Plane-waves approach to Energy Loss Spectroscopy

Features, tools and results

Francesco Sottile

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Ecole Polytechnique, Palaiseau - France
European Theoretical Spectroscopy Facility (ETSF)

Imperial College - London, 24 April 2009

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Outline

1. Energy Loss Spectroscopy
2. Microscopic-Macroscopic connection
3. ELS in *ab initio*: a schematic overview
4. Theory and Numerical support
5. The codes

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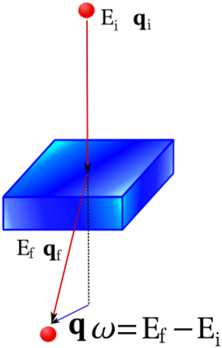
Spectroscopy: Electron Scattering



$$\frac{d^2\sigma}{d\Omega dE} \propto \mathrm{Im}\left\{\varepsilon^{-1}\right\}$$

$$\varepsilon_{\mathrm{M}}^{-1}(\mathbf{q}, \omega)$$

frequency-momentum dependent inverse Macroscopic dielectric function

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Microscopic-Macroscopic Connection

Theoretical definition

$$\mathbf{E}(\mathbf{r},\omega) = \int d\mathbf{r}\ \varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)\mathbf{D}(\mathbf{r}',\omega)$$

constitutive closure to Maxwell equations

The connection ?

$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) \Longrightarrow \varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega)$$

microscpic macroscopic

Microscopic-Macroscopic Connection

Finite systems

Photo-absorption cross section:

$$\sigma(\omega) = \frac{\omega}{c} \mathrm{Im} \int d\mathbf{r} d\mathbf{r}' \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$$

Electron scattering or Raman scattering:

$$R(\mathbf{q}, \omega) = \frac{q^2}{4\pi} \int d\mathbf{r} d\mathbf{r}' e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')} \mathrm{Im} \varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega)$$

Microscopic-Macroscopic Connection

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Dielectric Function in Crystals

A better representation: Fourier space

$$\mathbf{E}(\mathbf{r},\omega)=\sum_{\mathbf{G}}\int\frac{d\mathbf{q}d\omega}{(2\pi)^4}\mathbf{E}(\mathbf{q}+\mathbf{G},\omega)e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}$$

$$\varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega)=\sum_{\mathbf{G}\mathbf{G}'}\int\frac{d\mathbf{q}d\omega}{(2\pi)^4}\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}$$

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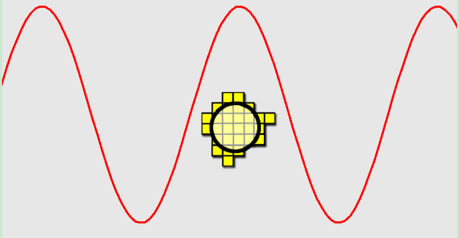
Dielectric Function in Crystals

Macroscopic average



$$\varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega) = \int_{\Omega} \varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) d\mathbf{r} d\mathbf{r}' = \sum_{\mathbf{G},\mathbf{G}'} \varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q},\omega) \int e^{-i\mathbf{G}\cdot\mathbf{r}} \int e^{-i\mathbf{G}'\cdot\mathbf{r}'}$$

$$\varepsilon_{\mathrm{M}}^{-1}(\mathbf{q},\omega) = \varepsilon_{00}^{-1}(\mathbf{q},\omega)$$

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Ab initio approach to calculate ε

Full polarizability

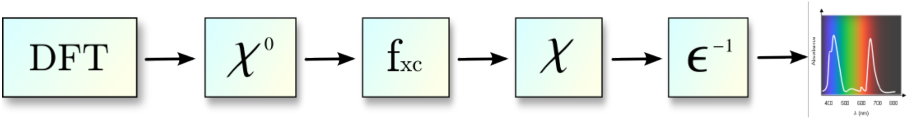
- TDDFT :: $\chi = \chi^0 + \chi^0 \left(v + f_{xc} \right) \chi$
- BSE :: ${}^4\chi = {}^4\chi^0 + {}^4\chi^0 \left({}^4v + {}^4\Xi \right) {}^4\chi$

Dielectric function

$$\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q},\omega) = 1 + v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

Ab initio approach to calculate ε

TDDFT::



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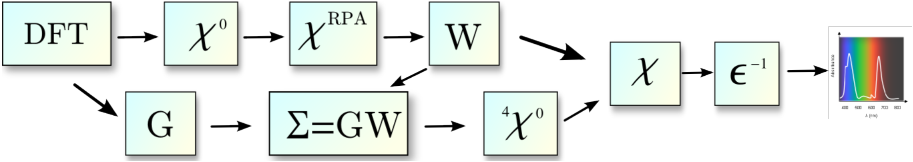
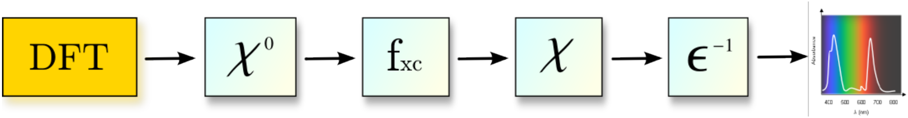


First step: the ground state calculation



$\mathrm{DFT} \rightarrow \chi^{0} \rightarrow \mathrm{f}_{\mathrm{xc}} \rightarrow \chi \rightarrow \epsilon^{-1} \rightarrow$

- DFT with plane waves basis $\psi(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$
- Cutoff energy $E_{\mathrm{cutoff}} = \frac{|\mathbf{G}_{\mathrm{max}}|^2}{2}$ as a unique convergence parameter
- pseudopotential (norm-conserving)
- LDA, GGA exchange-correlation potential

Results :: Eigenvalues (and eigenvectors)

$$\psi_{nk}, \epsilon_{nk}, f_{nk}$$

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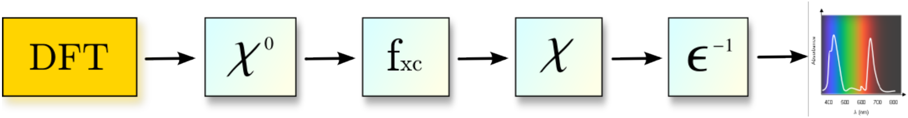

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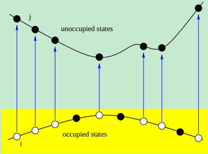
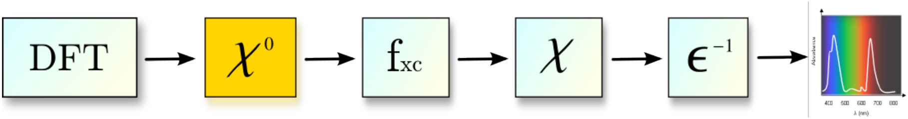


Second step: the Independent Particle Polarizability (IPA)



$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega-(\epsilon_i-\epsilon_j)}$$

$$\chi^0_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) = \sum_{ij} \frac{<\phi_i|e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}}|\phi_j><\phi_i|e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}|\phi_j>}{\omega-(\epsilon_i-\epsilon_j)}$$

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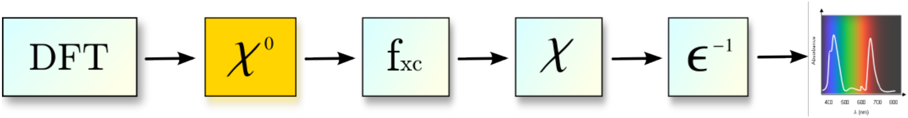
DFT → χ^0 → f_{xc} → χ → ϵ^{-1} →

IPA :: the easy way

$$\varepsilon_{\mathbf{GG'}}(\mathbf{q},\omega) = 1 - v_{\mathbf{G}}(\mathbf{q})\chi^0_{\mathbf{G},\mathbf{G'}}(\mathbf{q},\omega)$$

$$\varepsilon_{00}(\mathbf{q},\omega) = 1 - v_0(\mathbf{q})\chi^0_{00}(\mathbf{q},\omega)$$

$$\mathrm{ELS} = \mathrm{Im}\left\{\frac{1}{\varepsilon_{00}(\mathbf{q},\omega)}\right\}$$

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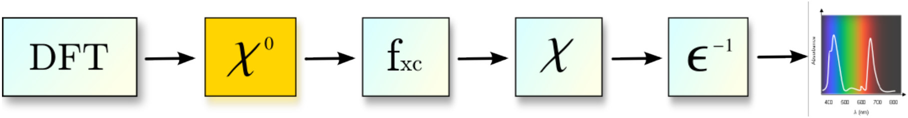

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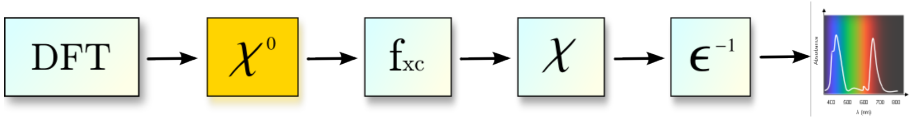

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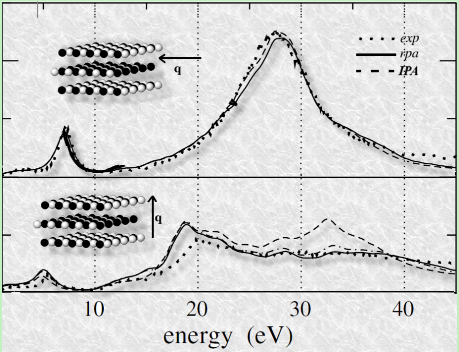
Independent Particle Polarizability

Some good results ... (graphite)



A.Marinopoulos *et al.* Phys.Rev.Lett **89**, 76402 (2002)

ELS within RPA

RPA :: the inclusion of local fields

$$\varepsilon_{\mathbf{GG'}}(\mathbf{q},\omega) = 1 - v_{\mathbf{G}}(\mathbf{q})\chi^{0}_{\mathbf{G},\mathbf{G'}}(\mathbf{q},\omega)$$

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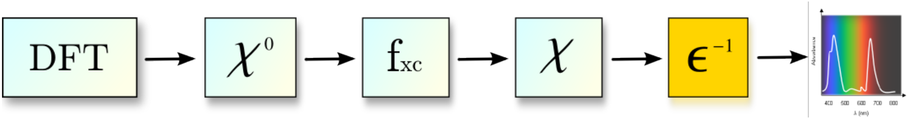

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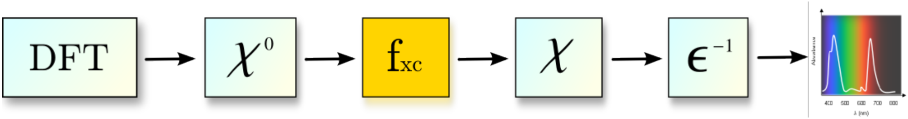
Ab initio approach

Full polarizability :: RPA

- TDDFT :: $\chi = \chi^0 + \chi^0 \left(v + \cancel{f_{xc}} \right) \chi$

Beyond RPA :: through a kernel

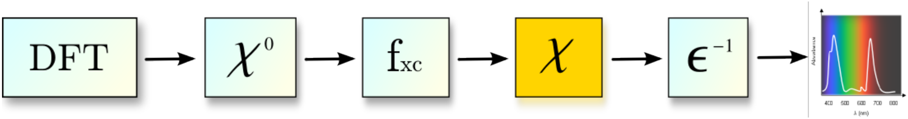


DFT → χ^0 → f_{xc} → χ → ϵ^{-1} →

ALDA kernel (GGA, EXX, etc.)

$$f_{xc} = \frac{\delta V_{xc}^{\mathrm{LDA}}}{\delta n}\delta(\mathbf{r},\mathbf{r}')(\omega = 0)$$

Beyond RPA :: through a kernel



Full polarizability :: ALDA

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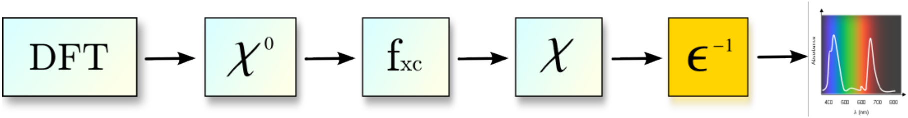
Beyond RPA :: through a kernel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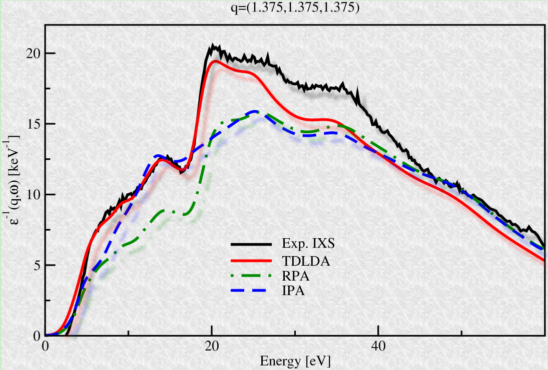
Dielectric function

$$\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = 1 + v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$$

ALDA results

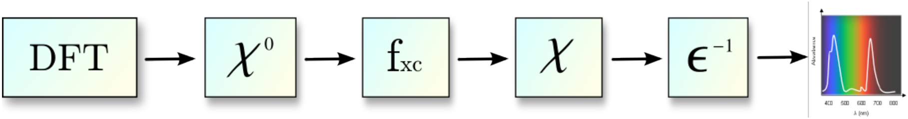
ALDA on IXS of Silicon



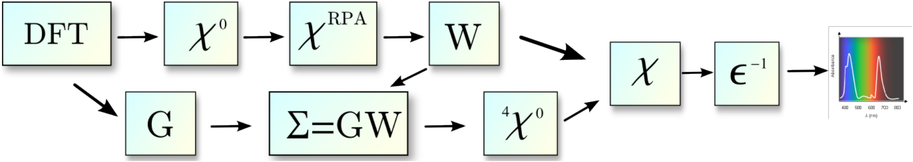
H-C. Weissker *et al.*, Physical Review Letters **97**, 237602 (2006)

Ab initio approach to calculate ε

TDDFT::



BSE::



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Why the numerical approach is important

- Analysis
- Prediction

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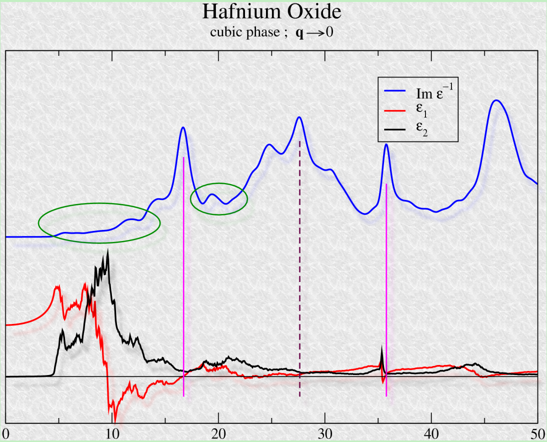
Analysis

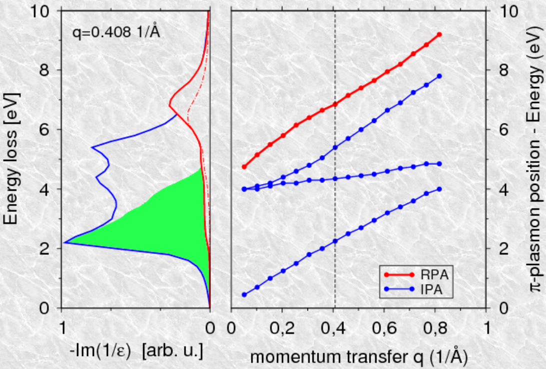
ELS of Hafnium Oxide



Zobelli and Sottile, to be published.

Analysis

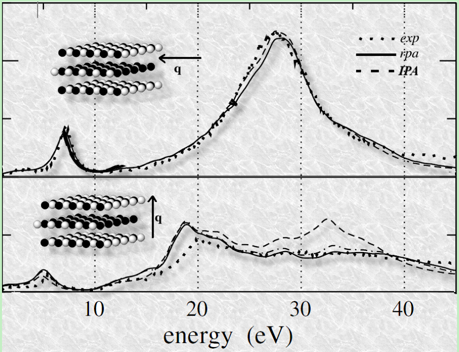
ELS of Nanotubes



Kramberger *et al.*, Phys. Rev. Lett. **100**, 196803 (2008)

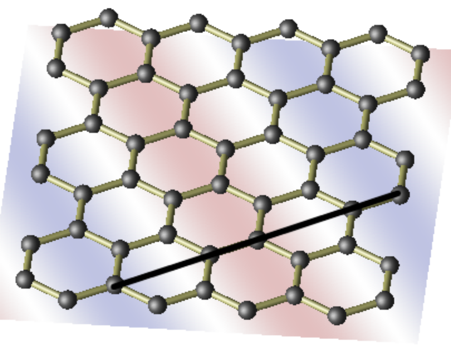
Analysis

Plasmons in graphite



Graphite: π–Plasmon

Induced charge fluctuations $\rho^{ind} = \chi\varphi^{ext}$



- plane wave perturbation

$$\varphi^{ext}(\mathbf{r},\omega) \propto e^{-i(\omega t-\mathbf{qr})}$$

- $|\mathbf{q}| = 0.74$ Å^{-1}, $\lambda = 8.5$ Å
- $\hbar\omega = 7eV$

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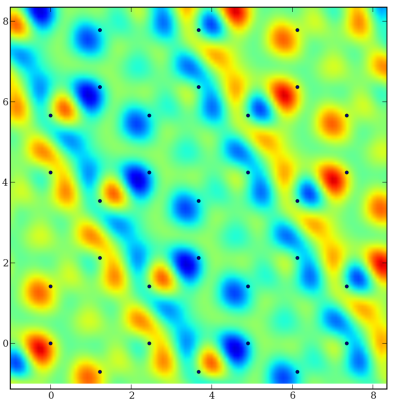

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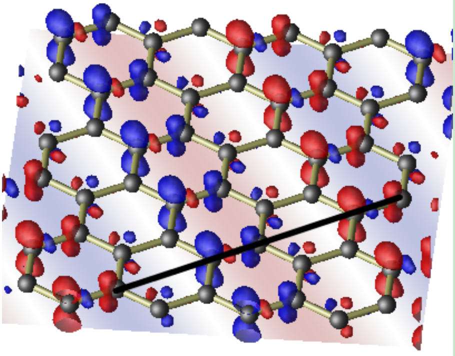
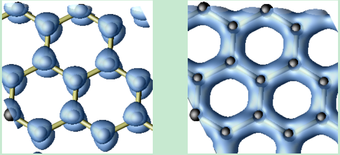


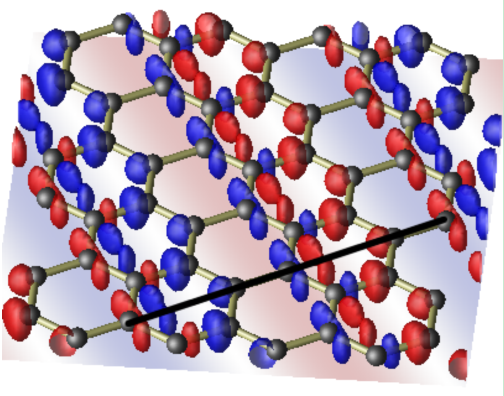
ground state density



p_z - orbitals sp^2 - orbitals

Graphite: $\pi + \sigma$–Plasmon

Induced charge fluctuations $\rho^{ind} = \chi\varphi^{ext}$



- plane wave perturbation

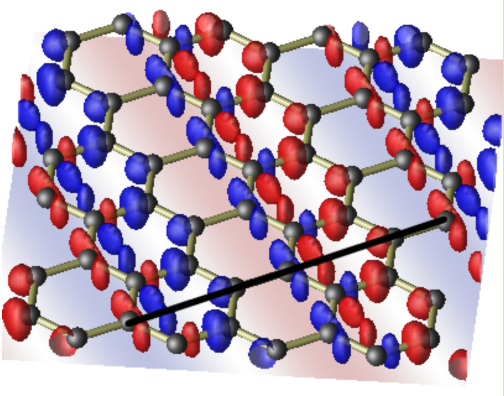
$$\varphi^{ext}(\mathbf{r},\omega) \propto e^{-i(\omega t - \mathbf{qr})}$$

- $|\mathbf{q}| = 0.74\ \text{Å}^{-1}$, $\lambda = 8.5$ Å
- $\hbar\omega = 30eV$

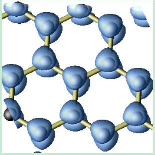
R. Hambach *et al.*, to be published.

Graphite: $\pi + \sigma$–Plasmon

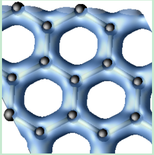
Induced charge fluctuations $\rho^{ind} = \chi\varphi^{ext}$



(partial) ground state density



p_z - orbitals



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R. Hambach *et al.*, to be published.

Prediction

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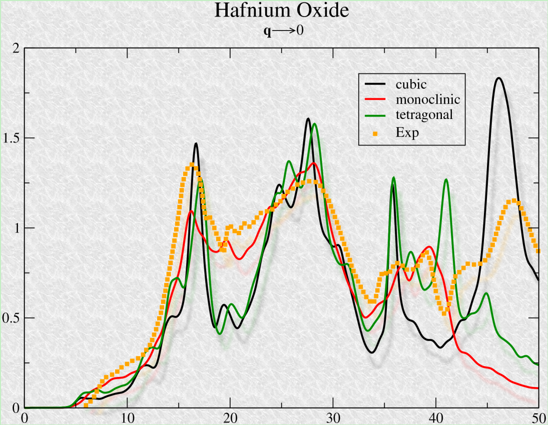

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Theoretical Spectroscopy :: plane wave approach

Theoretical support and analysis

Technical aspects

- Easy convergence
- Spectra in absolute value
- whole dielectric 2-rank tensor
- CIXS, circular dichroism with EELS

Limits

- 100-1000 atoms
- 0-100 eV

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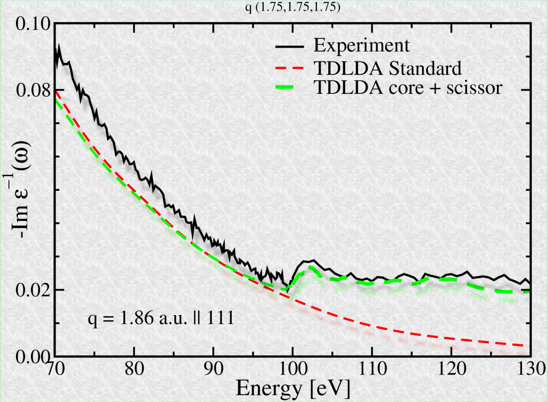
The Codes

- `www.abinit.org`
- `www.dp-code.org`
- `www.bethe-salpeter.org`

Semi-core states

L-edge of Silicon



Luppi *et al.* Phys. Rev. B **78**, 245124 (2008)

Theoretical Spectroscopy :: plane wave approach

Technical aspects

- Easy convergence parameters (cutoff, kpoints, bands, etc.)
- Spectra in absolute value
- whole dielectric 2-rank tensor
- non diagonal response (CIXS, circular dichroism with EELS)

Analysis

- transition-based analysis
- graphical tools
- real, imaginary part analysis

In progress

- non-linear response
- spactially resolved EELS (Ralf)
- tackle challenging materials (bio, strongly correlated, **semi-core states**, etc.)