Spatial Resolution in Electron Energy-Loss Spectroscopy

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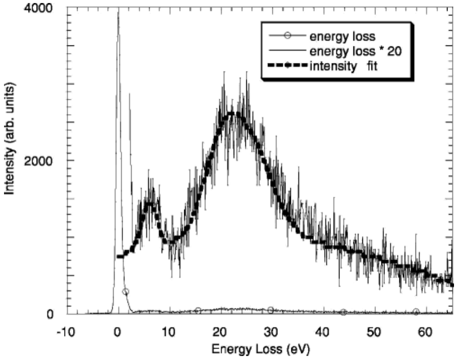
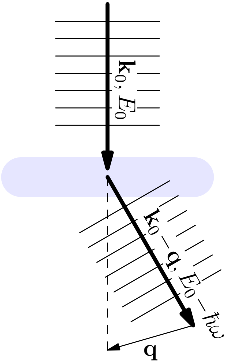
23. 03. 2009 — DPG09, Dresden

What is EELS?

angular resolved

- broad beam geometry
- momentum transfer $\boldsymbol{q}$, energy loss $\hbar\omega$
- resolution: $\Delta\boldsymbol{q} \approx 0.05$ Å^{-1}, $\Delta\hbar\omega \approx 0.2\mathrm{eV}$





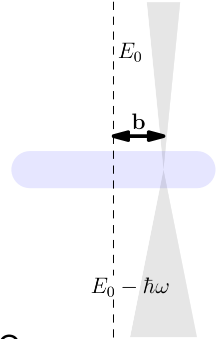
EELS for graphite
(π and $\pi + \sigma$ plasmon)

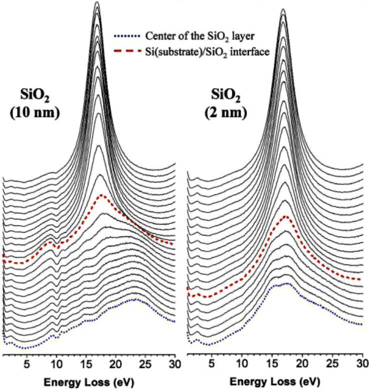
[M. Vos, PRB **63**, 033108 (2001).]

What is EELS?

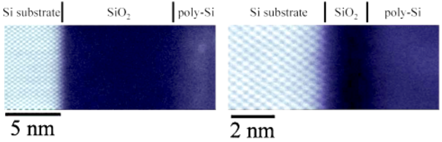
spatially resolved

- highly focussed beam
- impact parameter ***b***, energy loss $\hbar\omega$
- resolution: Δ***b*** $\approx$ 1 Å, $\Delta\hbar\omega \approx 0.5\text{eV}$





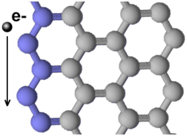
EELS for Si/SiO_2

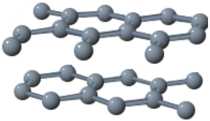


[M. Couillard *et. al.*, PRB **77**, 085318 (2008).]

Outlook

1. Methods and Theory
2. Spatially Resolved EELS: Graphene
3. Charge fluctuations in Graphite

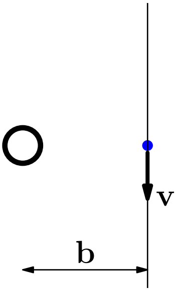




Semi-classical Theory

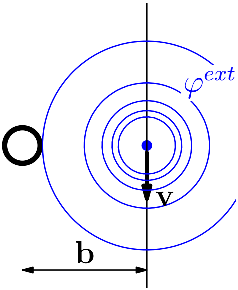
How do we calculate EELS ?

EELS: Classical Perturbation



1. electron flying along straight line
$$\rho^{ext}(\boldsymbol{r}, t) = -e\delta\big(\boldsymbol{r} - (\boldsymbol{b} + \boldsymbol{v}t)\big)$$
2. external potential (no retardation)
$$\Delta\varphi^{ext} = \rho^{ext}/\varepsilon_0$$
3. linear response of the medium
$$\rho^{ind} = \chi\varphi^{ext}, \qquad \epsilon^{-1} = 1 + v\chi$$
4. energy loss of the electron
$$\langle \frac{dW}{dt} \rangle_t = \int d\boldsymbol{r} \langle \boldsymbol{E}^{ind} \cdot \boldsymbol{j}^{ext} \rangle_t$$

EELS: Classical Perturbation



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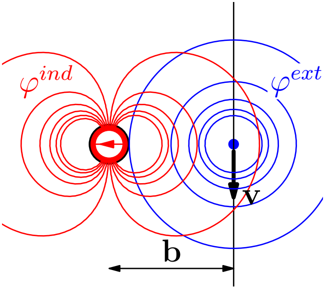

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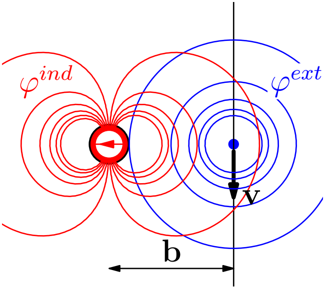

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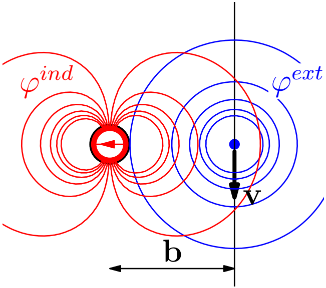

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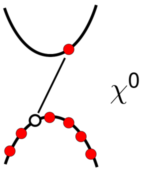
$$\langle \frac{dW}{dt} \rangle_t = \int d\boldsymbol{r} \langle \boldsymbol{E}^{ind} \cdot \boldsymbol{j}^{ext} \rangle_t$$

$\Rightarrow$ energy loss probability $S(\boldsymbol{b},\omega)$

EELS: Quantum Mechanical Response

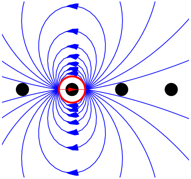
ab initio calculations (DFT)

1. ground state calculation gives ϕ_i^{KS}
2. independent-particle polarisability χ^0
3. RPA full polarisability $\chi = \chi^0 + \chi^0 v \chi$



non-local response of crystals

- $\rho^{ind}(\mathbf{r}, t) = \int \chi(\mathbf{r}, \mathbf{r}'; t - t')\varphi^{ext}(\mathbf{r}', t')$



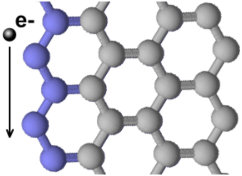
Codes:

ABINIT: X. Gonze *et al.*, Comp. Mat. Sci. **25**, 478 (2002)

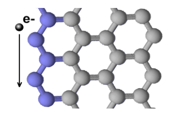
DP-code: `www.dp-code.org`; V. Olevano, *et al.*, unpublished.

Spatially Resolved EELS

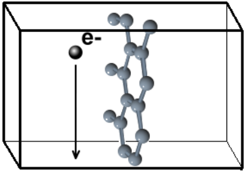
Aloof Spectroscopy for Graphene



Energy Loss for Graphene

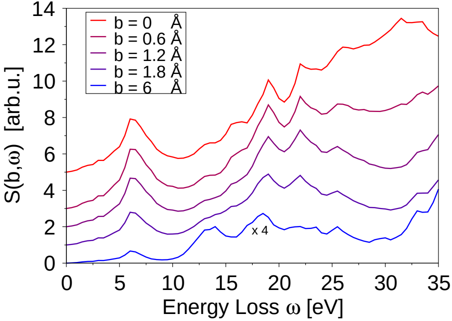


Electron parallel to sheet
(super-cell with 30 Å vac)



- non-dispersive modes
- surface plasmon: 6.2eV
- further excitations at 20eV and 32eV

Energy loss for different pos. ***b***



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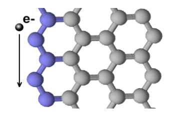
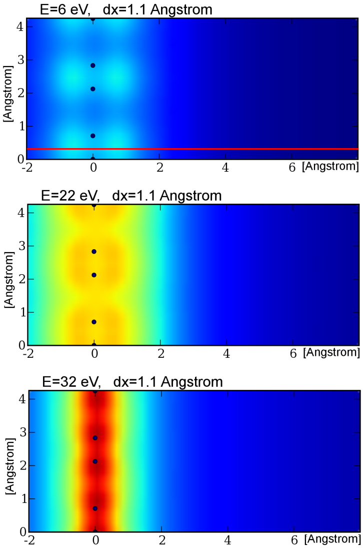
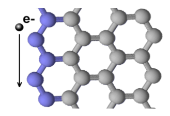
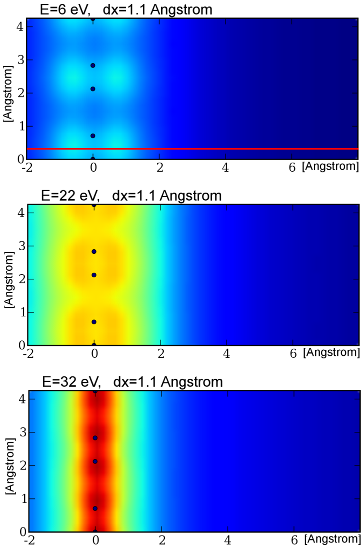




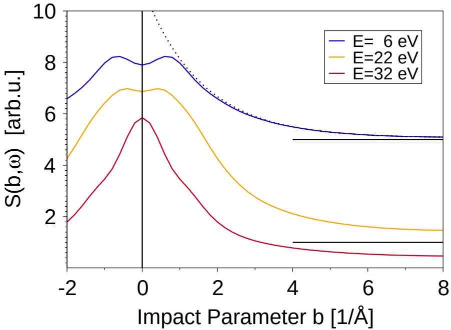
- spatial distribution of the loss probability for 6eV, 22eV and 32eV
- atomic resolution ($\Delta b = 1.1\,\text{Å}$)

Energy Loss for Graphene

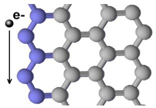




- exponential decay with *b*
- delocalization



Outlook



- Cerenkov radiation
- non-local effects
- experiments

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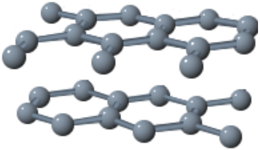
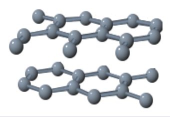
   $\langle \frac{dW}{dt} \rangle_t = \int d\boldsymbol{r} \langle \boldsymbol{E}^{ind} \cdot \boldsymbol{j}^{ext} \rangle_t$
5. non-local response $\chi(\boldsymbol{r}, \boldsymbol{r}', t - t')$

Induced Charge Density

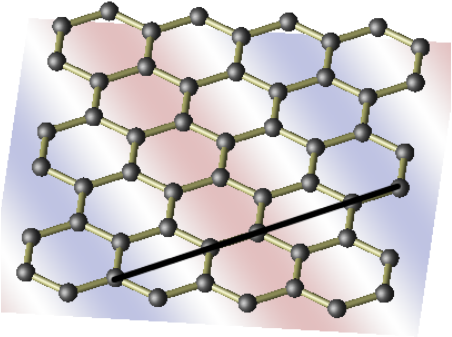
Looking at Plasmons in Graphite



Graphite: π–Plasmon



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

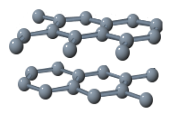


- plane wave perturbation

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

- $|\boldsymbol{q}| = 0.74$ Å^{-1}, $\lambda = 8.5$ Å
- $\hbar\omega = 9\text{eV}$

Graphite: π–Plasmon



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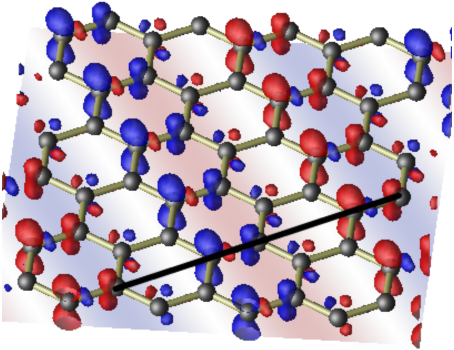

(resolution: 0.8 Å, isosurface at 50%)

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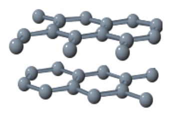

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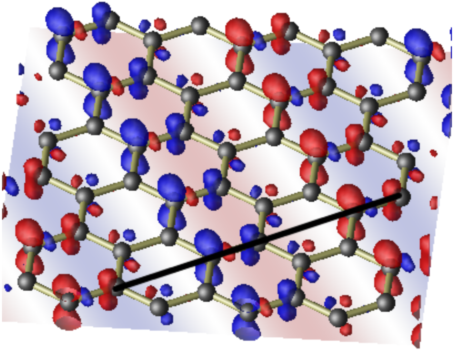
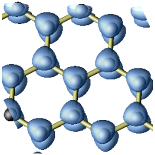
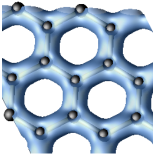


(resolution: 0.8 Å, isosurface at 50%)

(partial) ground state density

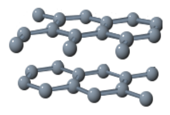


p_z - orbitals



sp^2 - orbitals

Graphite: $\pi + \sigma$–Plasmon



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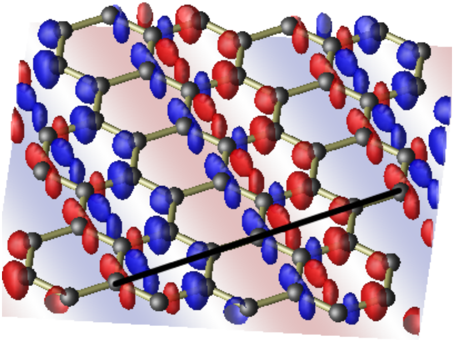


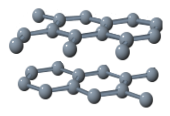
(resolution: 0.8 Å, isosurface at 35%)

- plane wave perturbation

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

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

Graphite: $\pi + \sigma$–Plasmon



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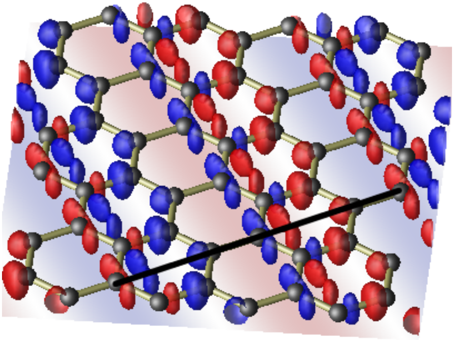

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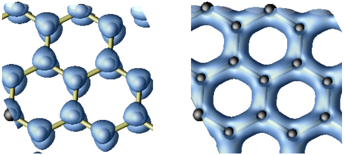
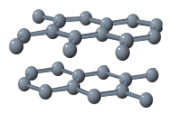


p_z - orbitals sp^2 - orbitals

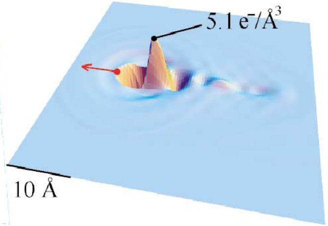
Outlook



- realistic external potential
  → electron in graphite
- relation with plasmons
- experimental accessibility

$9\mathrm{MeV}$ gold ion in water
(from IXS measurements)

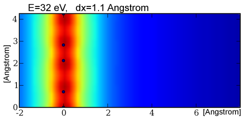
[P. Abbamonte, PRL **(92)**, 237401 (2004)]



Summary

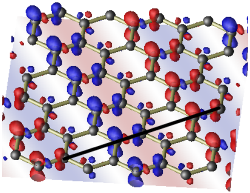
Spatially resolved EELS

1. atomic resolution in EELS calls for ab-initio calculations
2. first tests for graphene layer



induced charge density

3. visualisation of density fluctuations



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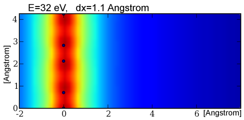

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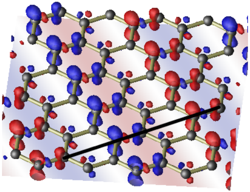
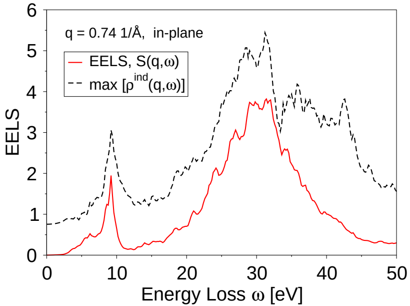


Thank you for your attention!

Relation with Plasmons

- **Def. Plasmon:** normal modes of the intrinsic electrons
  $\epsilon \boldsymbol{E}^{tot} = \boldsymbol{E}^{ext} \stackrel{!}{=} \mathbf{0}, \quad \Longleftrightarrow \quad \Re\epsilon = 0$
- plane wave perturbation excites normal mode(s)
  $\rho^{ind} = \chi\varphi^{ext}$



Energy Loss for an Electron

The energy loss in semi-classical approximation is given by

$$\langle \frac{dW}{dt} \rangle_t = \int d\boldsymbol{r} \langle \boldsymbol{E}^{ind} \cdot \boldsymbol{j}^{ext} \rangle_t$$
$$= \int d\omega \omega \iint d\boldsymbol{q} d\boldsymbol{q}' \;\; \varphi^{ext}(-\boldsymbol{q}, -\omega) i\chi(\boldsymbol{q}, \boldsymbol{q}'; \omega) \varphi^{ext}(\boldsymbol{q}', \omega),$$

and for an electron flying through a crystal

$$\langle \frac{dW}{dt} \rangle_t = -\int_0^\infty d\omega \omega 8\pi^2 e^2 \iint d\boldsymbol{q}_\perp d\boldsymbol{q}'_\perp \Im \Big[\frac{\chi(\boldsymbol{q}, \boldsymbol{q}'; \omega) e^{i\boldsymbol{b}(\boldsymbol{q}_\perp - \boldsymbol{q}'_\perp)}}{q^2 q'^2} \Big],$$

where $\boldsymbol{q}^{(')} = \boldsymbol{q}_\perp^{(')} + (w/v)\boldsymbol{e}_z$ is split into a part perpendicular and parallel to the direction of motion of the electron.