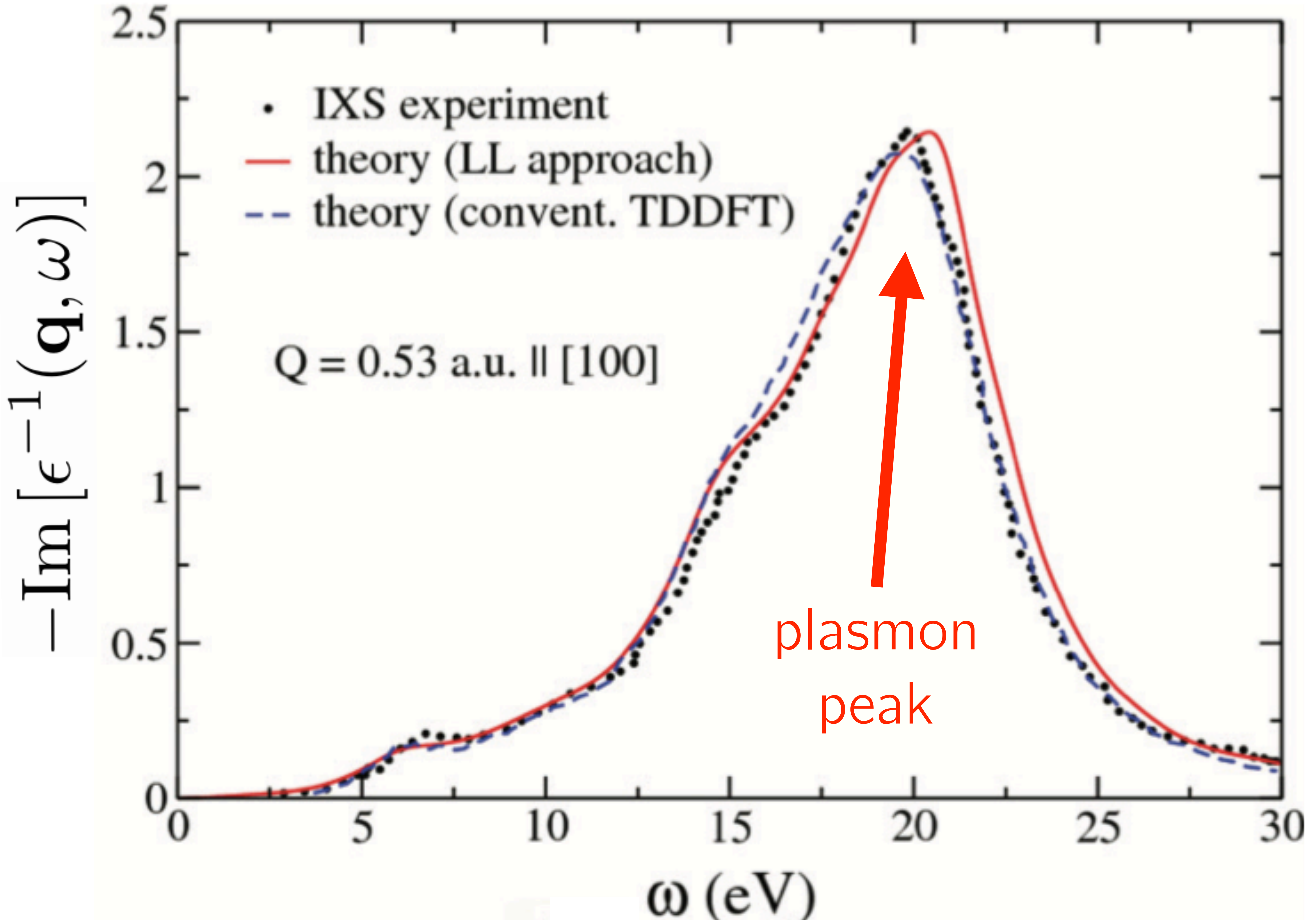
Double-differential cross section:

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

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

Electron energy loss in solids

EELS spectrum of bulk silicon



plasmon peak

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

Electron energy loss in solids

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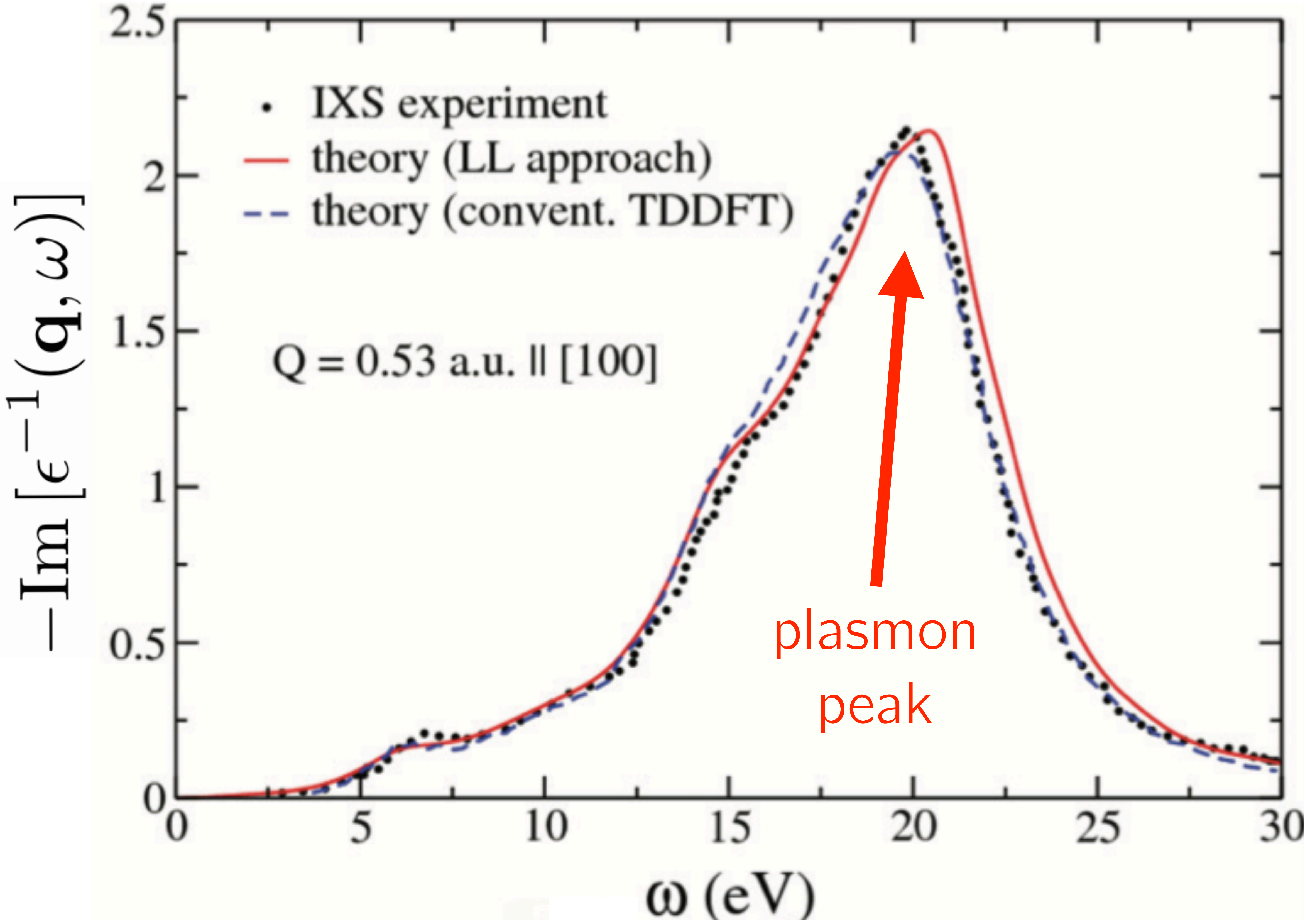

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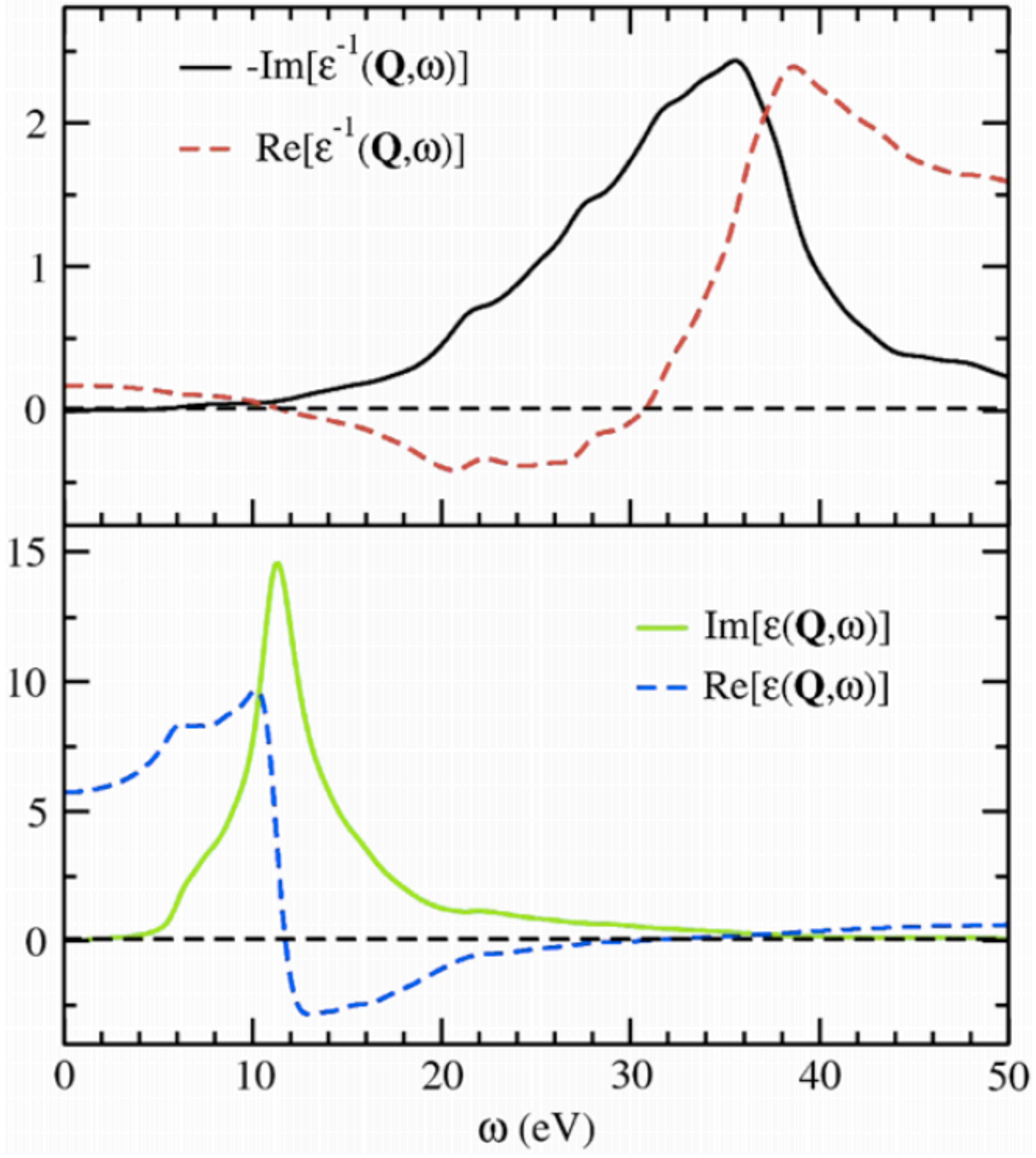
Phys. Rev. B **88**, 064301 (2013).

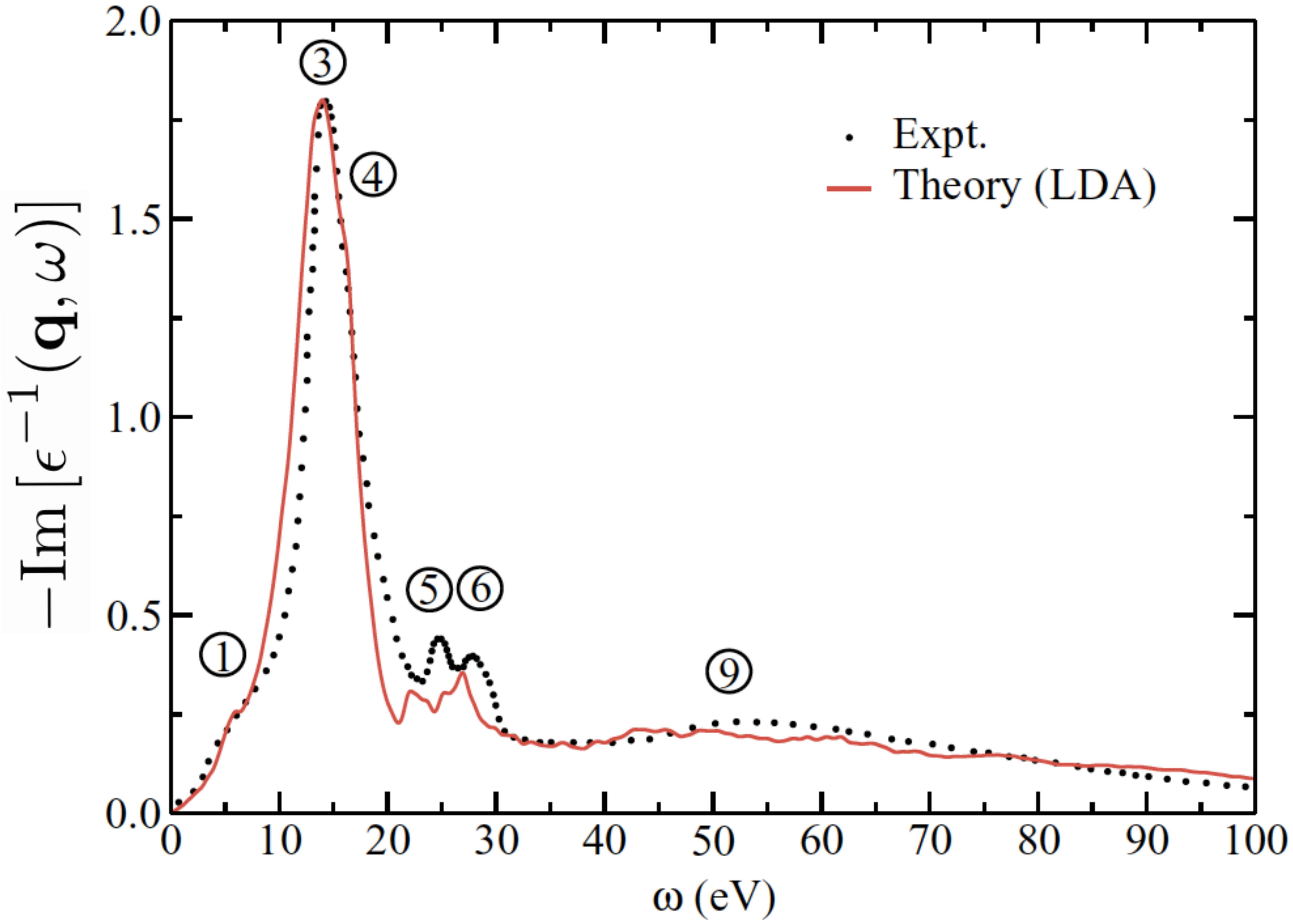
Bulk diamond



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

Electron energy loss in solids

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).

Electron energy loss in solids

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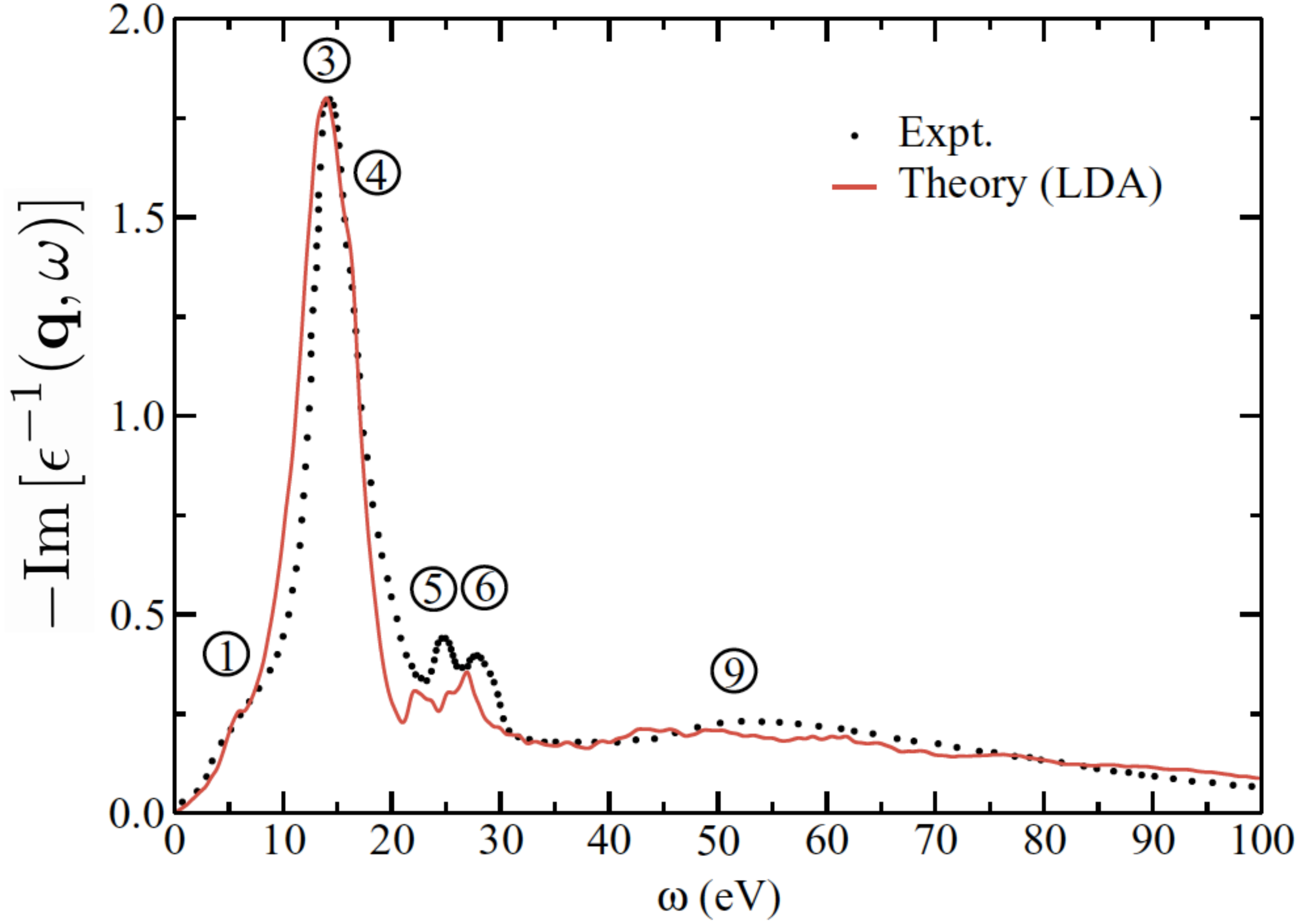
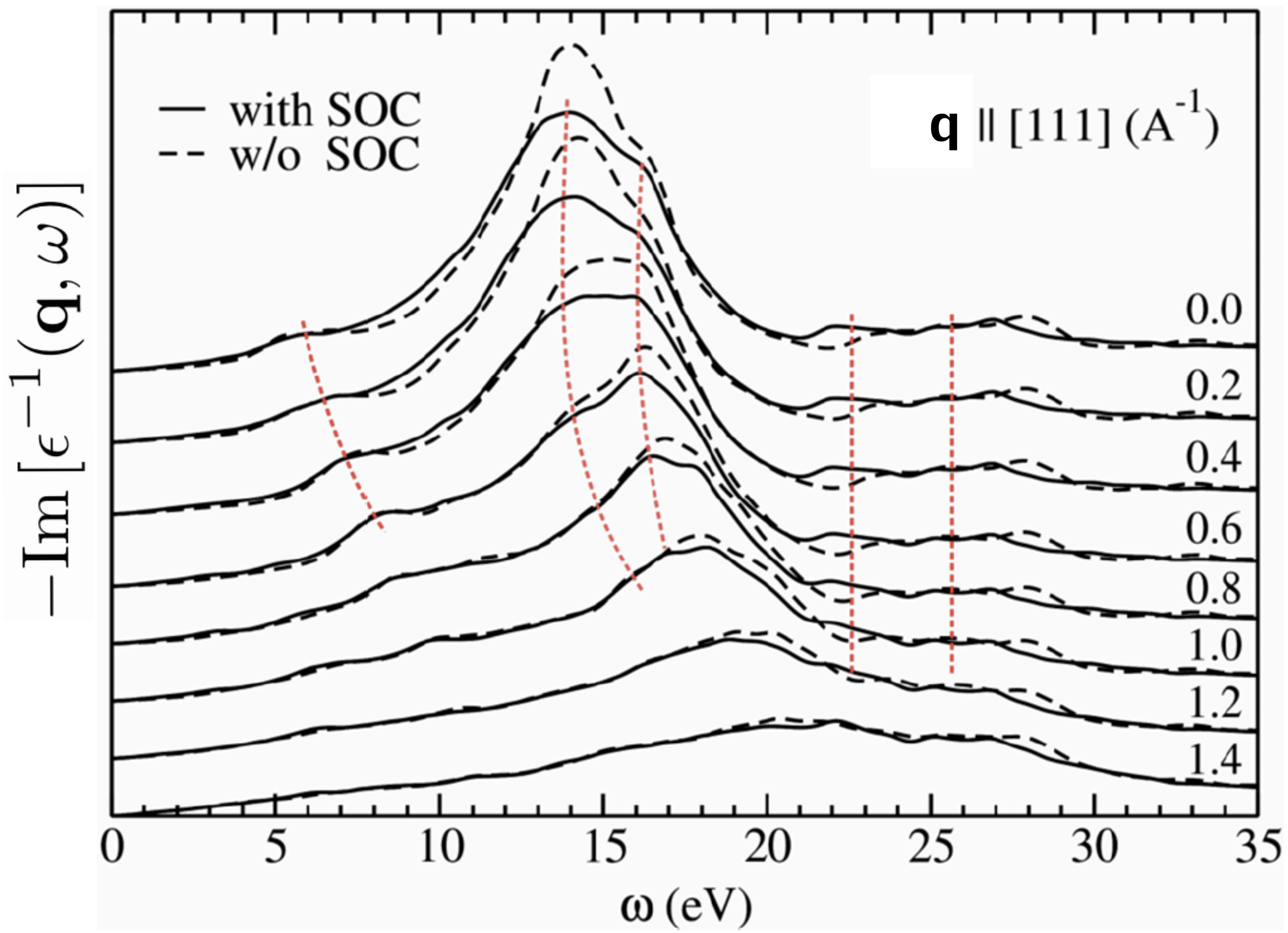


Peaks dispersion as a function of **q**



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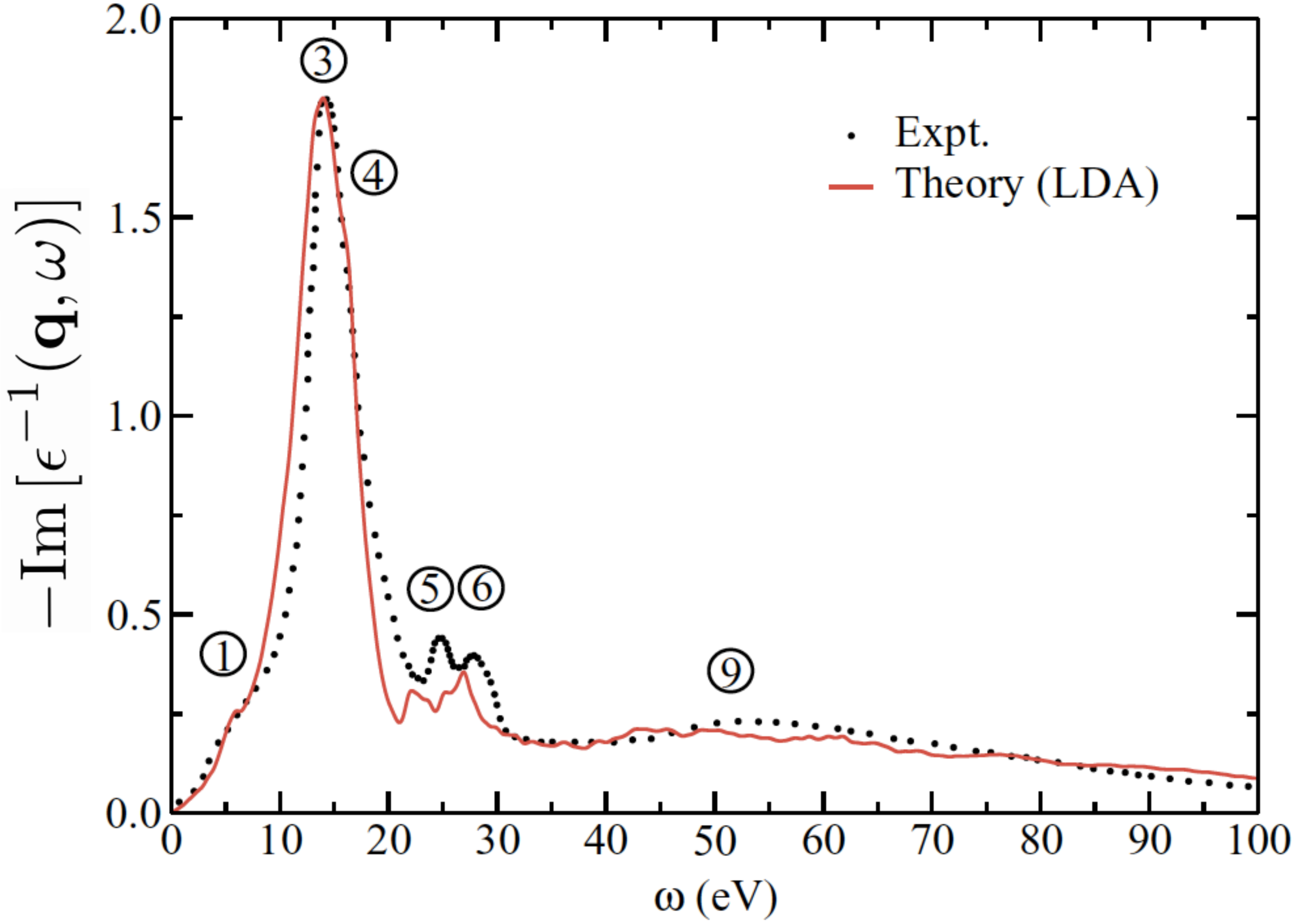

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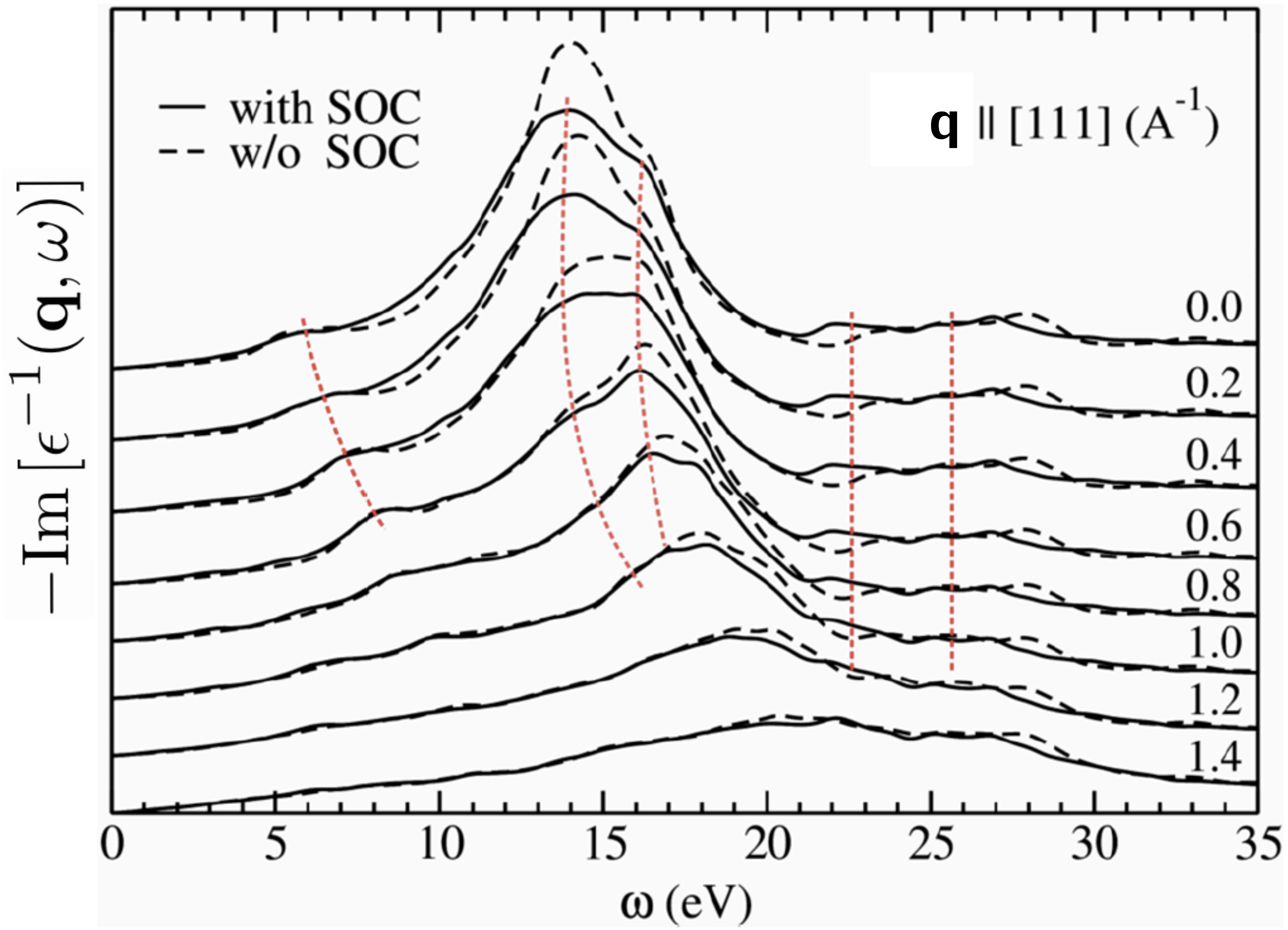


TDDFT@ALDA gives good results for EELS in solids (contrary to the optical absorption in solids)!

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).

Various spectroscopies from TDDFPT

TDDFPT

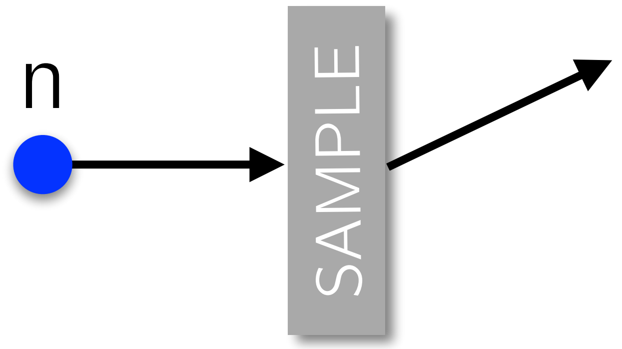
Optical absorption spectroscopy

Electron energy loss spectroscopy

Inelastic neutron scattering spectroscopy

Inelastic neutron scattering in solids

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



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

Inelastic neutron scattering in solids

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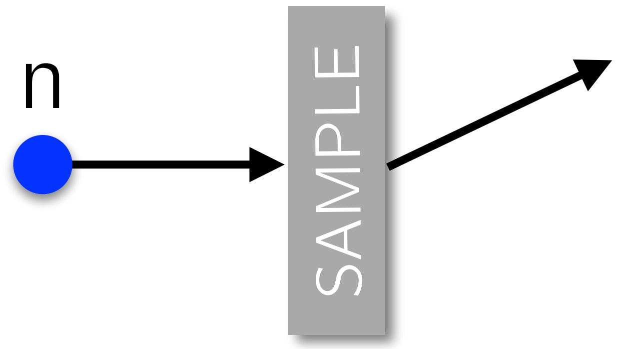

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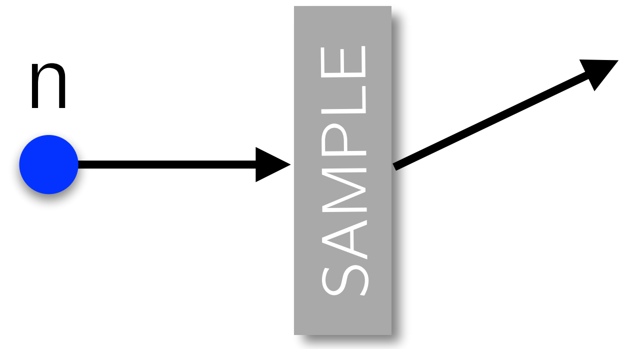

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This allows us to compute the following quantity:

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

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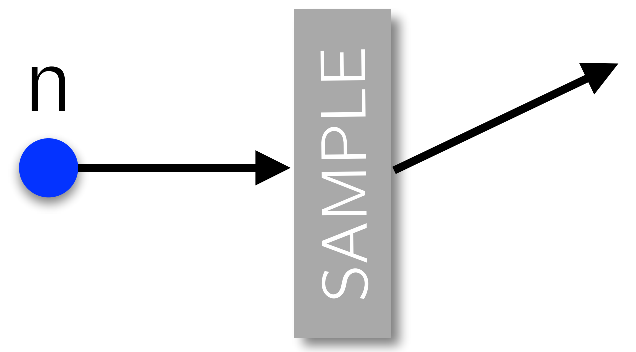

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➡

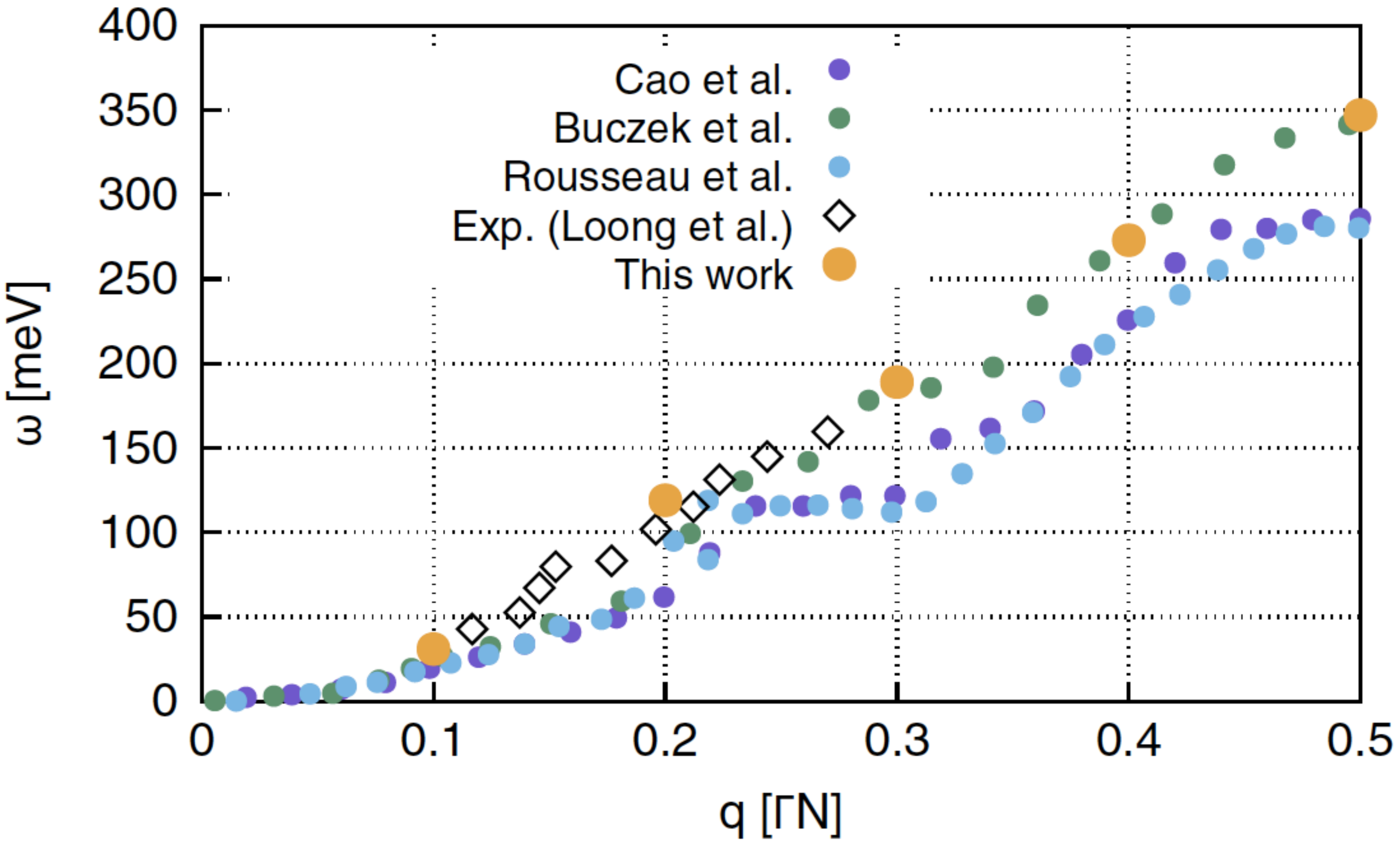
Double-differential cross section:

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

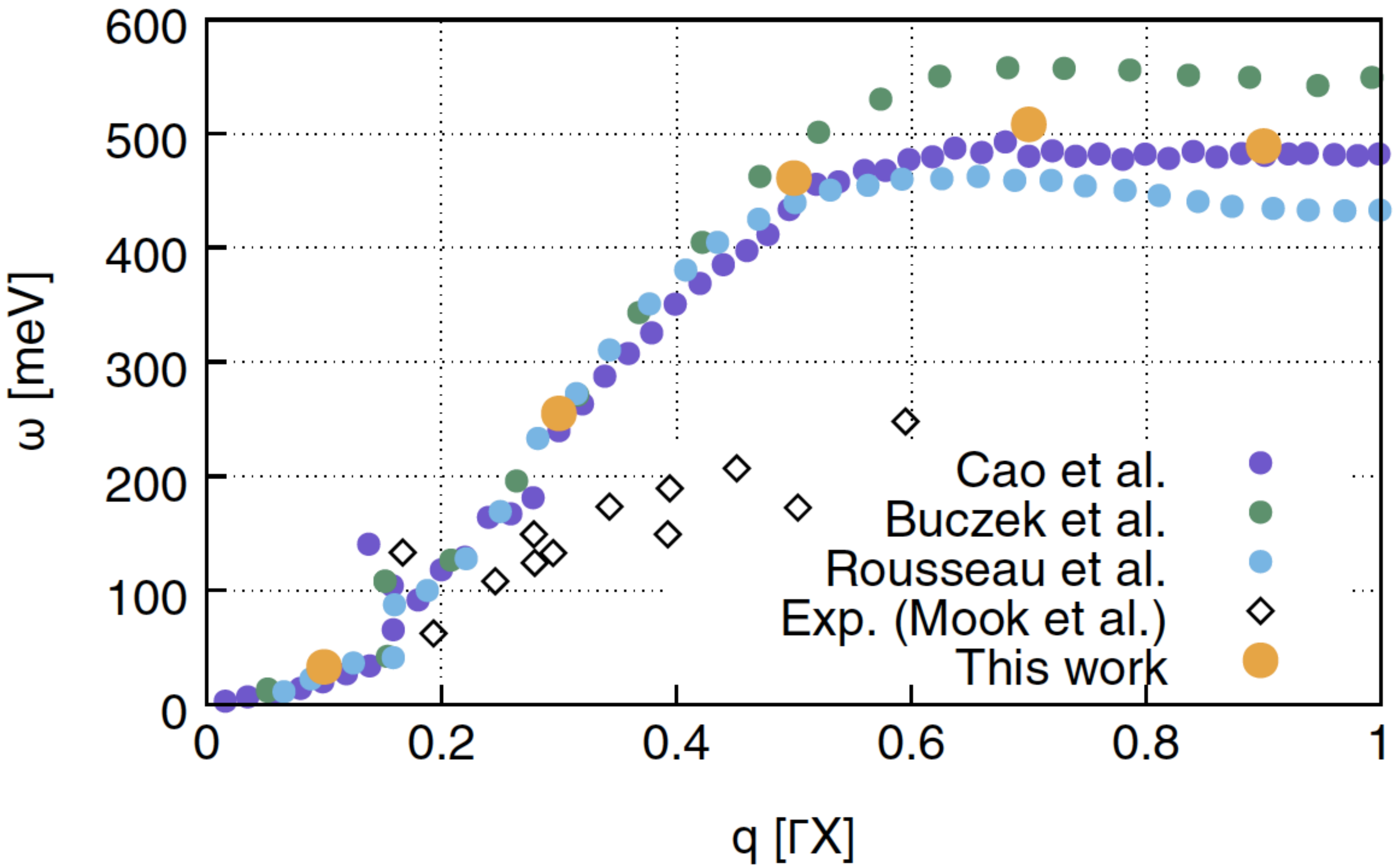
Currently, the code to compute INS spectra is being ported to the public version of Quantum ESPRESSO.

Inelastic neutron scattering in solids

Magnon dispersion in bulk iron



Magnon dispersion in bulk nickel



TDDFT@ALDA gives excellent results for Fe but overestimates magnon energies by 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 in solids, sometimes also magnons in solids, etc.). 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 soon will contain also the code for modelling of magnons in magnetic solids.