Time-dependent density functional perturbation theory

Iurii Timrov and Tommaso Gorni

SISSA – Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy

Advanced Quantum ESPRESSO developers' meeting: linear response
ICTP, Trieste, Italy

19 January 2016

Outline

1. Introduction to the TDDFPT module of QE

2. Absorption spectroscopy for finite systems

3. Electron energy loss spectroscopy for periodic systems

4. Conclusions

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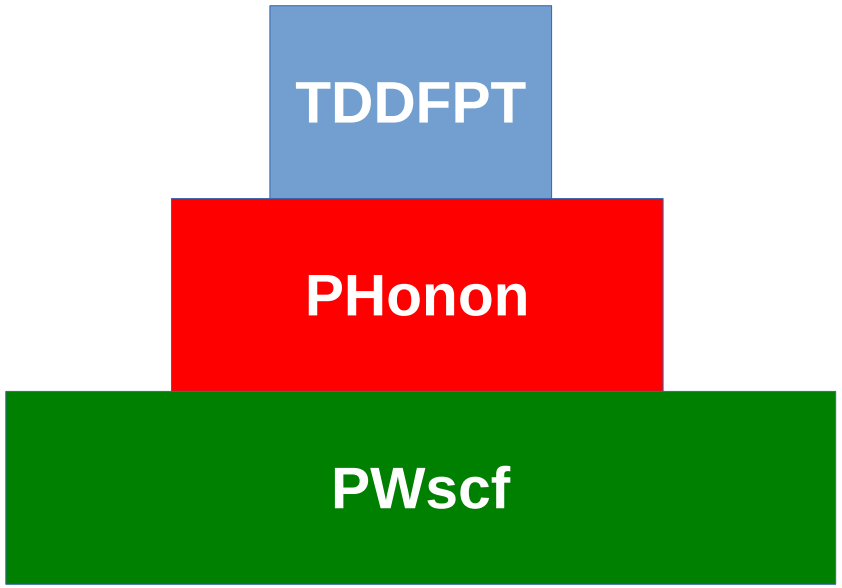
Developers of the TDDFPT module

- Stefano Baroni (2004 – present), coordinator
- Ralph Gebauer (2004 – present)
- Brent Walker (2004 – 2006)
- Dario Rocca (2006 – 2012)
- Baris Malcioglu (2008 – 2010)
- Simon Binnie (2010 – 2012)
- Xiaochuan Ge (2010 – present)
- Iurii Timrov (2010 – present)
- Tommaso Gorni (2014 - present)

The timing is approximate.

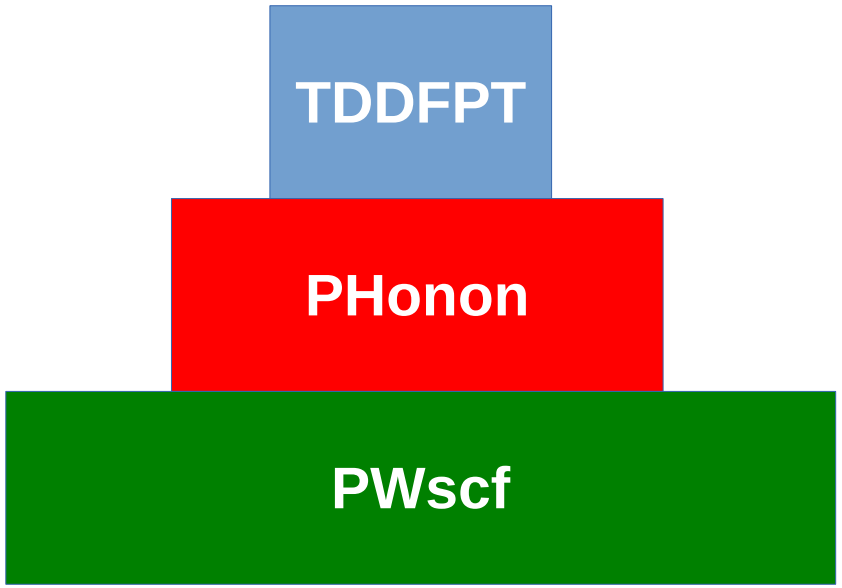
Schematic illustration of the dependencies

What is now

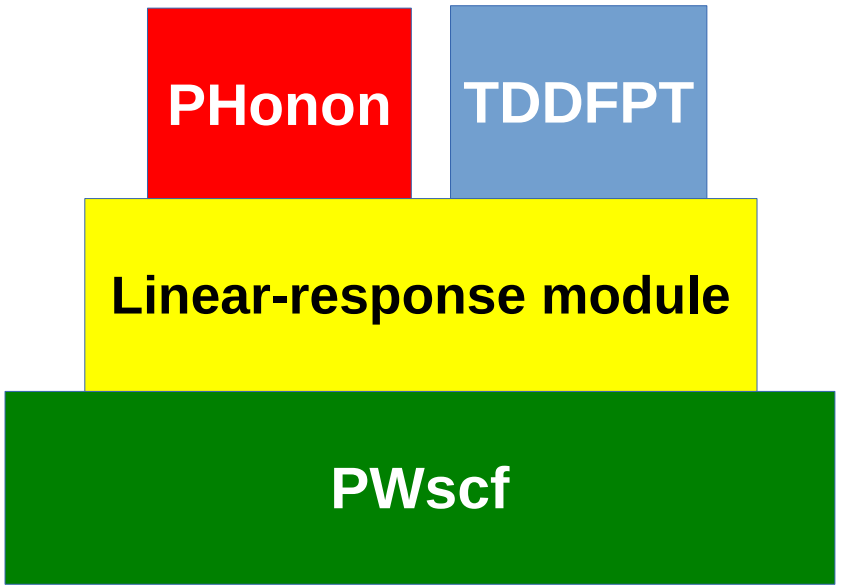


Schematic illustration of the dependencies

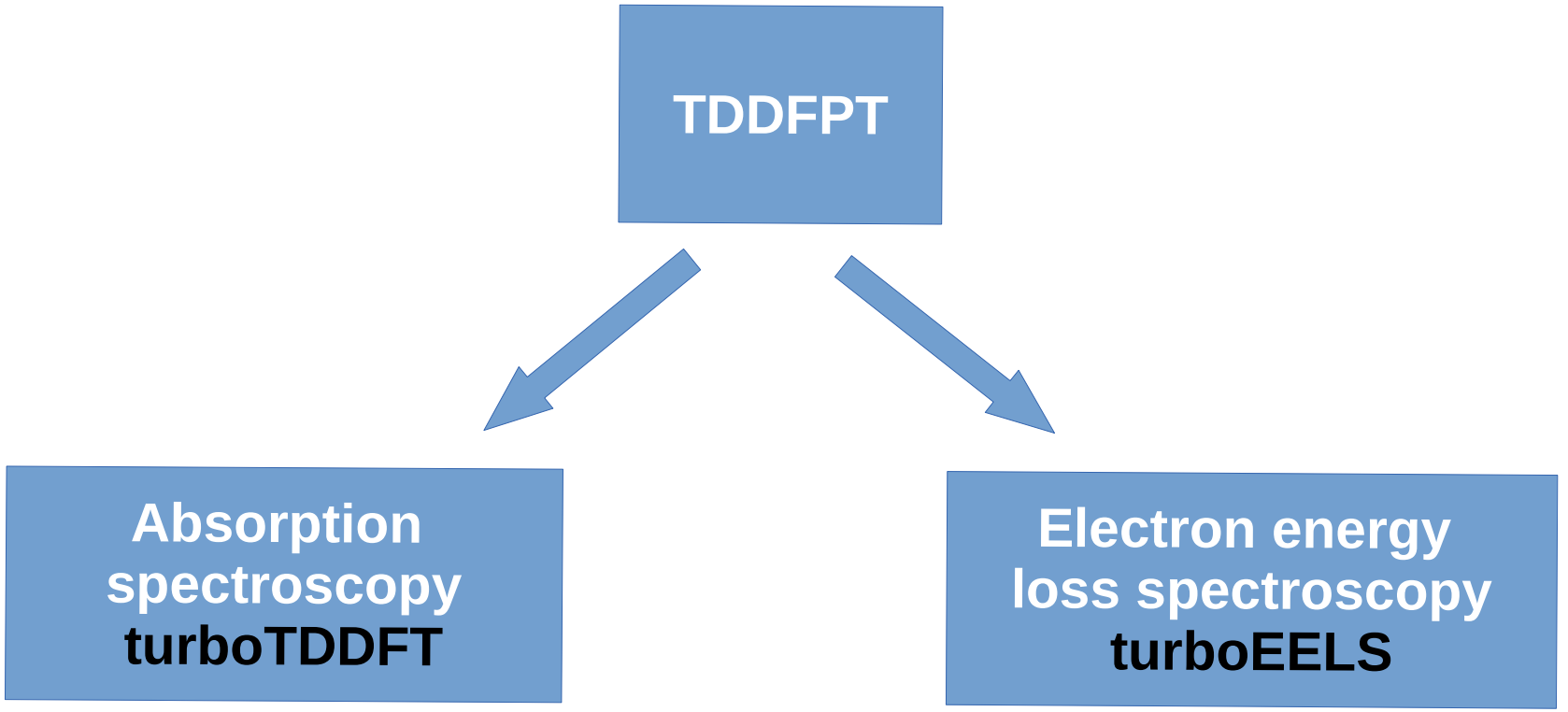
What is now



What is desired...

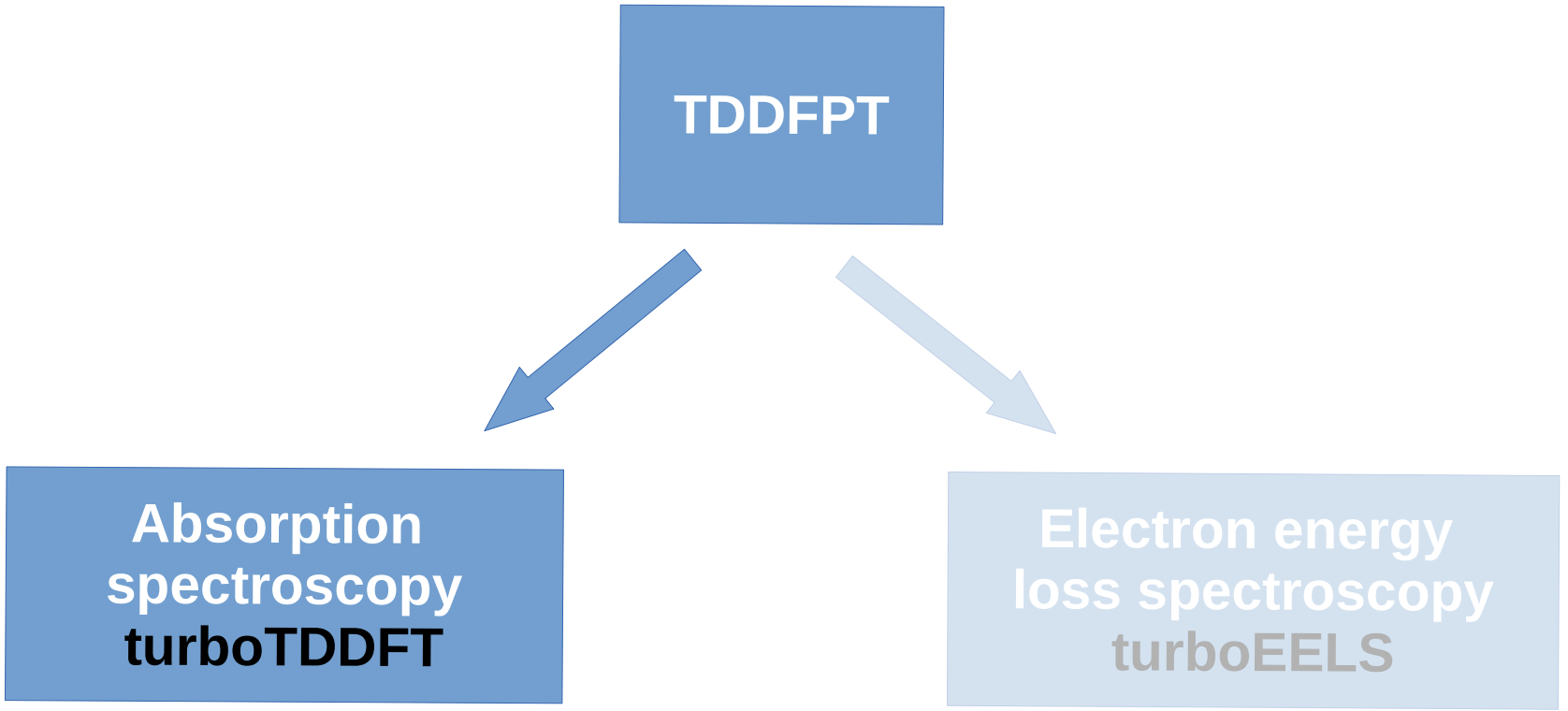


Components of the TDDFPT module



These two codes are strongly interleaved and reside in the same repository, namely **`TDDFPT/src`** .

Components of the TDDFPT module



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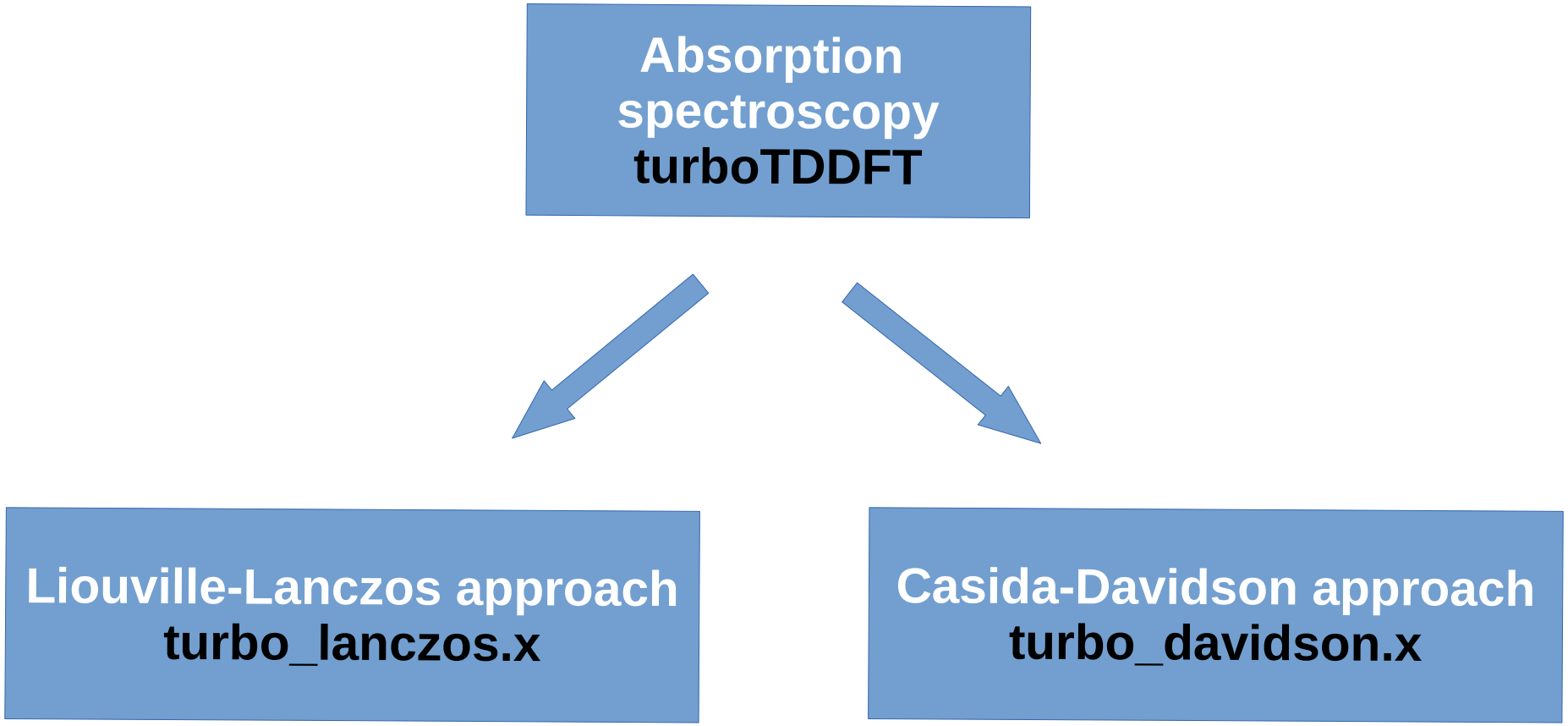
Absorption spectroscopy
turboTDDFT
Liouville-Lanczos approach
turbo_lanczos.x
Casida-Davidson approach
turbo_davidson.x

Bibliography

1. B. Walker, R. Gebauer,
Ultrasoft pseudopotentials in time-depepndent density-functional theory,
J. Chem. Phys. **127**, 164106 (2007).

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Turbo charging time-dependent density-functional theory with Lanczos chains, J. Chem. Phys. **128**, 154105 (2008).

3. O. Malcioglu, R. Gebauer, D. Rocca, and S. Baroni,
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4. S. Baroni and R. Gebauer,
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5. X. Ge, S. Binnie, D. Rocca, R. Gebauer, and S. Baroni,
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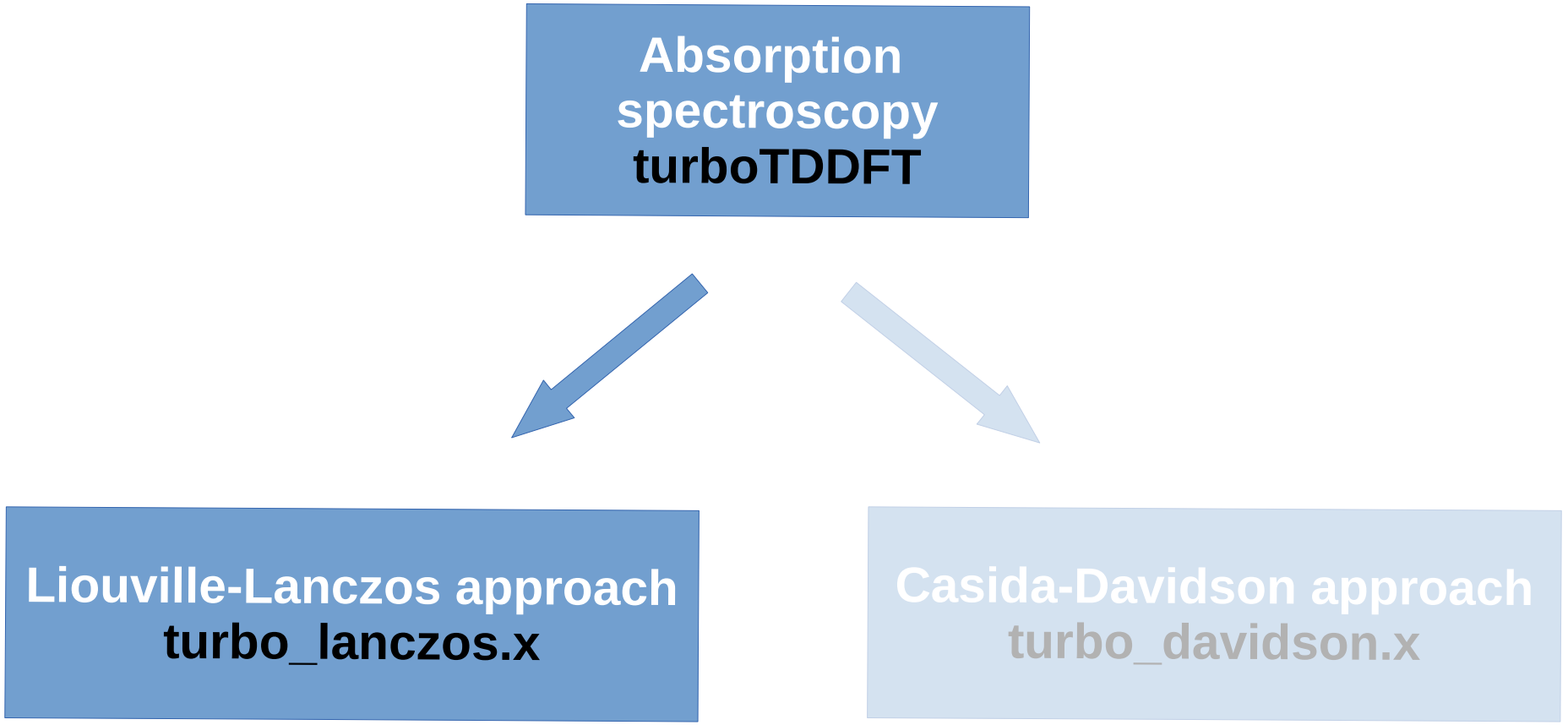
Comp. Phys. Comm. **185**, 2080 (2014).

6. I. Timrov, O. Andreussi, A. Biancardi, N. Marzari, and S. Baroni,
Self-consistent continuum solvation for optical absorption of complex molecular systems in solution, J. Chem. Phys. **142**, 034111 (2015).

Restrictions of the turboTDDFT code

- Linear-response regime.
- Use of only the Γ point (`gamma_only`) and supercells.
  $k = 0$ or many k points algorithm seems working well, but nobody have ever performed an extensive testing. It may be used at your own risk!
- Supports NC and US pseudopotentials. No PAW.
- Hybrid functional are supported, but only with NC PP's
- Adiabatic XC kernels only.
- Only unpolarized systems are allowed (`nspin=1`). Collinear (`nspin=2`) and noncollinear (`noncolin=.true.`) cases are not supported.
- No relativistic effects: spin-orbit coupling is not implemented.
- Parallelization: PWs, bands, task groups (only NC PP's, experimental).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Liouville-Lanczos approach: basic equations

Coupled linear-response TDDFPT equations (resonant and anti-resonant):

perturbation

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

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

interaction terms

These equations can be re-written as a quantum Liouville equation:

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

$$\hat{\mathcal{L}} \cdot \hat{\rho}' \equiv [\hat{H}^{\circ}, \hat{\rho}'] + [\hat{V}'_{\mathrm{HXC}}, \hat{\rho}^{\circ}]$$

Absorption coefficient is computed as:

$$\alpha(\omega) = -(\hat{\mathbf{r}}, (\omega - \hat{\mathcal{L}})^{-1}[\hat{\mathbf{r}}, \hat{\rho}^{\circ}])$$

Lanczos algorithm is used to solve recursively quantum Liouville equation in the standard batch representation. This allows us to avoid inversions and multiplications of large matrices.

Liouville-Lanczos approach: implementation

$$(\hat{H}^\circ - \varepsilon_v - \omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^*_v(\mathbf{r},-\omega)]\,\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})$$

$$(\hat{H}^\circ - \varepsilon_v + \omega)\tilde{\varphi}'^*_v(\mathbf{r},-\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^*_v(\mathbf{r},-\omega)]\,\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})$$

perturbation

TDDFPT/lr_dvpsi_e.f90

(analogue of PH/dvpsi_e.f90)

External electric field inducing a dipole moment:

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

$$\langle\varphi^\circ_c|\,\hat{\mathbf{r}}\,|\varphi^\circ_v\rangle = \frac{\langle\varphi^\circ_c|\,[\hat{H}^\circ,\hat{\mathbf{r}}]\,|\varphi^\circ_v\rangle}{\varepsilon_c - \varepsilon_v}$$

PH/commutator_Hx_psi.f90

Projector on empty states:

$$\hat{P}_c = 1 - \sum_{v=1}^{N_{occ}} |\varphi^\circ_v\rangle\langle\varphi^\circ_v|$$

PH/orthogonalize.f90

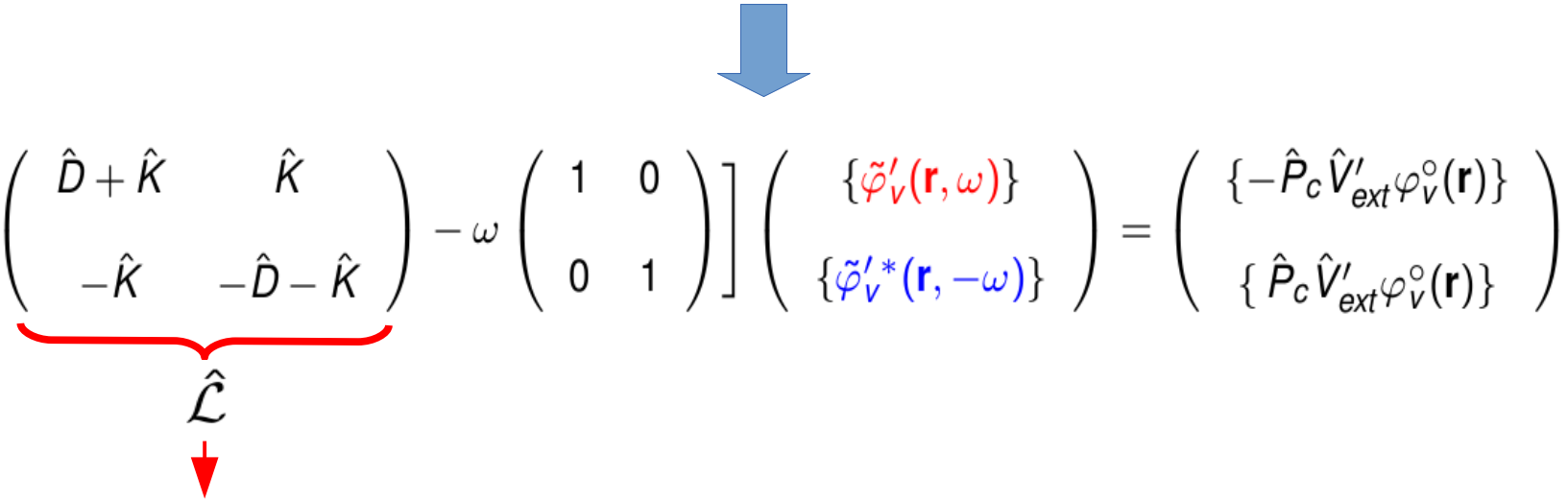
S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. ***73****, 515 (2001)*

No empty states!

Liouville-Lanczos approach: implementation

$$(\hat{H}^\circ - \varepsilon_v - \omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})$$

$$(\hat{H}^\circ - \varepsilon_v + \omega)\tilde{\varphi}'^{*}_v(\mathbf{r},-\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})$$



$$\left[\underbrace{\begin{pmatrix} \hat{D}+\hat{K} & \hat{K} \\ -\hat{K} & -\hat{D}-\hat{K} \end{pmatrix}}_{\hat{\mathcal{L}}} - \omega \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \begin{pmatrix} \{\tilde{\varphi}'_v(\mathbf{r},\omega)\} \\ \{\tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)\} \end{pmatrix} = \begin{pmatrix} \{-\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})\} \\ \{\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})\} \end{pmatrix}$$

TDDFPT/lr_apply_liouvillian.f90

Liouville-Lanczos approach: implementation

$$(\hat{H}^\circ - \varepsilon_v - \omega)\tilde{\varphi}'_v(\mathbf{r},\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})$$

$$(\hat{H}^\circ - \varepsilon_v + \omega)\tilde{\varphi}'^{*}_v(\mathbf{r},-\omega) + \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}[\tilde{\varphi}'_v(\mathbf{r},\omega), \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)]\,\varphi^\circ_v(\mathbf{r}) = -\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})$$

$$\left[\underbrace{\begin{pmatrix} \hat{D}+\hat{K} & \hat{K} \\ -\hat{K} & -\hat{D}-\hat{K} \end{pmatrix}}_{\hat{\mathcal{L}}} - \omega \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \begin{pmatrix} \{\tilde{\varphi}'_v(\mathbf{r},\omega)\} \\ \{\tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)\} \end{pmatrix} = \begin{pmatrix} \{-\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})\} \\ \{\hat{P}_c\,\hat{V}'_{ext}\varphi^\circ_v(\mathbf{r})\} \end{pmatrix}$$

TDDFPT/lr_apply_liouvillian.f90

$\hat{D} \longrightarrow (\hat{H}^\circ - \varepsilon_v)$

PW/h_psi.f90

$\hat{K} \longrightarrow \hat{P}_c\,\hat{V}'_{\mathrm{HXC}}\varphi^\circ_v(\mathbf{r})$

$$\tilde{V}'_{\mathrm{HXC}}(\mathbf{r},\omega) = \int \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \kappa_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')\right) \tilde{n}'(\mathbf{r}',\omega)\,d\mathbf{r}' \longrightarrow \textbf{PH/dv\_of\_drho.f90}$$

$$\tilde{n}'(\mathbf{r}',\omega) = 2\sum_v \varphi^\circ_v(\mathbf{r})\left[\tilde{\varphi}'_v(\mathbf{r},\omega) + \tilde{\varphi}'^{*}_v(\mathbf{r},-\omega)\right] \longrightarrow \textbf{TDDFPT/lr\_calc\_dens.f90}$$

Liouville-Lanczos approach: SBR

In the actual implementation of the Liouville-Lanczos approach, the so called *standard batch representation* **(SBR)** is used (rotation of 45 degrees):

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

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

In the SBR, the matrix linear-response equation have a block-diagonal form:

$$\left[\underbrace{\begin{pmatrix} 0 & -\hat{D} \\ -\hat{D}-\hat{K} & 0 \end{pmatrix}}_{\hat{\mathcal{L}}} + \omega \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \begin{pmatrix} \{q_v(\mathbf{r})\} \\ \{p_v(\mathbf{r})\} \end{pmatrix} = \begin{pmatrix} 0 \\ \{\hat{P}_c \hat{V}'_{ext} \varphi^{\circ}_v(\mathbf{r})\} \end{pmatrix}$$

This allows us to decrease the number of operations by a factor of 2.

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

Liouville-Lanczos approach: Lanczos algorithm

Iterative (recursive) solver of the matrix linear-response equation in SBR.

$$\left[\begin{pmatrix} 0 & -\hat{D} \\ -\hat{D}-\hat{K} & 0 \end{pmatrix} + \omega \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \begin{pmatrix} \{q_v(\mathbf{r})\} \\ \{p_v(\mathbf{r})\} \end{pmatrix} = \begin{pmatrix} 0 \\ \{\hat{P}_c \hat{V}'_{ext} \varphi^{\circ}_v(\mathbf{r})\} \end{pmatrix}$$

Tridiagonal matrix is generated

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

TDDFPT/lr_lanczos.f90

Two flavors of the Lanczos algorithm:

- Non-Hermitian
- Pseudo-Hermitian (2 times faster)

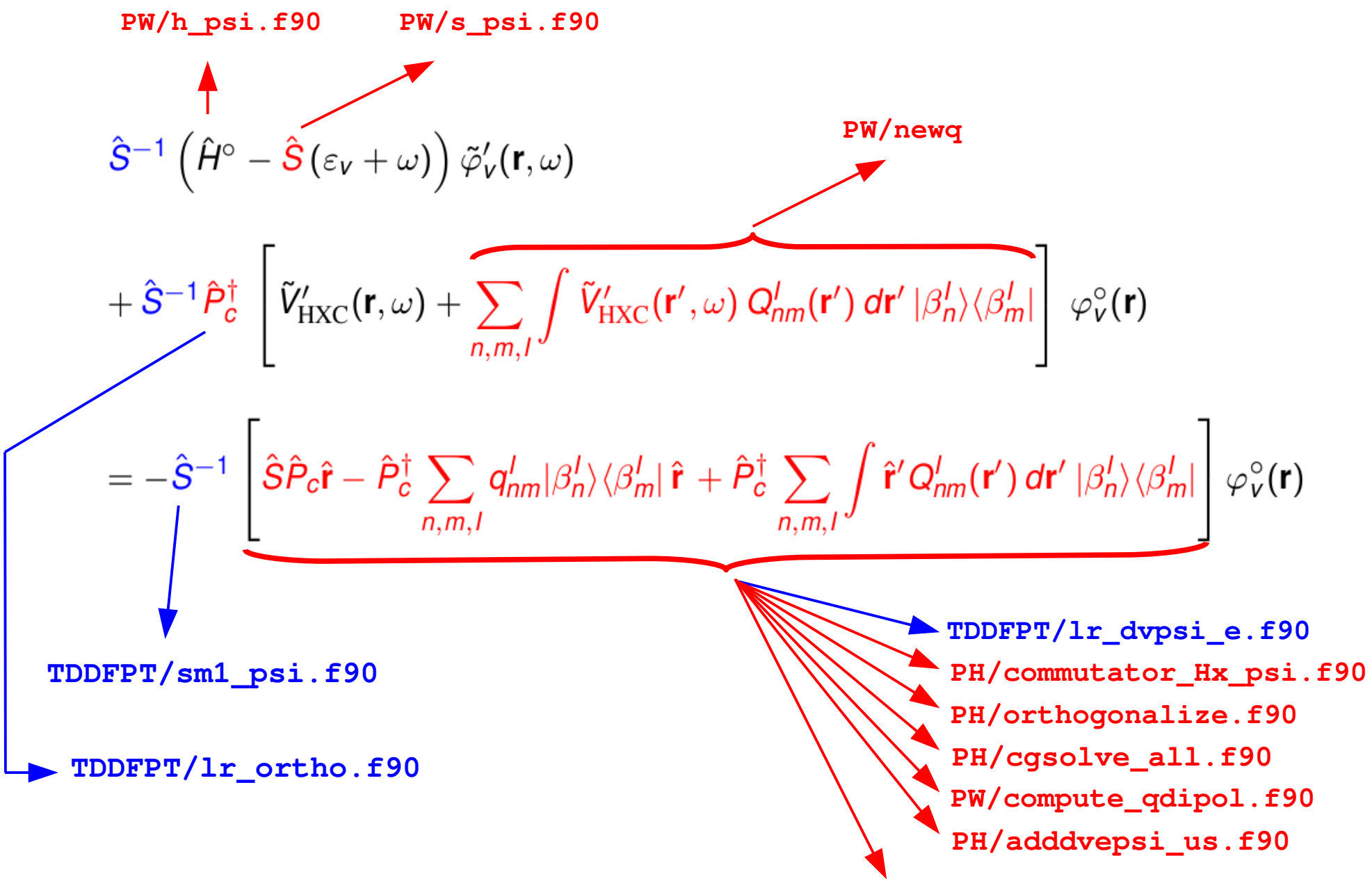
ζ_N coefficients are computed on the fly

Post-processing calculation of the absorption coefficient at various frequencies:

TDDFPT/tools/lr_calculate_spectrum.f90

$$\alpha(\omega) = (\zeta_N, (\omega - \hat{T}_N)^{-1} \cdot \mathbf{e}_1^N)$$

Liouville-Lanczos approach: ultrasoft case



*B. Walker and R. Gebauer, JCP **127**, 164106 (2007)*

*J. Tobik and A. Dal Corso, JCP **120**, 9934 (2004).*

Liouville-Lanczos approach: ultrasoft case

The response charge-density reads:

$$\tilde{n}'(\mathbf{r},\omega) = 2\sum_v \varphi_v^\circ(\mathbf{r})\left[\tilde{\varphi}_v'(\mathbf{r},\omega)+\tilde{\varphi}_v'^*(\mathbf{r},-\omega)\right] + 2\sum_v \sum_{n,m,I} Q_{nm}^I(\mathbf{r})\langle\varphi_v^\circ|\beta_n^I\rangle\langle\beta_m^I|\left[\tilde{\varphi}_v'(\mathbf{r},\omega)+\tilde{\varphi}_v'^*(\mathbf{r},-\omega)\right]\rangle$$

TDDFPT/lr_calc_dens.f90

The projector on empty states:

$$\hat{P}_c = 1 - \sum_{v=1}^{N_{occ}} |\varphi_v^\circ\rangle\langle\varphi_v^\circ|\hat{S}$$

$$\hat{P}_c^\dagger = 1 - \sum_{v=1}^{N_{occ}} \hat{S}|\varphi_v^\circ\rangle\langle\varphi_v^\circ|$$

TDDFPT/lr_ortho.f90

(analogue of PH/orthogonalize.f90)

$$\hat{S}^{-1}\hat{P}_c^\dagger = \hat{P}_c\,\hat{S}^{-1}$$

*B. Walker and R. Gebauer, JCP **127**, 164106 (2007)*

Liouville-Lanczos approach: hybrid functionals

In hybrid functionals, a fraction of the local exchange potential is replaced by the same fraction of the non-local exact-exchange (EXX) potential (e.g. in PBE0, $\alpha = 1/4$).

$$(\hat{H}^{\circ\alpha} + \alpha\hat{V}^{\circ}_{\mathrm{EXX}} - \varepsilon_v - \omega)\tilde{\varphi}'_v(\mathbf{r},\omega)$$

$$+ \hat{P}_c \left[\hat{V}'_{\mathrm{H}}(\omega) + \hat{V}'^{\alpha}_{\mathrm{XC}}(\omega) + \alpha\hat{V}'_{\mathrm{EXX}}(\omega)\right] \varphi^{\circ}_v(\mathbf{r}) = -\hat{P}_c \hat{V}'_{ext}\varphi^{\circ}_v(\mathbf{r})$$

$$\hat{V}^{\circ}_{\mathrm{EXX}}\,\tilde{\varphi}'_v(\mathbf{r},\omega) = -\sum_{v'}\varphi^{\circ}_{v'}(\mathbf{r})\int \frac{\varphi^{\circ}_{v'}(\mathbf{r}')\,\tilde{\varphi}'_v(\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$$

PW/exx.f90

$$\hat{V}'_{\mathrm{EXX}}(\omega)\,\varphi^{\circ}_v(\mathbf{r}) = -\sum_{v'}\int \frac{\left[\varphi^{\circ}_{v'}(\mathbf{r})\,\tilde{\varphi}'^{*}_{v'}(\mathbf{r}',-\omega) + \tilde{\varphi}'_{v'}(\mathbf{r},\omega)\,\varphi^{\circ}_{v'}(\mathbf{r}')\right]\varphi^{\circ}_v(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}'$$

TDDFPT/lr_exx_kernel.f90

X. Ge, S. Binnie, D. Rocca, R. Gebauer, S. Baroni, Comp. Phys. Commun. ***185****, 2080 (2014).*

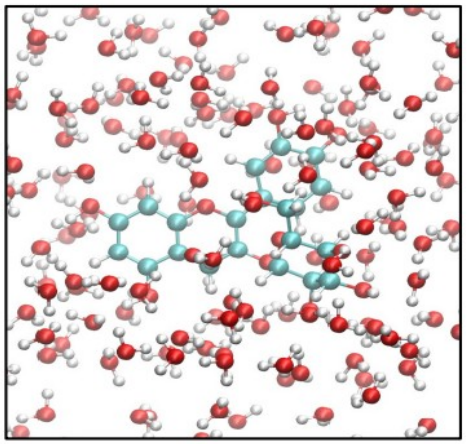
Liouville-Lanczos approach + EN VIR ON

www.quantum-environment.org

Inclusion of the environmental effects is very important for the correct prediction of the optical properties of the molecular systems.

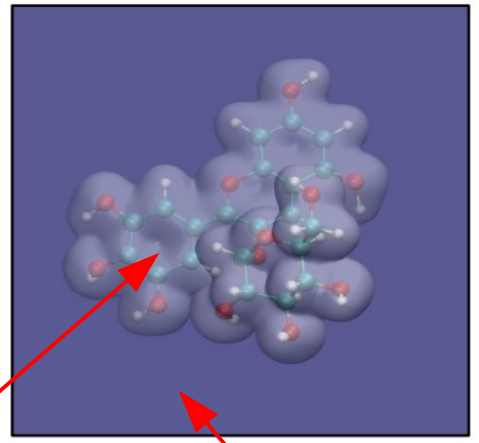
explicit solvent

(atomistically resolved)



continuum solvent

(homogeneous dielectric medium)



inside of the cavity
there is vacuum

outside of the cavity
there is a dielectric medium
with a dielec. constant of the solvent

O. Andreussi, I. Dabo, N. Marzari, J. Chem. Phys. ***136****, 064102 (2012).*

Liouville-Lanczos approach +

turboTDDFT code is interfaced with the **Environ** module.

Environ/solvent.f90

$$(\hat{H}^{\circ}_{\text{vacuum}} + \hat{V}^{\circ}_{\text{polarization}} + \hat{V}^{\circ}_{\text{interface}} - \varepsilon_v - \omega)\tilde{\varphi}'_v(\mathbf{r},\omega)$$

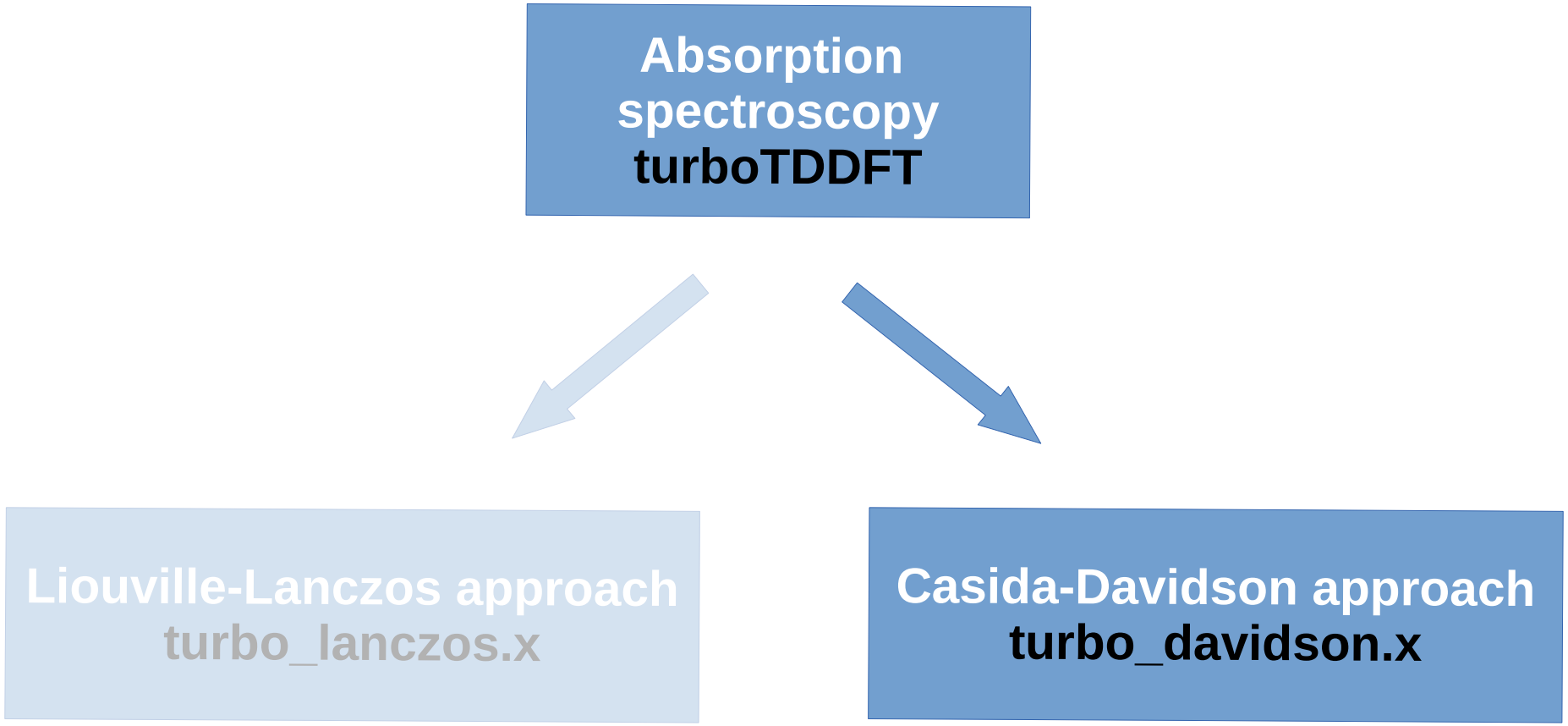
$$+ \hat{P}_c \left[\hat{V}'_{\text{HXC,vacuum}}(\omega) + \hat{V}'_{\text{polarization}}(\omega) + \hat{V}'_{\text{interface}}(\omega)\right] \varphi^{\circ}_v(\mathbf{r}) = -\hat{P}_c \hat{V}'_{ext}\varphi^{\circ}_v(\mathbf{r})$$

Environ/solvent_tddfpt.f90

In the present implementation (QE 5.3.0), Environ-related routines in TDDFPT are inside of the **`#ifdef __ENVIRON`** … **`#endif`** condition.

In the future releases, Environ-related routines in TDDFPT are planned to be patched as e.g. in PW.

I. Timrov, O. Andreussi, A. Biancardi, N. Marzari, and S. Baroni, J. Chem. Phys. ***142****, 034111 (2015).*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Casida-Davidson approach: basic equations

Coupled linear-response TDDFPT equations (resonant and anti-resonant):

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

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

These equations can be re-written as Casida's matrix equation:

$$\begin{pmatrix} 0 & \hat{D} \\ \hat{D} + \hat{K} & 0 \end{pmatrix} \begin{pmatrix} Q \\ P \end{pmatrix} = \omega \begin{pmatrix} Q \\ P \end{pmatrix}$$

interaction terms

where $\hat{D} \longrightarrow (\hat{H}^{\circ} - \varepsilon_v)$ and $\hat{K} \longrightarrow \hat{P}_c \hat{V}'_{\mathrm{HXC}} \varphi^{\circ}_v(\mathbf{r})$

Davidson algorithm is used to solve the Casida's equations and to obtain the eigenvalues of the Liouvillian, which are used for a calculation of the absorption coefficient.

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

Casida-Davidson approach

- The **`turbo_davidson.x`** code supports the same features as the **`turbo_lanczos.x`** code:

  (i.e. ultrasoft implementation, hybrid functionals, Environ, etc.).

- All Davidson subroutines are collected in one module **`TDDFPT/lr_dav_routines.f90`**

- The dependencies of **`turbo_davidson.x`** on **PW** and **PHonon** codes are the same as of **`turbo_lanczos.x`**.

The details of the theory about the Casida-Davidson approach can be found here:

X. Ge, PhD thesis "Seeing colors with TDDFT", SISSA (2013).

Liouville-Lanczos approach

turbo_lanczos.x

Solution method: Computes an absorption coefficient directly without computing eigenvalues of the Liouvillian, using the Lanczos recursion algorithm.

☺ Spectrum is computed *at once* in the large frequency range (only one Lanczos recursion is needed).

☺ No empty states (use of DFPT techniques)

☺ No large-matrix inversions (Lanczos recursion instead)

☹ No information about individual electronic transitions

Casida-Davidson approach

turbo_davidson.x

Solution method: Computes eigenvalues of the Liouvillian by diagonalizing it, and then computes the absorption coefficient from them.

☹ Many eigenvalues are required to compute spectrum in the large energy range.

☺ No empty states (use of DFPT techniques)

☹ Large-matrix diagonalization (Davidson-like solver) ⇒ high RAM

☺ Information about individual electronic transitions

!!!

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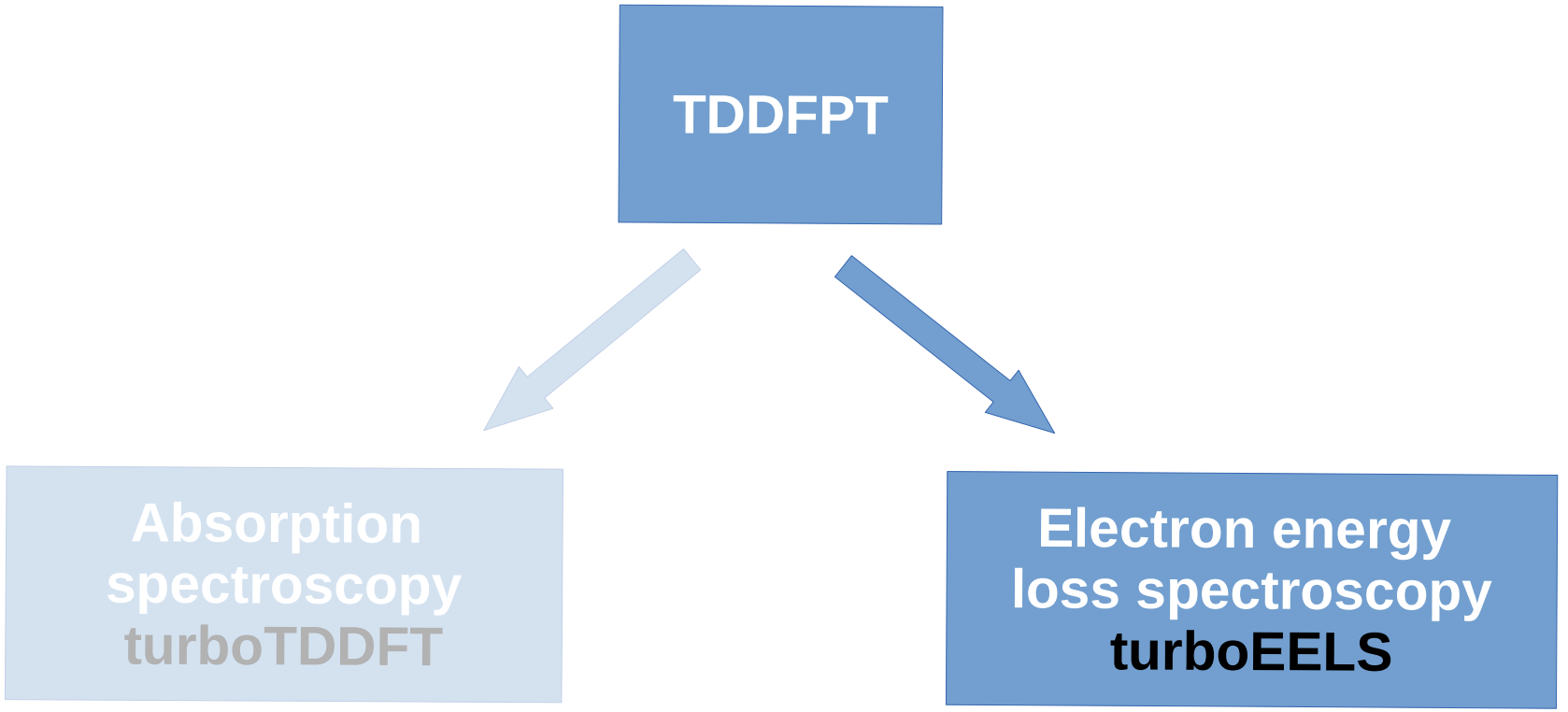
4. Conclusions

Components of the TDDFPT module



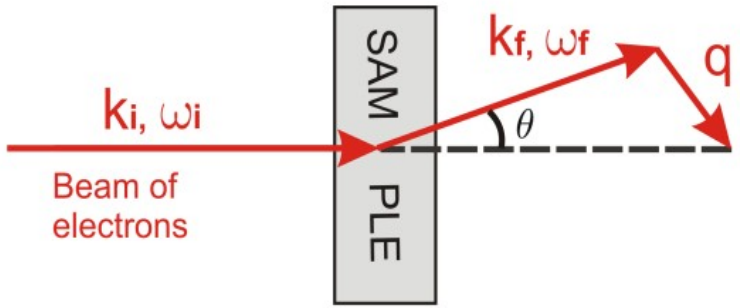
These two codes are strongly interleaved and reside in the same repository, namely **`TDDFPT/src`** .

Restrictions of the turboEELS code

- Linear response regime
- General **k** points algorithm. No **gamma_only** tricks.
- Supports NC and US pseudopotentials. No PAW.
- Hybrid functionals are not supported.
- Adiabatic XC kernels only.
- Unpolarized (`nspin=1`) and noncollinear (`noncolin=.true.`) cases are supported, while the collinear case (`nspin=2`) is not.
- Relativistic effects (spin-orbit coupling) are supported, but only with norm-conserving pseudopotentials.
- Parallelization: PWs, k points.

Electron energy loss spectroscopy (EELS)

Inelastic scattering of incoming electrons



$q = k_i - k_f$ - transferred momentum

$\omega = \omega_i - \omega_f$ - energy loss

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

Single-particle excitations and collective excitations (plasmons)

Perturbation: incoming electrons (plane waves)

$$\tilde{V}'_{\mathrm{ext}}(\mathbf{r},\omega) = \sum_{\mathbf{q}} \tilde{V}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega) = \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \underbrace{\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)}_{=1}$$

- Use of lattice-periodicity
- Use of time-reversal symmetry
- Use of monochromatic decomposition wrt **q**

$$\varphi^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$\tilde{\varphi}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) = e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}\, \tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega)$$

I. Timrov, PhD thesis, École Polytechnique (LSI), France (2013).

*I. Timrov, N. Vast, R. Gebauer, and S. Baroni, PRB **88**, 064301 (2013); ibid. **91**, 139901 (2015).*

Liouville-Lanczos approach for EELS: basic equations

Coupled linear-response TDDFPT equations (resonant and anti-resonant):

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega) + \hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{\,*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) + \hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

interaction terms **perturbation**

These equations can be re-written as a quantum Liouville equation:

$$(\omega - \hat{\mathcal{L}}_{\mathbf{q}}) \cdot \hat{\rho}'_{\mathbf{q}}(\omega) = [\hat{V}'_{\mathrm{ext},\mathbf{q}}(\omega), \hat{\rho}^{\circ}]$$

$$\hat{\mathcal{L}}_{\mathbf{q}} \cdot \hat{\rho}'_{\mathbf{q}} \equiv [\hat{H}^{\circ}, \hat{\rho}'_{\mathbf{q}}] + [\hat{V}'_{\mathrm{HXC},\mathbf{q}}, \hat{\rho}^{\circ}]$$

Susceptibility

$$\chi(\mathbf{q},\mathbf{q};\omega) = \left(\hat{n}_{\mathbf{q}}, (\omega - \hat{\mathcal{L}}_{\mathbf{q}})^{-1} \cdot [\hat{V}'_{\mathrm{ext},\mathbf{q}}(\omega), \hat{\rho}^{\circ}]\right)$$

Loss function: $$-\mathrm{Im}[\epsilon^{-1}(\mathbf{q},\omega)] = -\frac{4\pi}{|\mathbf{q}|^2}\,\mathrm{Im}[\chi(\mathbf{q},\mathbf{q};\omega)]$$

Liouville-Lanczos approach for EELS: implementation

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) \;+\; \hat{P}_c^{\mathbf{k}+\mathbf{q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k}+\mathbf{q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k}+\mathbf{q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) + \hat{P}_c^{\mathbf{k}+\mathbf{q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k}+\mathbf{q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

perturbation

TDDFPT/lr_dvpsi_eels.f90

$$\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega) = 1 \quad \Rightarrow \quad \hat{P}_c^{\mathbf{k}+\mathbf{q}}\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) - \sum_{n'}^{N_{occ}} u^{\circ}_{n',\mathbf{k}+\mathbf{q}}(\mathbf{r})\,\langle u^{\circ}_{n',\mathbf{k}+\mathbf{q}} | u^{\circ}_{n,\mathbf{k}} \rangle$$

PH/orthogonalize.f90

Projector on empty states:

$$\hat{P}_c^{\mathbf{k}+\mathbf{q}} = 1 - \sum_{n'}^{N_{occ}} |u^{\circ}_{n',\mathbf{k}+\mathbf{q}}\rangle\langle u^{\circ}_{n',\mathbf{k}+\mathbf{q}}|$$

Non-SCF calculation at **k+q** is needed

TDDFPT/lr_setup_nscf.f90

(analogue of PH/set_defaults_pw.f90)

TDDFPT/lr_run_nscf.f90

(analogue of PH/run_nscf.f90)

S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, RMP. ***73****, 515 (2001).*

No empty states!

Liouville-Lanczos approach for EELS: implementation

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega) \;+\; \hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k-q}}(\mathbf{r},-\omega) + \hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

perturbation

`TDDFPT/lr_dvpsi_eels.f90`

$$\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega) = 1 \quad \Rightarrow \quad \hat{P}_c^{\mathbf{k+q}}\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) - \sum_{n'}^{N_{occ}} u^{\circ}_{n',\mathbf{k+q}}(\mathbf{r})\,\langle u^{\circ}_{n',\mathbf{k+q}} | u^{\circ}_{n,\mathbf{k}} \rangle$$

Different ordering of the **G** vectors

`PH/cft_wave.f90`

Inverse Fourier (+1) or Fourier (-1) transform of a wavefunction

+1 : order as **k+G**

-1 : order as **k+q+G**

Liouville-Lanczos approach for EELS: implementation

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega) \;+\; \hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) + \hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$\left[\underbrace{\begin{pmatrix} \hat{D}_{\mathbf{q}} + \hat{K}_{\mathbf{q}} & \hat{K}_{\mathbf{q}} \\ -\hat{K}_{\mathbf{q}} & -\hat{D}_{\mathbf{q}} - \hat{K}_{\mathbf{q}} \end{pmatrix}}_{\hat{\mathcal{L}}_{\mathbf{q}}} - \omega \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \begin{pmatrix} \{\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega)\} \\ \{\tilde{u}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega)\} \end{pmatrix} = \begin{pmatrix} \{-\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})\} \\ \{-\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})\} \end{pmatrix}$$

TDDFPT/lr_apply_liouvillian_eels.f90

Liouville-Lanczos approach for EELS: implementation

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega) \;+\; \hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} + \omega)\,\tilde{u}'^{*}_{n,-\mathbf{k-q}}(\mathbf{r},-\omega) + \hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$\left[\begin{pmatrix} \hat{D}_{\mathbf{q}} + \hat{K}_{\mathbf{q}} & \hat{K}_{\mathbf{q}} \\ -\hat{K}_{\mathbf{q}} & -\hat{D}_{\mathbf{q}} - \hat{K}_{\mathbf{q}} \end{pmatrix} - \omega \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\right] \begin{pmatrix} \{\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega)\} \\ \{\tilde{u}'^{*}_{n,-\mathbf{k-q}}(\mathbf{r},-\omega)\} \end{pmatrix} = \begin{pmatrix} \{-\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})\} \\ \{-\hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})\} \end{pmatrix}$$

$$\hat{\mathcal{L}}_{\mathbf{q}}$$

TDDFPT/lr_apply_liouvillian_eels.f90

$$\hat{D}_{\mathbf{q}} \longrightarrow (\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}})$$

PH/h_psiq.f90

$$\hat{K}_{\mathbf{q}} \longrightarrow \hat{P}^{\mathbf{k+q}}_{c}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,u^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

TDDFPT/lr_dv_of_drho_eels.f90

$$\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega) = \int \left(\frac{1}{|\mathbf{r}-\mathbf{r}'|} + \kappa_{\mathrm{XC}}(\mathbf{r},\mathbf{r}')\right) \tilde{n}'_{\mathbf{q}}(\mathbf{r}',\omega)\, e^{-i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}\, d\mathbf{r}'$$

TDDFPT/lr_calc_dens_eels.f90

$$\tilde{n}'_{\mathbf{q}}(\mathbf{r}',\omega) = 2\sum_{n,\mathbf{k}} u^{\circ *}_{n,\mathbf{k}}(\mathbf{r}) \left[\tilde{u}'_{n,\mathbf{k+q}}(\mathbf{r},\omega) + \tilde{u}'^{*}_{n,-\mathbf{k-q}}(\mathbf{r},-\omega)\right]$$

Liouville-Lanczos approach for EELS: implementation

- In the actual implementation of the Liouville-Lanczos approach for EELS, the *standard batch representation* **(SBR)** is used (as in **turboTDDFT**).

- In the **turboEELS** code the same Lanczos algorithm is used as in **turboTDDFT**.

  `TDDFPT/lr_lanczos.f90`

  `TDDFPT/tools/lr_calculate_spectrum.f90`

- Use of the symmetry of the small group of **q**

  `TDDFPT/lr_sym_eels.f90` (analogue of `PH/symdvscf.f90`)
  `TDDFPT/lr_psym_eels.f90` (analogue of `PH/psymdvscf.f90`)
  `TDDFPT/lr_smallgq.f90` (analogue of `PH/smallg_q`, `PH/smallgq`)

- Description of the **turboEELS** code can be found here:

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

Liouville-Lanczos approach for EELS: spin-orbit coupling

The **turboEELS** code supports spin-orbit coupling, but only with norm-conserving pseudopotentials.

Two-component spinor wavefunctions

$$(\hat{H}^{\circ}_{\mathbf{k+q}} - \varepsilon^{\circ}_{n,\mathbf{k}} - \omega)\,\tilde{U}'_{n,\mathbf{k+q}}(\mathbf{r},\omega) \;+\; \hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)\,\mathbb{1}\,U^{\circ}_{n,\mathbf{k}}(\mathbf{r}) = -\hat{P}_c^{\mathbf{k+q}}\,\tilde{v}'_{\mathrm{ext},\mathbf{q}}(\mathbf{r},\omega)\,\mathbb{1}\,U^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

Contains the spin-orbit coupling term

- Non-collinear case
- Requires fully relativistic PP's

`PH/apply_dpot.f90`

`PH/addusdbec_nc.f90`

`PH/set_dbecsum_nc`

Liouville-Lanczos approach for EELS: ultrasoft case

PH/h_psiq.f90

PH/newdq.f90

PH/adddvscf.f90

$$\hat{S}^{-1}\left(\hat{H}^{\circ}-\hat{S}\left(\varepsilon^{\circ}_{n,\mathbf{k}}+\omega\right)\right)\tilde{\varphi}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega)$$

$$+\hat{S}^{-1}\hat{P}_c^{\dagger}\left[\tilde{V}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r},\omega)+\sum_{n,m,I}\int \tilde{V}'_{\mathrm{HXC},\mathbf{q}}(\mathbf{r}',\omega)\,Q^{I}_{nm}(\mathbf{r}')\,d\mathbf{r}'\,|\beta^{I}_{n}\rangle\langle\beta^{I}_{m}|\right]\varphi^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

$$=-\hat{S}^{-1}\hat{P}_c^{\dagger}\left[e^{i\mathbf{q}\cdot\mathbf{r}}+\sum_{n,m,I}\int e^{i\mathbf{q}\cdot\mathbf{r}'}\,Q^{I}_{nm}(\mathbf{r}')\,d\mathbf{r}'\,|\beta^{I}_{n}\rangle\langle\beta^{I}_{m}|\right]\varphi^{\circ}_{n,\mathbf{k}}(\mathbf{r})$$

TDDFPT/sm1_psi.f90

TDDFPT/lr_addus_dvpsi.f90

PH/orthogonalize.f90

I. Timrov, T. Gorni, A. Dal Corso, N. Vast, S. Baroni, et al. (unpublished).

Liouville-Lanczos approach for EELS: ultrasoft case

The response charge-density reads:

TDDFPT/lr_calc_dens_eels.f90

(analogue of PH/incdrhoscf.f90)

$$\tilde{n}'_{\mathbf{q}}(\mathbf{r},\omega) = 2\sum_{n,\mathbf{k}} \varphi^{\circ *}_{n,\mathbf{k}}(\mathbf{r}) \left[\tilde{\varphi}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \tilde{\varphi}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega)\right]$$

$$+2\sum_{n,\mathbf{k}}\sum_{n,m,I} Q^{I}_{nm}(\mathbf{r})\langle\varphi^{\circ}_{n,\mathbf{k}}|\beta'_{n}\rangle\langle\beta'_{m}|\left[\tilde{\varphi}'_{n,\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \tilde{\varphi}'^{*}_{n,-\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega)\right]\rangle$$

PH/addusdbec.f90

TDDFPT/lr_addusddens.f90

(analogue of PH/addusddens.f90)

I. Timrov, T. Gorni, A. Dal Corso, N. Vast, S. Baroni, et al. (unpublished).

Perspectives

- Generalization of TDDFPT to magnetic systems (magnons)
- Generalization of the **turboEELS** code to hybrid functionals (excitons)

Thank you for your attention!