Energy Loss Beamline

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European Theoretical Spectroscopy Facility (ETSF)

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Outline

Information about the Beamline

Calculation(microscopic)-Measurement(macroscopic) Connection

Underlying theory and approximations

Usefulness of Theory

Codes

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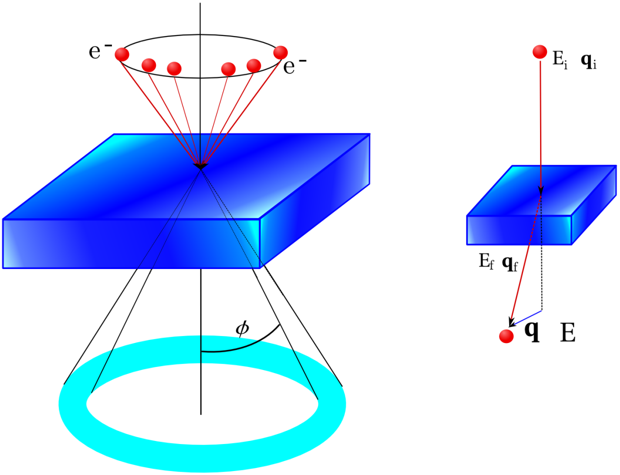
The Energy Loss Beamline

- Coordinator: Francesco Sottile
  (Palaiseau, `Francesco.Sottile@polytechnique.fr`)
- Experiments:
  - Electron Energy Loss Spectroscopy (EELS).
  - Reflection Electron Energy Loss Spectroscopy (REELS).
  - Inelastic and Coherent X-ray Scattering (IXS,CIXS).
- Systems:
  - Bulk, Surfaces and Nanostructures.
- Methods:
  - Density functional approach: DFT-KS, TDDFT.
  - Many-body techniques: Bethe-Salpeter Equation.
- Nodes involved:
  - Palaiseau, Rome, Milan, Grenoble

Spectroscopy: Electron or X Scattering

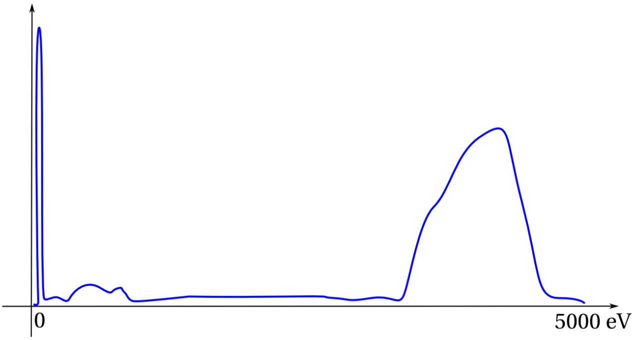


Spectroscopy: Electron or X Scattering

Energy Loss Function

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

Spectroscopy: Electron or X Scattering



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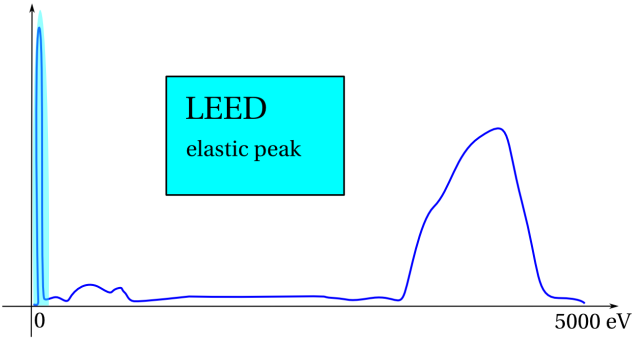

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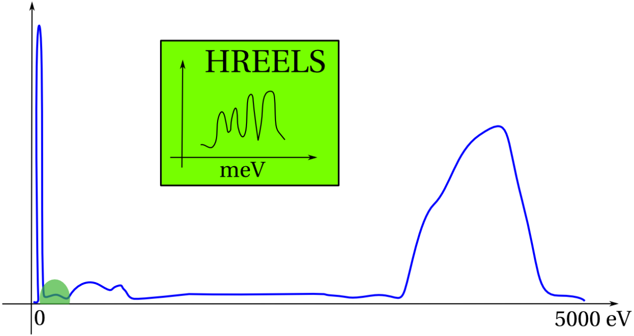

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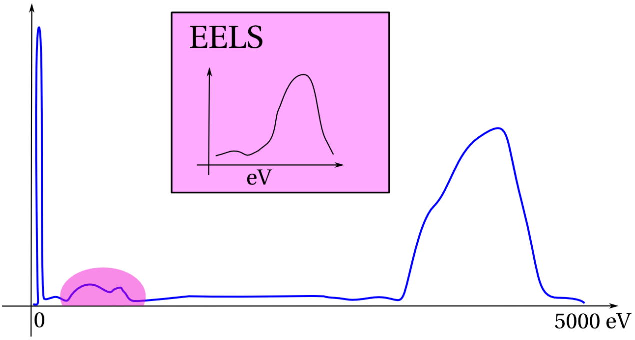
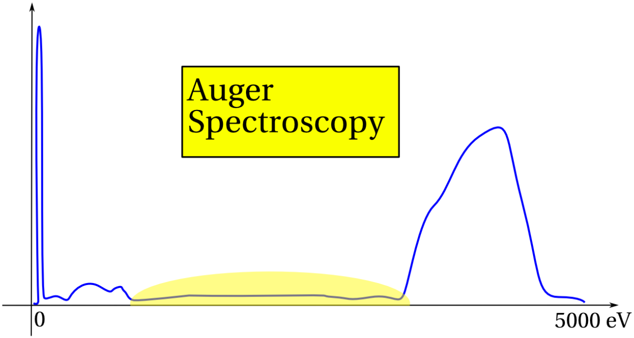


Spectroscopy: Electron or X Scattering



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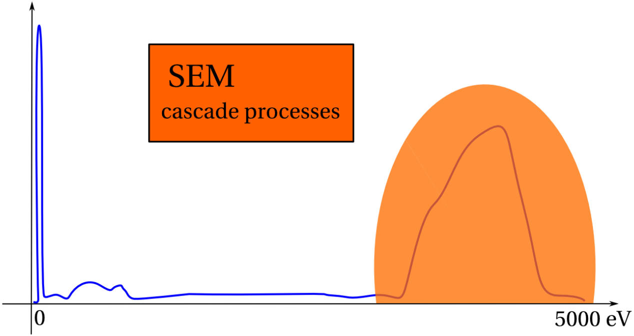
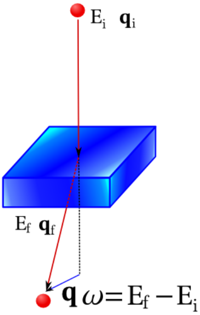


Spectroscopy: Electron or X Scattering



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

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

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

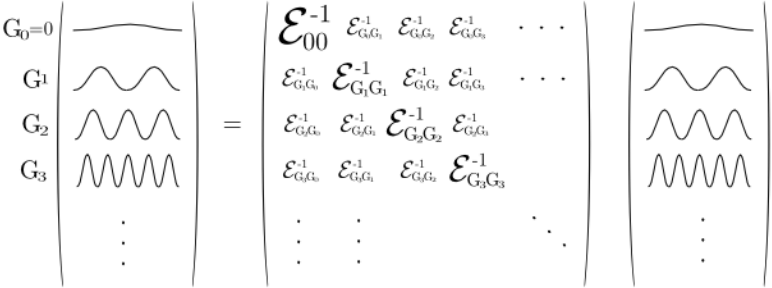
The connection ?

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

microscpic macroscopic

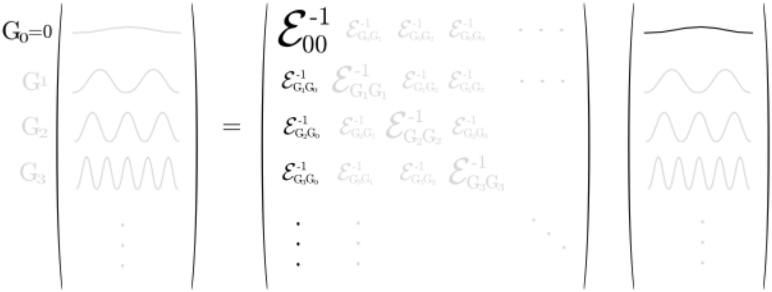
Theoretical definition in G space

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



Theoretical definition in G space

$$\mathbf{E}(\mathbf{q}+\mathbf{G},\omega) = \varepsilon^{-1}_{\mathbf{G},0}(\mathbf{q},\omega)\mathbf{D}(\mathbf{q}+0,\omega)$$



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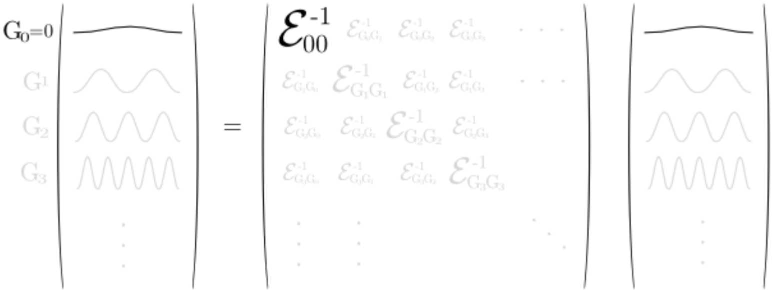

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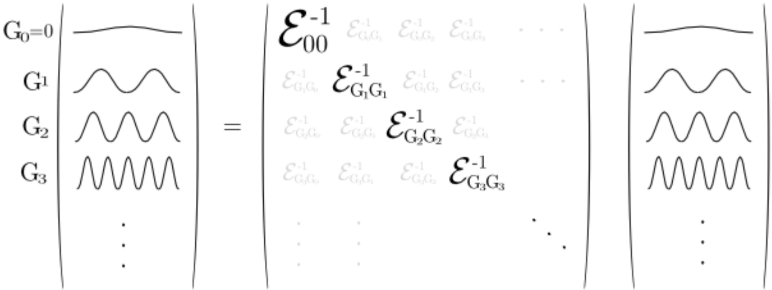

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Ab initio approach to calculate ε

Full polarizability

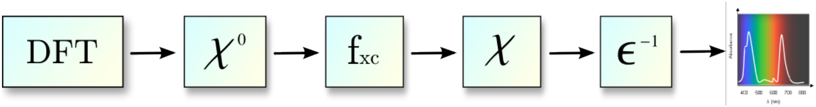
- TDDFT :: $\chi = \chi^0 + \chi^0 \left(v + f_{xc} \right) \chi$
- BSE :: ${}^4\chi = {}^4\chi^0 + {}^4\chi^0 \left({}^4 v + {}^4\Xi \right) {}^4\chi$

Dielectric function

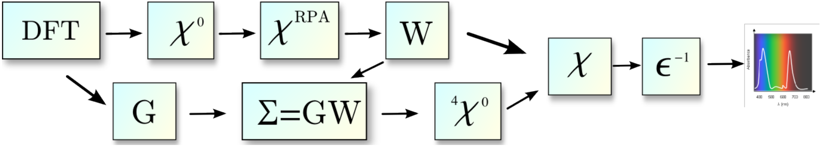
$$\varepsilon^{-1}_{\mathbf{GG}'}(\mathbf{q}, \omega) = 1 + v_{\mathbf{G}}(\mathbf{q}) \chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega)$$

Ab initio approach to calculate ε

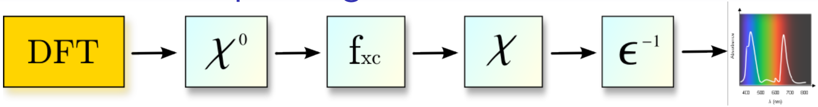
TDDFT::



BSE::



First step: the ground state calculation



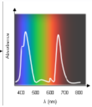
- DFT with plane waves basis $\psi(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$
- Cutoff energy $E_{\mathrm{cutoff}} = \frac{|\mathbf{G}_{\mathrm{max}}|^2}{2}$ as a unique convergence parameter
- pseudopotential (norm-conserving)
- LDA, GGA exchange-correlation potential

Results :: Eigenvalues (and eigenvectors)

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

First step: the ground state calculation

DFT → χ^0 → f_{xc} → χ → ϵ^{-1} →



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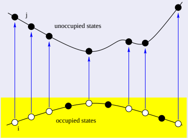
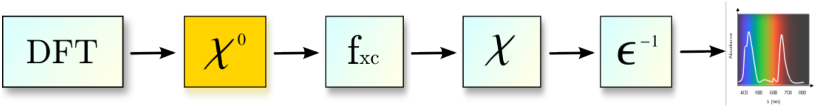


Second step: the Independent Particle Polarizability (IPA)



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

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

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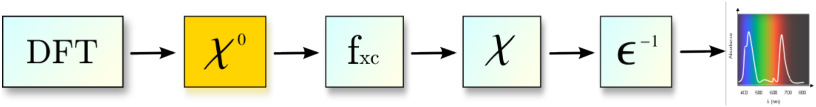


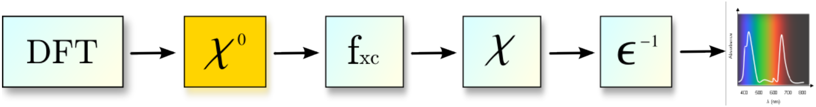
IPA :: the easy way

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

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

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

Second step: the Independent Particle Polarizability (IPA)



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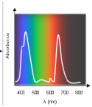
Second step: the Independent Particle Polarizability (IPA)

DFT → χ^0 → f_{xc} → χ → ϵ^{-1} → 

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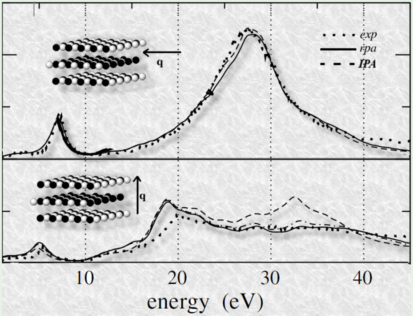
Independent Particle Polarizability

Some good results ... (graphite)



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

ELS within RPA

RPA :: the inclusion of local fields

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

$$\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) \quad \mapsto \quad \varepsilon^{-1}_{00}(\mathbf{q},\omega)$$

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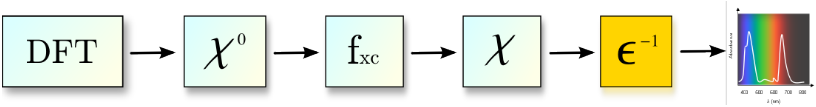

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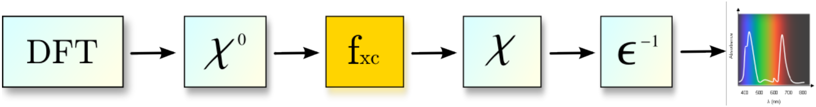
Ab initio approach

Full polarizability :: RPA

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

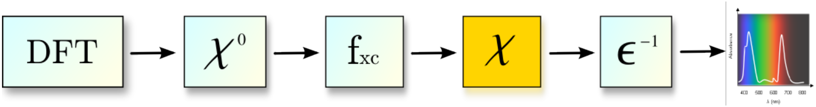
Beyond RPA :: through a kernel



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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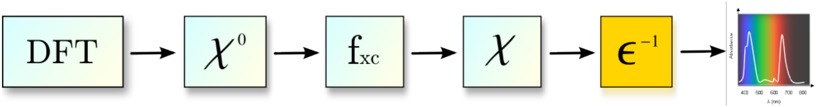
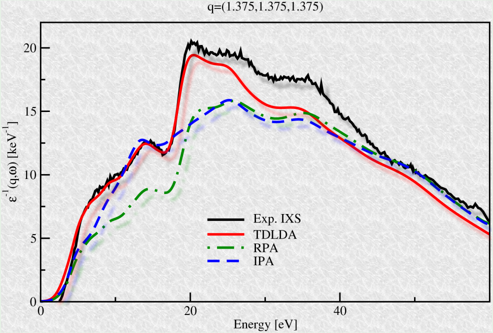


Dielectric function

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

ALDA results

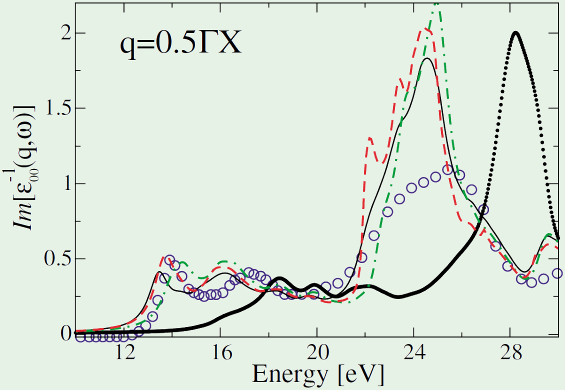
ALDA on IXS of Silicon



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

BSE results

LiF - Energy Loss small non-zero momentum transfer



A.Marini, R. Del Sole and A.Rubio, Physical Review Letters **91**, 256402 (2003)

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Codes

Why the numerical approach is important

- Analysis
- Prediction

Why the numerical approach is important

- Analysis
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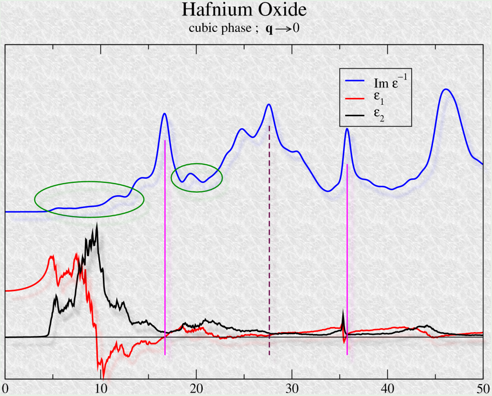
Analysis

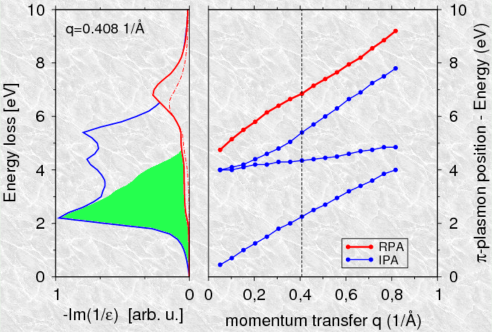
ELS of Hafnium Oxide



Zobelli and Sottile, to be published.

Analysis

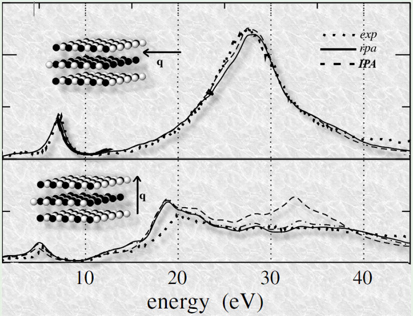
ELS of Nanotubes



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

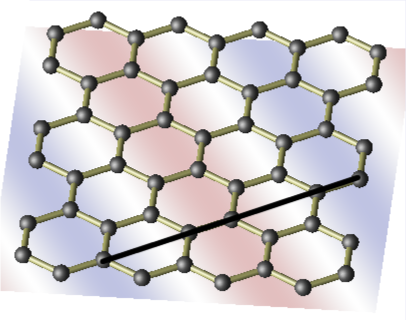
Analysis

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
- $\hbar\omega = 7eV$

Graphite: π–Plasmon

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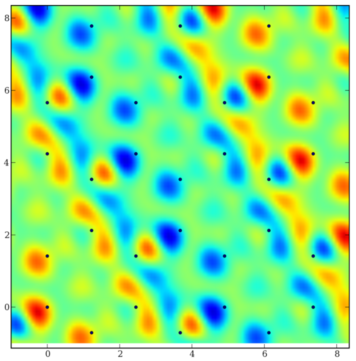

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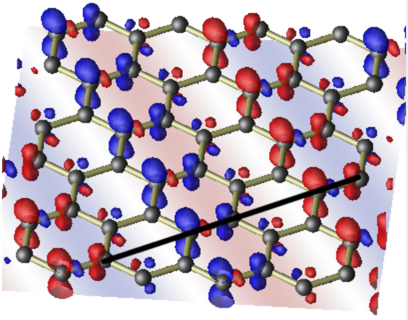
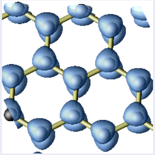
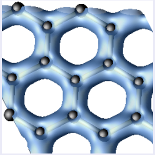


ground state density



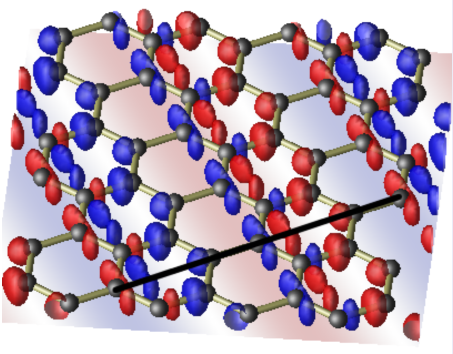
p_z - orbitals



sp^2 - orbitals

Graphite: $\pi + \sigma$–Plasmon

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



- plane wave perturbation

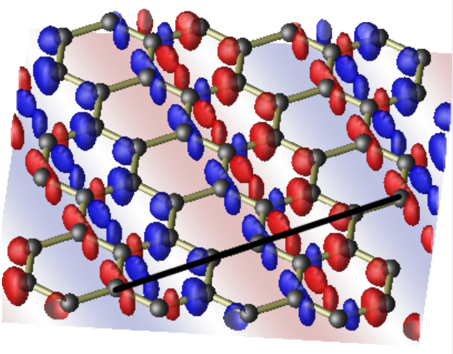
  $$\varphi^{ext}(\mathbf{r}, \omega) \propto e^{-i(\omega t - \mathbf{qr})}$$

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

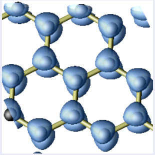
R. Hambach *et al.*, to be published.

Graphite: $\pi + \sigma$–Plasmon

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



(partial) ground state density



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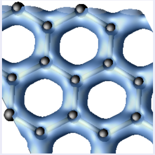

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R. Hambach *et al.*, to be published.

Prediction

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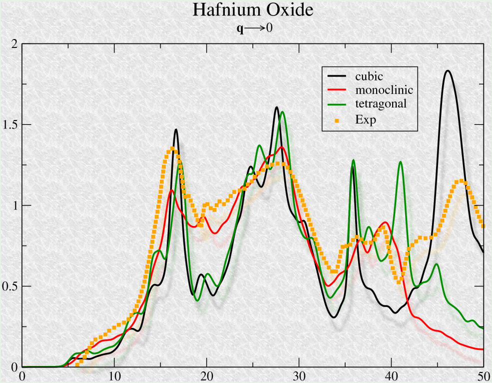


Zobelli and Sottile, to be published.

Valence Electron Loss Spectroscopy

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

Valence Electron Loss Spectroscopy

Theoretical support and analysis

Analysis

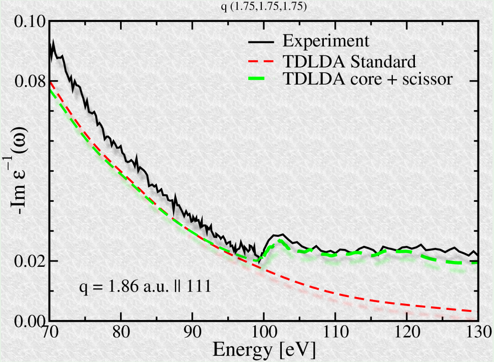
- transition-based analysis
- graphical tools
- real, imaginary part analysis

Limits

- 100-1000 atoms
- 0-100 eV

Semi-core states

L-edge of Silicon



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

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The Codes

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