Kubo-Greenwood Electric Conductivity Tensor: Essentials and Open-source Implementation

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Univ. Florida Orbital-Free DFT & Free-energy DFT Group

Sam Trickey: Today, Room 261, 9:24-9:36 am: Tunable non-interacting free-energy functionals
Jim Dufty: Monday, Room 267; 4:54 pm: Equivalence of exchange-correlation functionals for the inhomogeneous electron gas and jellium at finite temperature
Valentin Karasiev: Today, Room 289; 11:51 am: Generalized Gradient Approximation for Exchange-Correlation Free Energy
Lázaro Calderín: This talk

Kai Luo — **Affiliates: Frank Harris (U. Utah); Keith Runge (U. Arizona)**
Daniel Mejia — **Alumni: Deb Chakraborty, Támas Gál, Olga Shukruto, Travis Sjostrom**

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NERSC National Energy Research Scientific Computing Center

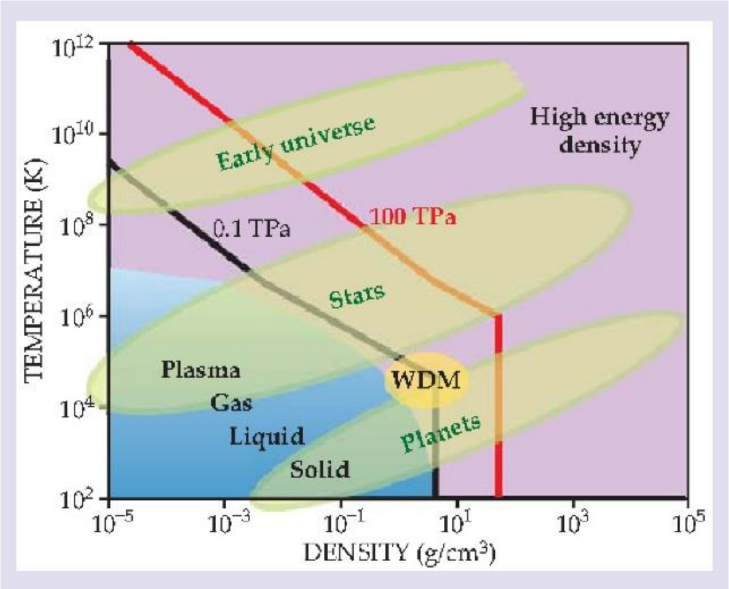
HiPerGator RESEARCH COMPUTING

Publications, preprints, local pseudopotentials, and codes at
http://www.qtp.ufl.edu/ofdft

Motivation

Schematic temperature-density diagram:
Aluminum [Phys. Today 63(6), 28 (2010)]

Number of States,
Size of the Basis Set,
Core States



Core States

- **Orbital Free Density Functional Theory for Molecular Dynamics**
- **Calculation of properties requires Kohn-Sham orbitals, but there is an overall gain in speed**
- **Electrical conductivity is an important property to predict, which needs a code that overcomes the mentioned difficulties**

Goal: full-featured post-processing tool for Quantum Espresso

KGEC: (K)ubo (G)reenwood (E)lectron (C)onductivity

Main features of KGEC

- **Coded in modular Fortran 90.**
- **Calculates the full complex conductivity tensor.**
- **Uses either the original KG formula or the most popular one (in terms of a Dirac delta function & approximation)**
- **Performs a decomposition into intra- and inter-band contributions as well as degenerate state contributions.**
- **Calculates the direct-current conductivity tensor directly.**
- **Provides both Gaussian and Lorentzian representations of the Dirac delta function. (A Lorentzian always is recommended.)**
- **MPI parallelized over k-points, bands, and plane waves, with an option to recover plane wave processes for their use in bands parallelization**
- **Allows for writing and reading of the gradient matrix elements.**
- **Fast convergence with respect to k-point density.**

Requires investigating details of the K-G formalism

Kubo-Greenwood Conductivity Tensor

$$\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega),$$

$$\sigma_1(\omega) = \frac{2e^2\hbar^3}{m_e^2 V} \sum_m \sum_{m'} \frac{\Delta f_{m'm}}{\Delta\epsilon_{mm'}} \langle m|\nabla|m'\rangle\langle m'|\nabla|m\rangle \frac{\delta/2}{(\Delta\epsilon_{mm'} - \hbar\omega)^2 + \delta^2/4}$$

$$\sigma_2(\omega) = \frac{2e^2\hbar^3}{m_e^2 V} \sum_m \sum_{m'} \frac{\Delta f_{m'm}}{\Delta\epsilon_{mm'}} \langle m|\nabla|m'\rangle\langle m'|\nabla|m\rangle \frac{(\Delta\epsilon_{mm'} - \hbar\omega)}{(\Delta\epsilon_{mm'} - \hbar\omega)^2 + \delta^2/4}$$

$$\Delta f_{m'm} = f(\epsilon_{m'}) - f(\epsilon_m)$$

$$\Delta\epsilon_{mm'} = \epsilon_m - \epsilon_{m'}$$

Kubo-Greenwood Conductivity Tensor

For small δ, the Lorentzian in $\sigma_1(\omega)$ behaves like a Dirac delta function, that is

$$\frac{\delta/2}{(\Delta\epsilon_{mm'} - \hbar\omega)^2 + \delta^2/4} \approx \pi\delta(\Delta\epsilon_{mm'} - \hbar\omega),$$

which allows $\sigma_1(\omega)$ to be written as

$$\sigma_1(\omega) = \frac{2\pi e^2\hbar^3}{m_e^2 V} \sum_m \sum_{m'} \frac{\Delta f_{m'm}}{\Delta\epsilon_{mm'}} \langle m|\nabla|m'\rangle\langle m'|\nabla|m\rangle\delta(\Delta\epsilon_{mm'} - \hbar\omega).$$

or

$$\sigma_1(\omega) = \frac{2\pi e^2\hbar^2}{m_e^2 V\omega} \sum_m \sum_{m'} \Delta f_{m'm} \langle m|\nabla|m'\rangle\langle m'|\nabla|m\rangle\delta(\Delta\epsilon_{mm'} - \hbar\omega).$$

Approximation by introducing only the Dirac delta function keeps all contributions and allows for recovery of original KG expression. Needs a careful treatment for *m=m'*, and degeneracies

Usual KG formula, typically approximated:
1) By introducing the Dirac delta function,
2) Taking into account only inter-band contributions
No recovery of the KG expression possible

Kubo-Greenwood Conductivity Tensor in Bloch States (Real Part):

$$\sigma_1(\omega) = -\frac{2e^2\hbar^3}{m_e^2\Omega}\sum_{\mathbf{k}} w_{\mathbf{k}}\Big[\sum_n \frac{\partial f(\epsilon_{n\mathbf{k}})}{\partial \epsilon_{n\mathbf{k}}}\Re\big(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle\big)\frac{\delta/2}{(\hbar\omega)^2+\delta^2/4}$$
$$+\sum_{\substack{n\neq n' \\ \epsilon_{n\mathbf{k}}=\epsilon_{n'\mathbf{k}}}} \frac{\partial f(\epsilon_{n\mathbf{k}})}{\partial \epsilon_{n\mathbf{k}}}\Re\big(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n'\mathbf{k}}\rangle\langle\Psi_{n'\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle\big)\frac{\delta/2}{(\hbar\omega)^2+\delta^2/4}$$
$$-\sum_{\substack{n\neq n' \\ \epsilon_{n\mathbf{k}}\neq\epsilon_{n'\mathbf{k}}}} \frac{\Delta f_{n'\mathbf{k},n\mathbf{k}}}{\Delta \epsilon_{n\mathbf{k},n'\mathbf{k}}}\Re\big(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n'\mathbf{k}}\rangle\langle\Psi_{n'\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle\big)\frac{\delta/2}{(\Delta\epsilon_{n\mathbf{k},n'\mathbf{k}}-\hbar\omega)^2+\delta^2/4}\Big]$$

Decomposition into intra-band contribution, degeneracy contribution, and inter-band contribution

(similarly for the imaginary part)

DC Component

$$\sigma_{dc} = -\frac{2e^2\hbar^3}{m_e^2\Omega}\sum_{\mathbf{k}} w_{\mathbf{k}}\Big[\frac{2}{\delta}\sum_{n}\frac{\partial f(\epsilon_{n\mathbf{k}})}{\partial \epsilon_{n\mathbf{k}}}\Re(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle)$$
$$+\frac{2}{\delta}\sum_{\substack{n\neq n' \\ \epsilon_{n\mathbf{k}}=\epsilon_{n'\mathbf{k}}}}\frac{\partial f(\epsilon_{n\mathbf{k}})}{\partial \epsilon_{n\mathbf{k}}}\Re(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n'\mathbf{k}}\rangle\langle\Psi_{n'\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle)$$
$$-\sum_{\substack{n\neq n' \\ \epsilon_{n\mathbf{k}}\neq\epsilon_{n'\mathbf{k}}}}\frac{\Delta f_{n'\mathbf{k},n\mathbf{k}}}{\Delta \epsilon_{n\mathbf{k},n'\mathbf{k}}}\Re(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n'\mathbf{k}}\rangle\langle\Psi_{n'\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle)\frac{\delta/2}{(\Delta\epsilon_{n\mathbf{k},n'\mathbf{k}})^2+\delta^2/4}\Big]$$

Drude Component (no inter-band contribution)

$$\sigma_{dc}^{D} = -\frac{2e^2\hbar^2\tau}{m_e^2\Omega}\sum_{\mathbf{k}} w_{\mathbf{k}}\Big[\sum_{n}\frac{\partial f(\epsilon_{n\mathbf{k}})}{\partial \epsilon_{n\mathbf{k}}}\Re(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle)$$
$$+\sum_{n\neq n'}\delta_{\epsilon_{n\mathbf{k}}\epsilon_{n'\mathbf{k}}}\frac{\partial f(\epsilon_{n\mathbf{k}})}{\partial \epsilon_{n\mathbf{k}}}\Re(\langle\Psi_{n\mathbf{k}}|\nabla|\Psi_{n'\mathbf{k}}\rangle\langle\Psi_{n'\mathbf{k}}|\nabla|\Psi_{n\mathbf{k}}\rangle)\Big]$$

$\tau = \frac{2\hbar}{\delta} \longrightarrow$ **Defines the delta-width as the inverse of the average inter-collision time**

Analytical expressions for the DC components also obtained for the approximated KG formulas

Sum Rule for a particular state:

$$\frac{2}{m_e} \sum_{\substack{m'=1 \\ m' \neq n \\ \epsilon_{m'} \neq \epsilon_n}}^{\infty} \frac{|\langle m' | \hat{p}_\alpha | n \rangle|^2}{(\epsilon_{m'} - \epsilon_n)} = 1$$

Sum Rule in terms of the occupation numbers:

$$S_f = \frac{2}{3 m_e N_e} \sum_{\alpha=1}^{3} \sum_{m=1}^{\infty} \sum_{\substack{n=1 \\ n \neq m \\ \epsilon_n \neq \epsilon_m}}^{\infty} (f(\epsilon_n) - f(\epsilon_m)) \frac{|\langle m | \hat{p}_\alpha | n \rangle|^2}{(\epsilon_m - \epsilon_n)} = 1$$

Sum Rule for the integral of the average trace:

$$S_\omega = \frac{2 m_e V}{3 \pi e^2 N_e} \int_0^\infty d\omega \, Tr(\sigma_1(\omega)) \geq 1$$

Because of intra-band and degeneracy contributions

Sum Rule for a particular state:

Finite Number of States

$$\frac{2}{m_e} \sum_{\substack{m'=1 \\ m' \neq n \\ \epsilon_{m'} \neq \epsilon_n}}^{N_s} \frac{|\langle m'|\hat{p}_\alpha|n\rangle|^2}{(\epsilon_{m'} - \epsilon_n)} \neq 1$$

→ **Not valid**

↓

Sum Rule in terms of the occupation numbers:

$$S_f = \frac{2}{3 m_e N_e} \sum_{\alpha=1}^{3} \sum_{m=1}^{N_s} \sum_{\substack{n=1 \\ n \neq m \\ \epsilon_n \neq \epsilon_m}}^{N_s} (f(\epsilon_n) - f(\epsilon_m)) \frac{|\langle m|\hat{p}_\alpha|n\rangle|^2}{(\epsilon_m - \epsilon_n)} \neq 1$$

Incomplete sum

↓

Sum Rule for the integral of the average trace:

$$S_\omega = \frac{2 m_e V}{3 \pi e^2 N_e} \int_0^\infty d\omega \, Tr(\sigma_1(\omega)) \neq 1$$

← **Can be either greater or less than 1.**

Similar problem for the conductivity

...

Gradient Matrix Elements for PAW datasets

$$\langle \Psi_{n\mathbf{k}}|\nabla|\Psi_{n'\mathbf{k}}\rangle = \langle \tilde{\Psi}_{n\mathbf{k}}|\nabla|\tilde{\Psi}_{n'\mathbf{k}}\rangle + \\ + \sum_i \sum_{\ell m} \sum_{\ell' m'} \langle \tilde{\Psi}_{n\mathbf{k}}|\tilde{p}_{i\ell m}\rangle \left[\langle \varphi_{i\ell m}|\nabla|\varphi_{i\ell' m'}\rangle - \langle \tilde{\varphi}_{i\ell m}|\nabla|\tilde{\varphi}_{i\ell' m'}\rangle\right] \langle \tilde{p}_{i\ell' m'}|\tilde{\Psi}_{n'\mathbf{k}}\rangle$$

Calculated in the one-center approximation

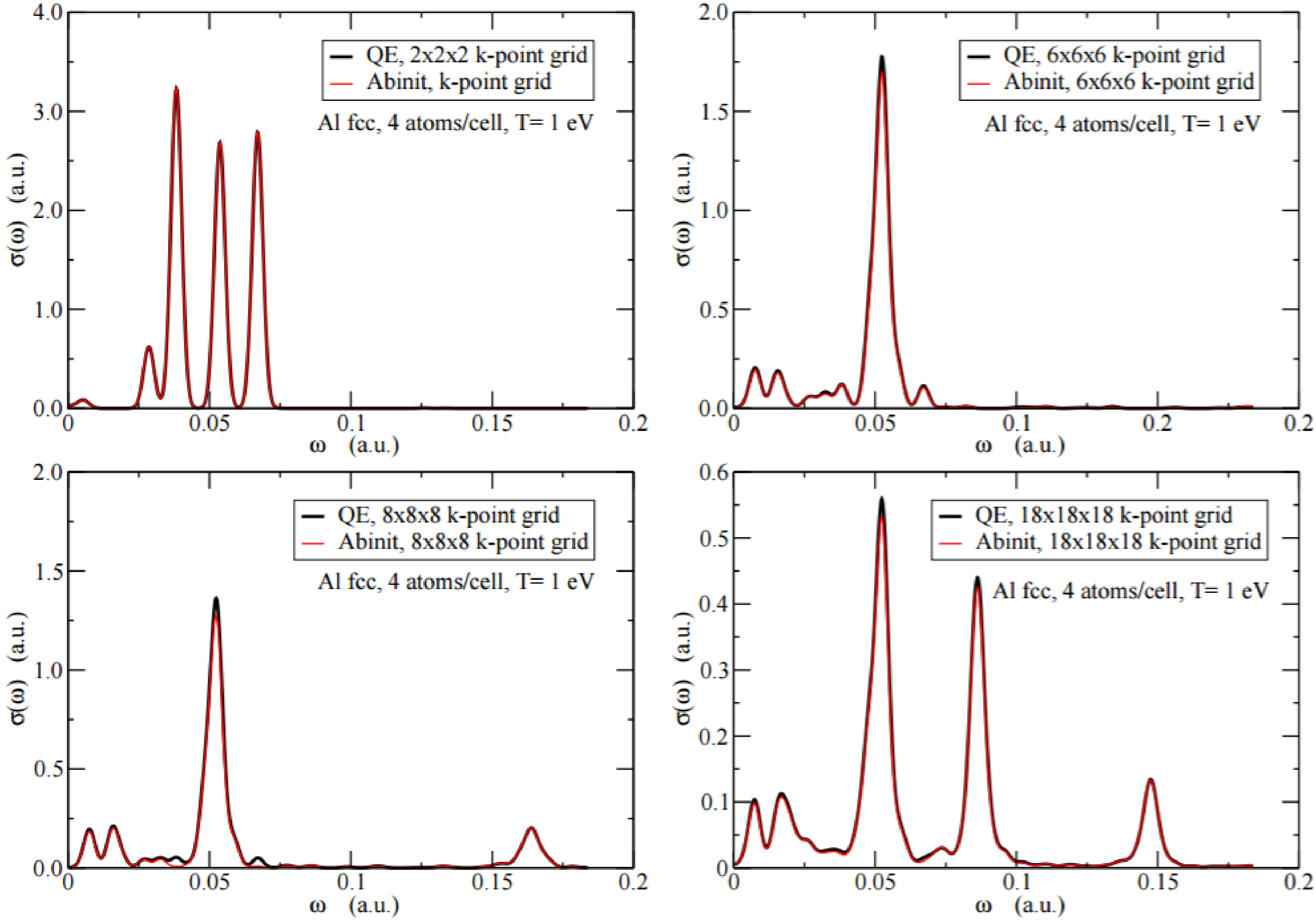
$$\varphi_{i\ell m}(\mathbf{r}-\mathbf{R}_i) = R_{i\ell}(|\mathbf{r}-\mathbf{R}_i|)Y_{\ell m}(\theta,\phi)$$ ⟶ **Atomic Orbitals**

$$\tilde{\varphi}_{ilm}(\mathbf{r}-\mathbf{R}_i) = \tilde{R}_{i\ell}(|\mathbf{r}-\mathbf{R}_i|)Y_{\ell m}(\theta,\phi)$$ ⟶ **Pseudo Orbitals**

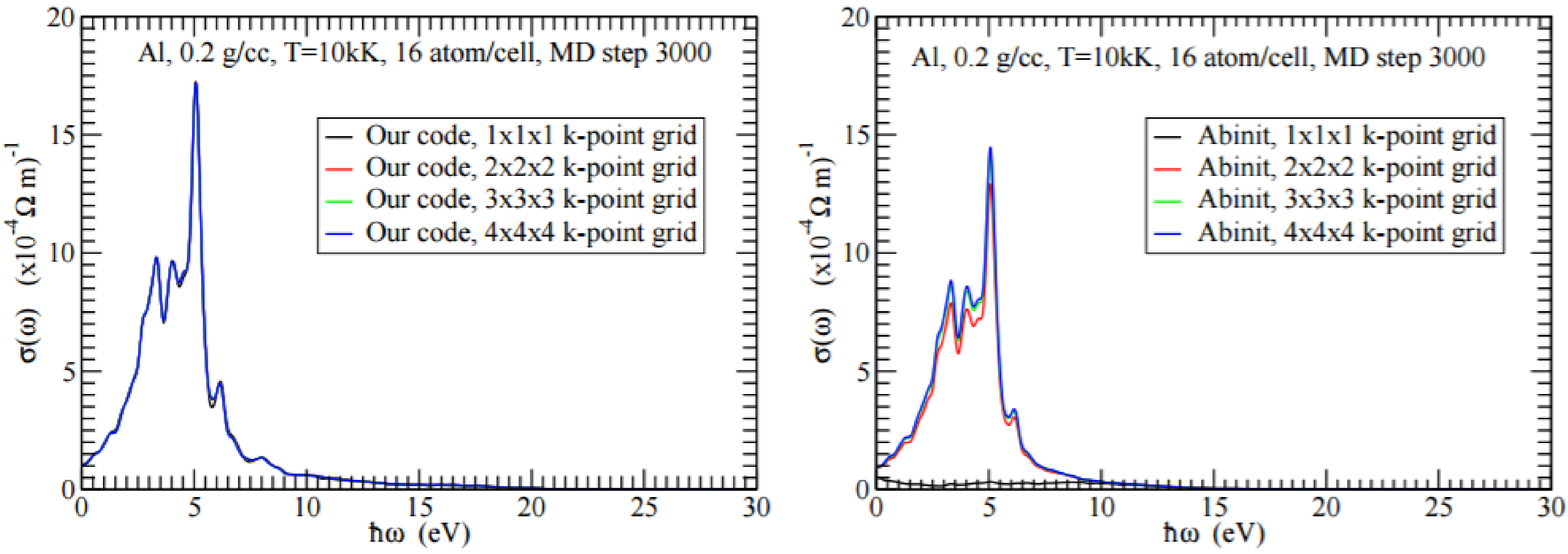
$$\tilde{p}_{i\ell m}(\mathbf{r}-\mathbf{R}_i) = \tilde{p}_{i\ell}(|\mathbf{r}-\mathbf{R}_i|)Y_{\ell m}(\theta,\phi)$$ ⟶ **Projectors**

Angular integrals calculated analytically
Radial integrals calculated numerically

Comparison with Abinit (ordered system)



Comparison with Abinit (disordered system)



Remarks

- **Survey of the KG theory, leading to new analytical results, algorithm and code (KGEC).**
- **KGEC implemented as a post-processing tool for Quantum Espresso (from version 5.1 to version 6.0).**
- **KGEC is MPI parallelized taking into account the demanding computational conditions usually needed in WDM calculations. It is in the final stages of beta testing.**
- **Work still in progress to tackle the problems associated with finite numbers of states.**