Calculations of the optical and electrical properties within the PAW formalism

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Motivations

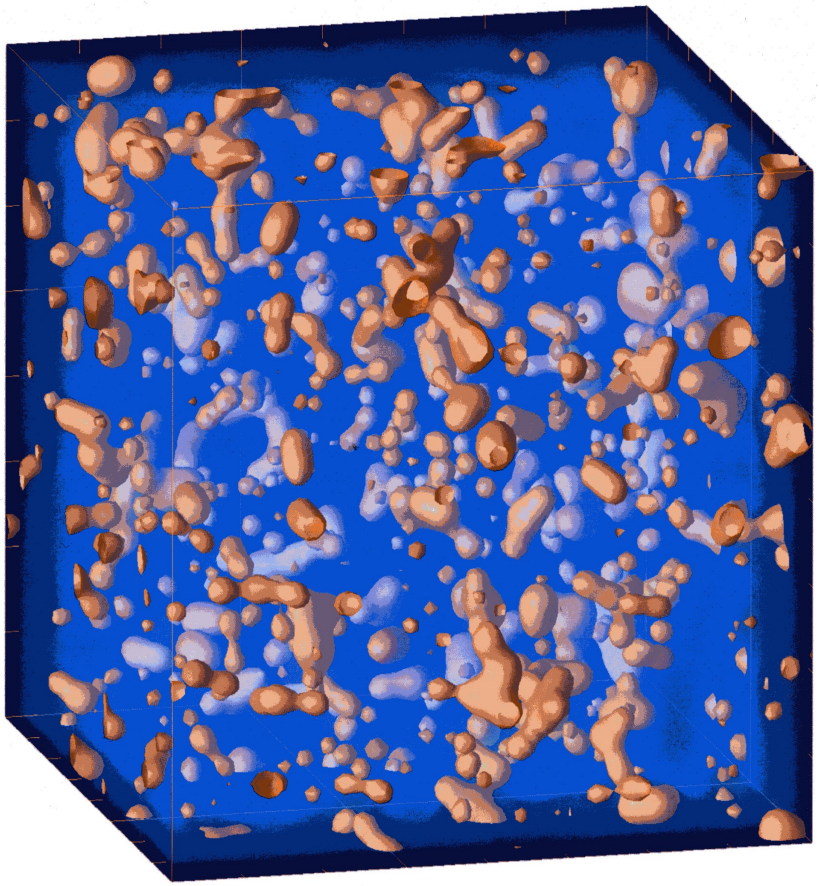

FIGURE: Dense hydrogen at $\rho = 1\text{g/cm}^3$ and T=3eV

- Studies of dense plasmas: $\sim \rho_0$ and T$\sim 1 - 10$eV
- Molecular dynamics simulations
- Finite temperature: few hundred states
- Gamma point; from 100 to 1000 particles
- Calculate the dynamical, electrical, and optical properties
- $\sigma_1(\mathbf{k},\omega)$ gives access to the other quantities

PAW formalism: X-ray spectra where core orbitals are involved

Kubo-Greenwood Formulation

Within the Kubo-Greenwood formulation, the real part of the conductivity is given by

$$\sigma_1(\mathbf{k},\omega) = \frac{2\pi}{3\omega\Omega}\sum_{\mathbf{j=1}}^{\mathbf{n_b}}\sum_{\mathbf{i=1}}^{\mathbf{n_b}}\sum_{\alpha=1}^{3} (F(\epsilon_{i,\mathbf{k}}) - F(\epsilon_{j,\mathbf{k}})) \times |\langle\psi_{j,\mathbf{k}}|\nabla_\alpha|\psi_{i,\mathbf{k}}\rangle|^2 \delta(\epsilon_{j,\mathbf{k}} - \epsilon_{i,\mathbf{k}} - \omega).$$

where

- m_e and e are the electron charge and the electron mass
- i and j are the sum over the n_b orbitals
- α stands for the 3 directions x, y, et z
- Ω is the volume of the simulation cell
- $\epsilon_{i,\mathbf{k}}$ and $\psi_{i,\mathbf{k}}$ are the i^{th} orbital for the k-point $\mathbf{k}$
- $F(\epsilon_{i,\mathbf{k}})$ are the occupations

Dipole matrix elements within the PAW formalism

Within the PAW formalism, $|\psi_{i,\mathbf{k}}\rangle$ is connected to $|\tilde{\psi}_{i,\mathbf{k}}\rangle$ by the linear operator T:

$$|\psi_{i,\mathbf{k}}\rangle = |\tilde{\psi}_{i,\mathbf{k}}\rangle + \sum_{\mathbf{R},n} \left(|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle \right) \langle \tilde{p}_{\mathbf{R},n} | \tilde{\psi}_{i,\mathbf{k}} \rangle .$$

In PAW the dipole matrix elements become:

$$\begin{aligned} \langle \psi_{m,\mathbf{k}} | \vec{\nabla} | \psi_{n,\mathbf{k}} \rangle = \quad & \langle \tilde{\psi}_{m,\mathbf{k}} | \vec{\nabla} | \tilde{\psi}_{n,\mathbf{k}} \rangle \\ & + \sum_{i,j} \langle \tilde{\psi}_{m,\mathbf{k}} | \tilde{p}_i \rangle \langle \tilde{p}_j | \tilde{\psi}_{n,\mathbf{k}} \rangle \left(\langle \phi_i | \vec{\nabla} | \phi_j \rangle - \langle \tilde{\phi}_i | \vec{\nabla} | \tilde{\phi}_j \rangle \right) \end{aligned}$$

where i and j stand for the sum over $\{\mathbf{R}, n\}$.

First term: plane wave contribution

We evaluate the first term in cartesian coordinates using the plane wave expansion

$$\psi_{m,\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \sum_{\vec{G}} C^m_{\vec{G}} e^{i(\vec{G}+\vec{k}).\vec{r}}$$

which leads to

$$\langle \tilde{\psi}_{m,\mathbf{k}} | \nabla_\alpha | \tilde{\psi}_{n,\mathbf{k}} \rangle = \sum_{\vec{G}} C^{*m}_{\vec{G}} C^n_{\vec{G}} (\vec{G}+\vec{k}).\vec{i}_\alpha$$

Second and third terms: atomic contributions

We use the standart separation of an atomic orbital into a radial and an angular parts $\phi(\vec{r}) = \frac{u_{n,l}(r)}{r} S_{l,m}(\hat{r})$ where $S_{l,m}(\hat{r})$ are the real spherical harmoniques, and express the gradient in spherical coordinates

$$\vec{\nabla} = \begin{pmatrix} \frac{\partial}{\partial r} \\ \frac{1}{r}\frac{\partial}{\partial \theta} \\ \frac{1}{r sin\theta}\frac{\partial}{\partial \phi} \end{pmatrix}, \quad \begin{aligned} \hat{r} &= \sin\theta\cos\phi\vec{i} + \sin\theta\sin\phi\vec{j} + \cos\theta\vec{k}, \\ \hat{\theta} &= \cos\theta\cos\phi\vec{i} + \sin\phi\cos\phi\vec{j} - \sin\theta\vec{k}, \\ \hat{\phi} &= -\sin\phi\vec{i} + \cos\phi\vec{j}. \end{aligned}$$

We also use the expression of $\hat{r}$, $\hat{\theta}$, et $\hat{\phi}$ in cartesienne coordinates. This leads to 2 types of radial integrals and 8 angular integrals

$$f^1 = \int dr u_{n,l}(r)\frac{\partial}{\partial r}u_{n',l'}(r),$$
$$f^2 = \int dr \frac{1}{r} u_{n,l}(r)u_{n',l'}(r).$$

Implementation in Abinit

- Ground state calculation with prtnabla=1 and prtwfk=1: call to optics_paw.F90 from outscfcv.F90 (in /11drive)
  - Subroutine optics_paw.F90 (in /11drive)
    - call to ctocprj.f: calculations of the projectors $\langle \tilde{p}_j | \tilde{\psi}_{n,\mathbf{k}} \rangle$
    - calculate the radial integrals f_1 and f_2 for $u_{n,l}(r)$ and $\tilde{u}_{n,l}(r)$
    - call to int_ang.F90 calculate the angular integrals
    - write the matrix elements in the file filename_OPT
- Postprocessing of the dipole matrix elements using conducti
  - read the matrix elements in filename_OPT
  - calculate the electrical and thermal conductivities
  - execution: conducti <filename.files
  - filename.in:
    2 ! 2 for PAW calculations
    filename_OPT ! optics filename
    filename_WFK ! ground state data file obtained with prtwfk=1
    0.0036749 !temperature
    1.000 ! K points weight
    0.073119 0.0000001 5.00 1000 !width, ω_{min}, ω_{max}, nbr pts

Aluminum conductivity

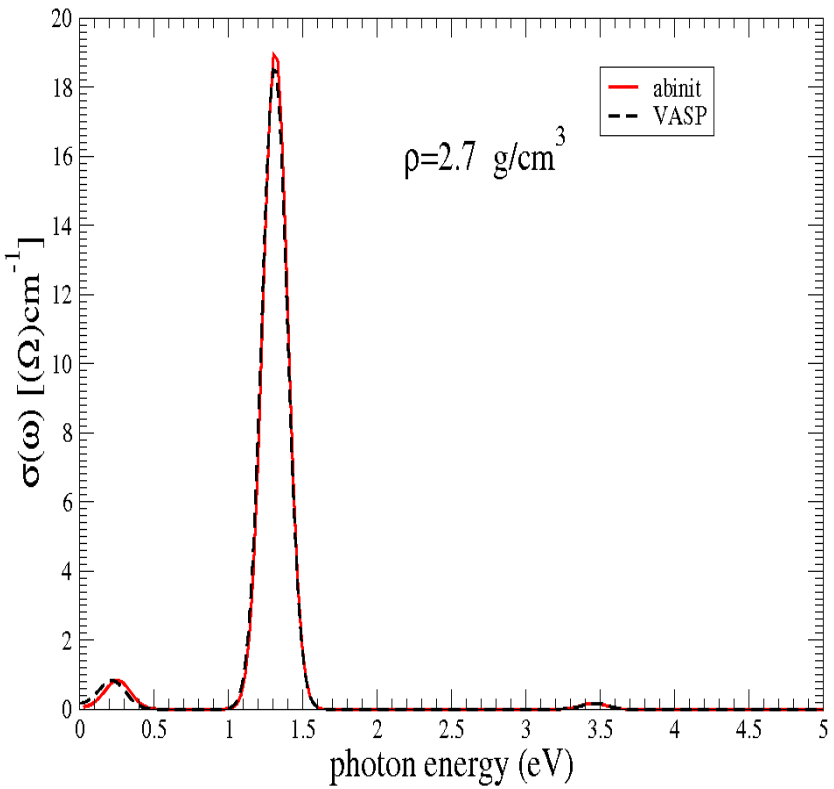

FIGURE: Aluminum conductivity

- 4 atoms in FCC position
- LDA pseudopotential
- Temperature of 1eV
- Very close agreement with a similar VASP calculation

X-ray absorption: Theory

- $\alpha(\omega)$ is directly related to the real part of the electrical conductivity $\alpha(\omega) = \sigma_1(\omega)/n(\omega)$ where $n(\omega)$ is the index of refraction.
- Include frozen orbitals ϕ_c in $\sigma_1(\mathbf{k},\omega)$.

$$\langle\psi_{m,\mathbf{k}}|\vec{\nabla}|\phi_c\rangle = \langle\tilde{\psi}_{m,\mathbf{k}}|\vec{\nabla}|\phi_c\rangle + \sum_i \langle\tilde{\psi}_{m,\mathbf{k}}|\tilde{p}_i\rangle \left(\langle\phi_i|\vec{\nabla}|\phi_c\rangle - \langle\tilde{\phi}_i|\vec{\nabla}|\phi_c\rangle\right).$$

- when $\phi_c = 0$ for $r > \Omega_{\mathbf{R}}$ the dipole matrix elements become

$$\langle\psi_{m,\mathbf{k}}|\vec{\nabla}|\phi_c\rangle = \sum_i \langle\tilde{\psi}_{m,\mathbf{k}}|\tilde{p}_i\rangle\langle\phi_i|\vec{\nabla}|\phi_c\rangle.$$

  where we use the fact that $\{|\tilde{\phi}\rangle\}$ represent a complete basis for $|\tilde{\psi}\rangle$ inside $\Omega_{\mathbf{R}}$
- Average on the different atomic sites **R**

Implementation in Abinit

- N.A. Holzwarth PAW pseudopotential generator
- Save the core WF when producing the PAW pseudopotential in Wfc.pseudoname
- Ground state calculation with prtnabla=1 and prtwfk=1: call to optics_paw_core.F90 from outscfcv.F90 (in /11drive)
- Subroutine optics_paw_core.F90 (in /11drive)
  - similar functions as optics_paw.F90
  - calculate the additional matrix elements including the core states
  - write the matrix elements in the file filename_OPT2
- Postprocessing of the dipole matrix elements using conducti

Preliminary results

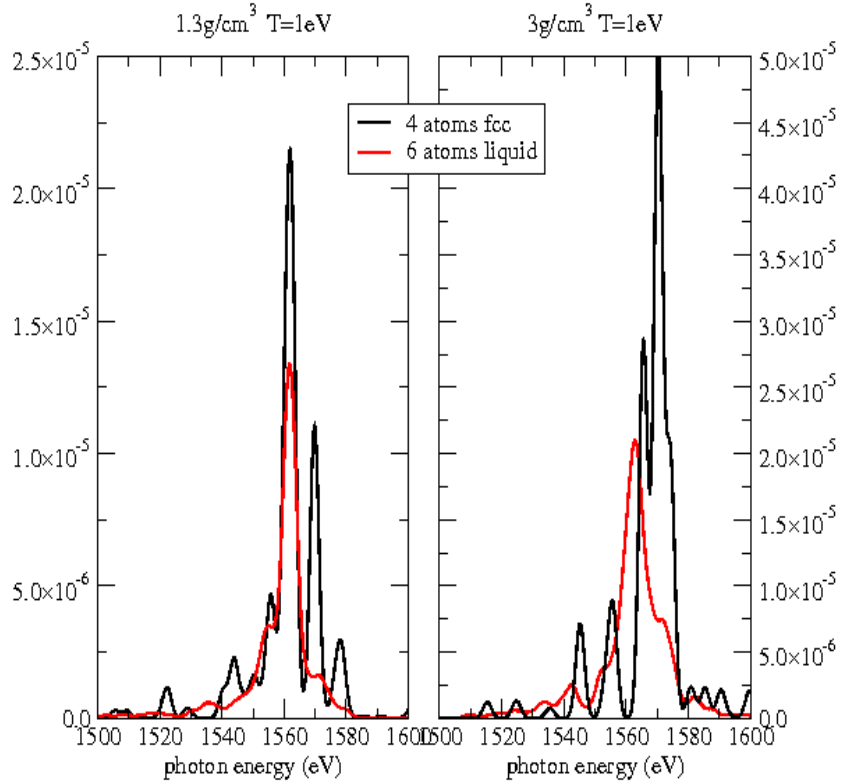

FIGURE: K shell absorption in Al

- 4 atoms in FCC position
- 6 atoms liquid
- LDA pseudopotential
- temperature of 1eV
- single **k**-point Γ
- 400 bands to converge
  ~ 100eV above the edge

Future work

- test on larger systems
- deal high energy states
- include in version 5.4