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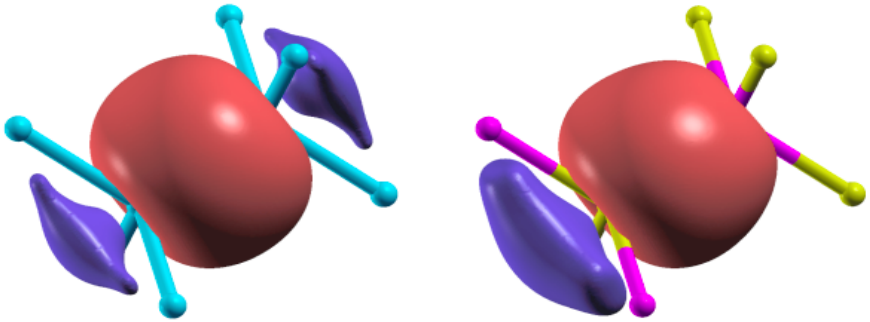
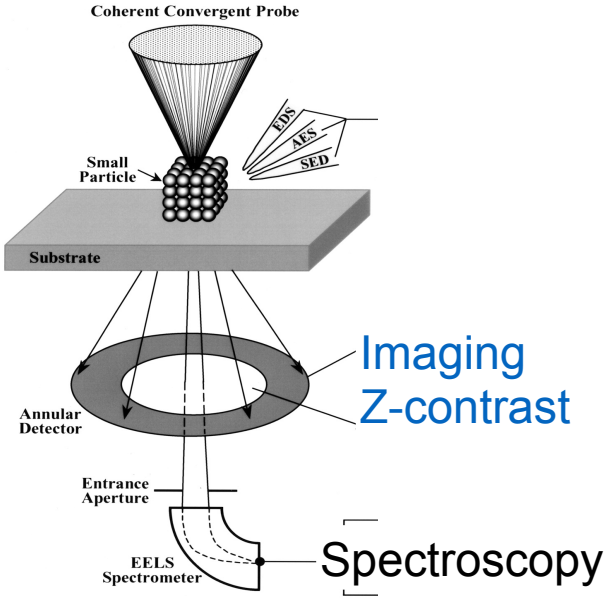
Electron energy loss spectroscopy (EELS)

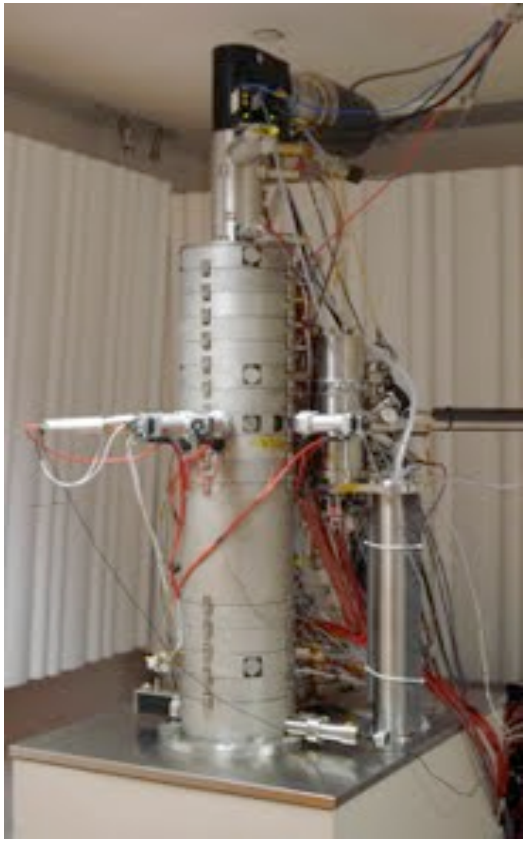


Phil Hasnip
Condensed Matter Dynamics Group
Department of Physics,
University of York, U.K.
http://www-users.york.ac.uk/~pjh503

Many slides courtesy of Jonathan Yates (University of Oxford)

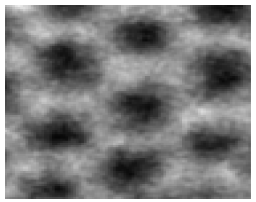
THE UNIVERSITY of York Scanning Transmission Electron Microscopy



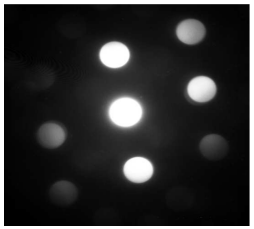


SuperSTEM II - Daresbury

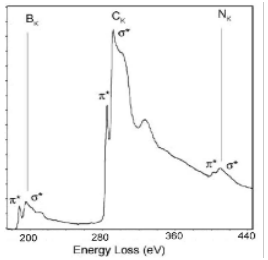
Imaging



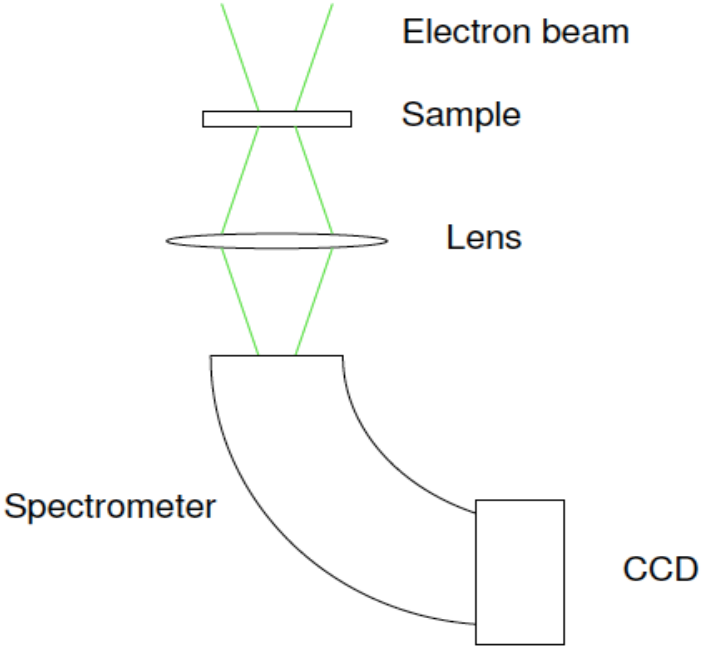
Diffraction



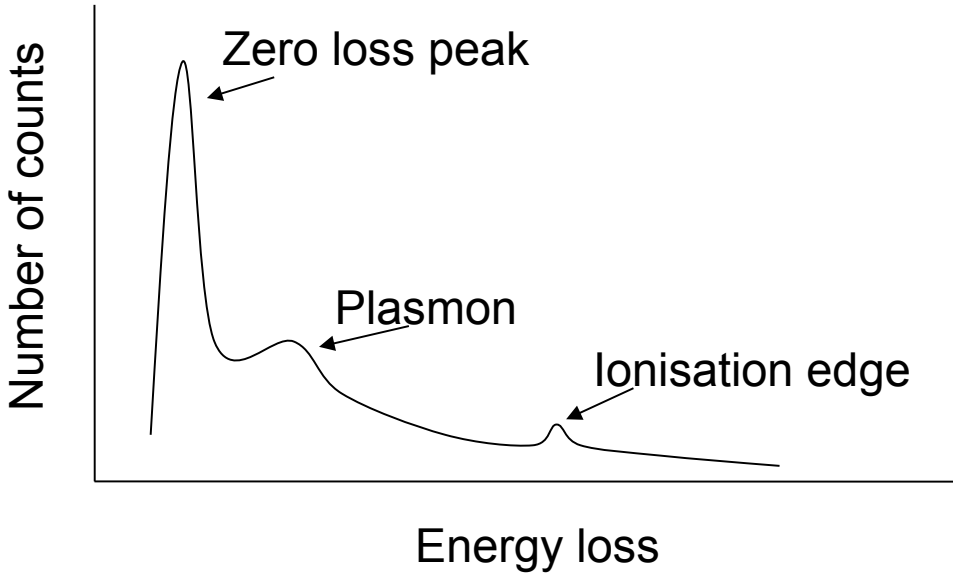
Spectroscopy



Electron Energy Loss



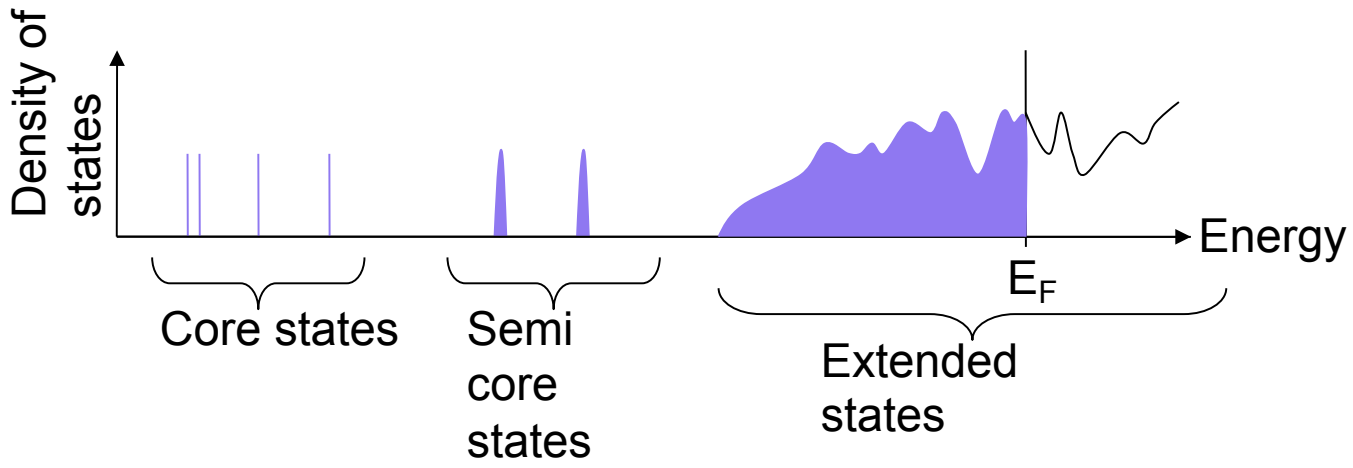
Plasmons ~ 5-30 eV
Single excitations ~50-2000eV



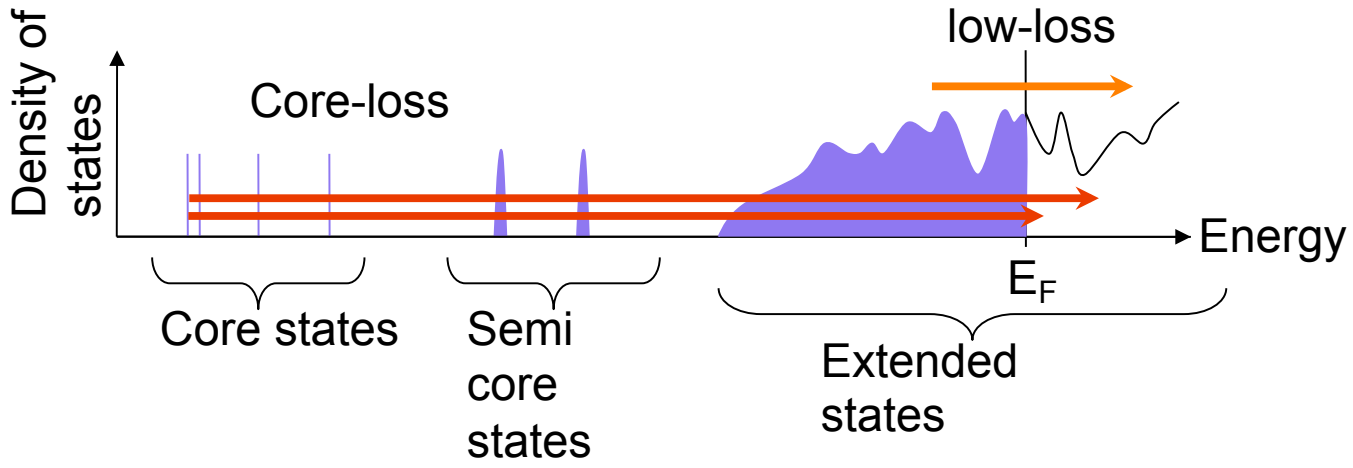
- Phonon Scattering
- Plasmon Scattering
- Single electron excitation
- Direct Radiation losses

Atomic picture

Electronic Structure



Electronic Structure



Fermi's Golden rule:

$$T_{i\to f} = \frac{2\pi}{\hbar} \left|\langle f \left|H\right| i\rangle\right|^2 \rho$$

Dielectric Response

The dielectric function $\varepsilon(\omega,\mathbf{q})$ tells us about the response of a material to an electric field

$$\mathbf{D}(\omega,\mathbf{q}) = \varepsilon(\omega,\mathbf{q})\,\mathbf{E}\,(\omega,\mathbf{q})$$

$$\varepsilon(\omega,\mathbf{q}) = \varepsilon_1(\omega,\mathbf{q}) + i\varepsilon_2(\omega,\mathbf{q})$$

Loss function:

$$\mathrm{Im}\left\{\frac{-1}{\varepsilon(\omega,\mathbf{q})}\right\}$$

Kramers-Kronig:

$$\varepsilon_1 \leftrightarrow \varepsilon_2$$

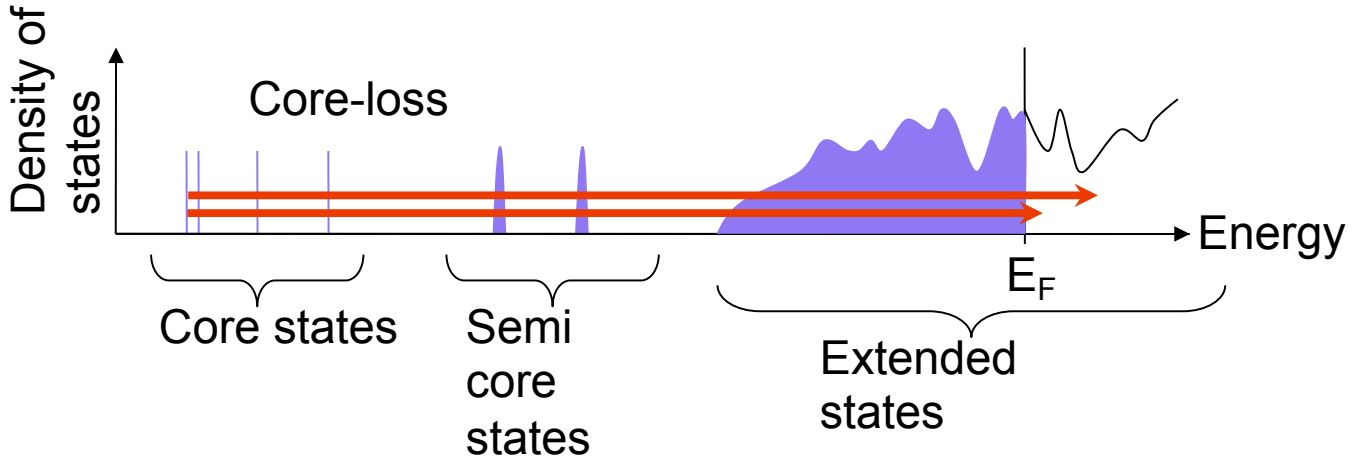
When an electron moves through a medium it creates a displacement field D. The loss function gives the rate of energy absorption.

Core-loss

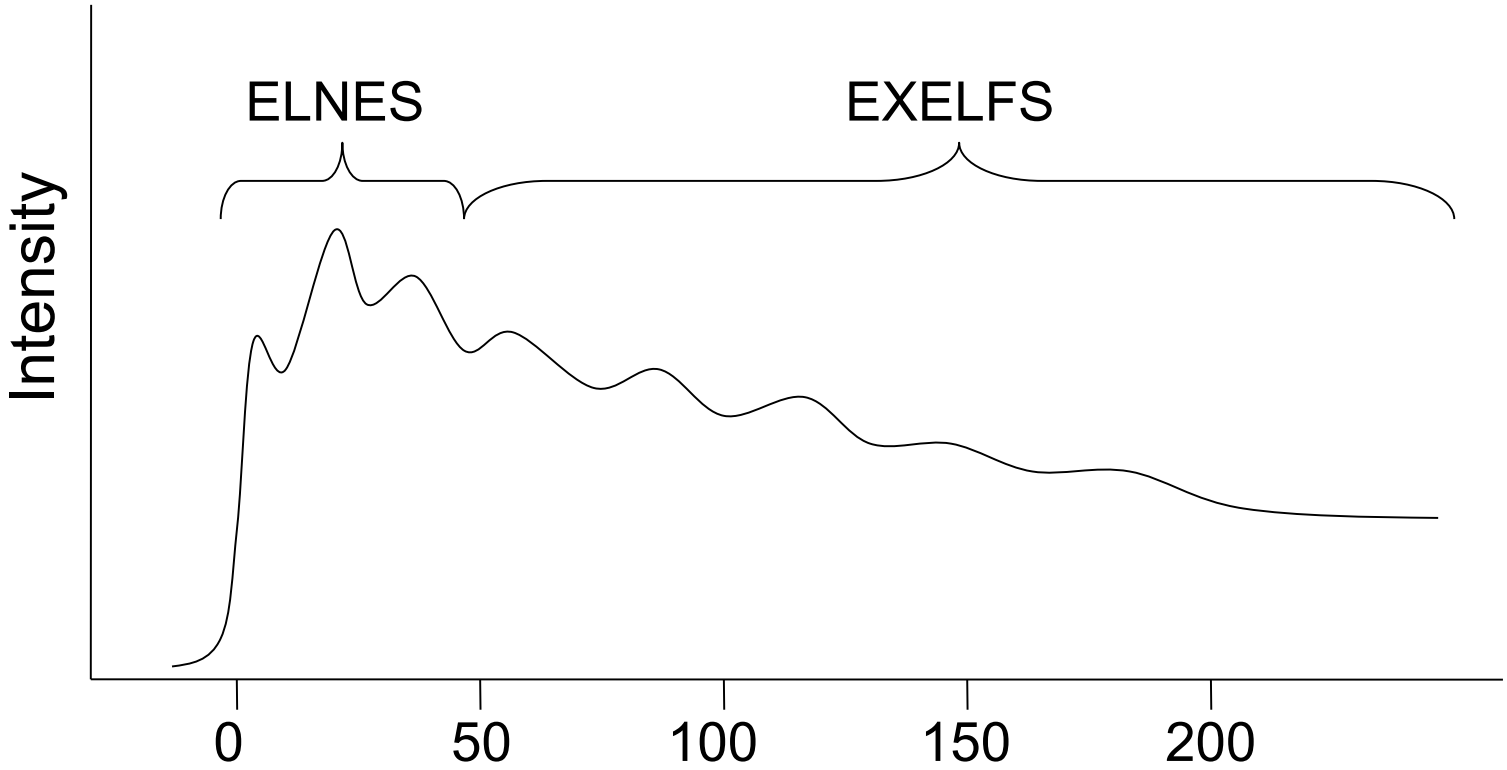
At high energies (i.e. transitions from core-states) the loss function is given by the imaginary part of the dielectric function.

$$Im\left\{\frac{-1}{\varepsilon(\mathbf{q},\omega)}\right\} = \varepsilon_2(\mathbf{q},\omega)$$

$$\varepsilon_2(\mathbf{q},E) = \frac{4\pi e^2}{\Omega q^2}\sum_{n,\mathbf{k}} |\langle\psi^n_{\mathbf{k}}|e^{i\mathbf{q}.\mathbf{r}}|\mathrm{c}\rangle|^2\delta(E^c_{\mathbf{k}} - E_{1\mathrm{s}} - E)$$



Near-edge spectra



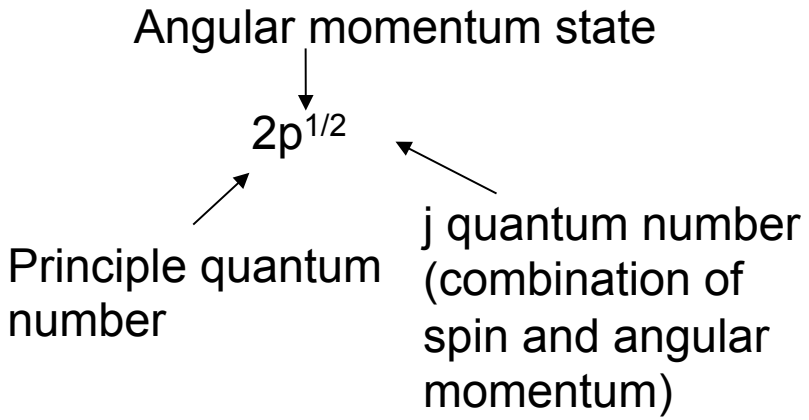
bonding”

“nearest neigbour”

ELNES - Energy Loss Near Edge Structure
EXELFS - Extended Energy Loss Fine Structure

Core Edges

Core electron	Edge
$1s^{1/2}$	K
$2s^{1/2}$	L_1
$2p^{1/2}$	L_2
$2p^{3/2}$	L_3
$3s^{1/2}$	M_1
$3p^{1/2}$	M_2
$3p^{3/2}$	M_3
$3d^{3/2}$	M_4
$3d^{5/2}$	M_5



Dipole Rule

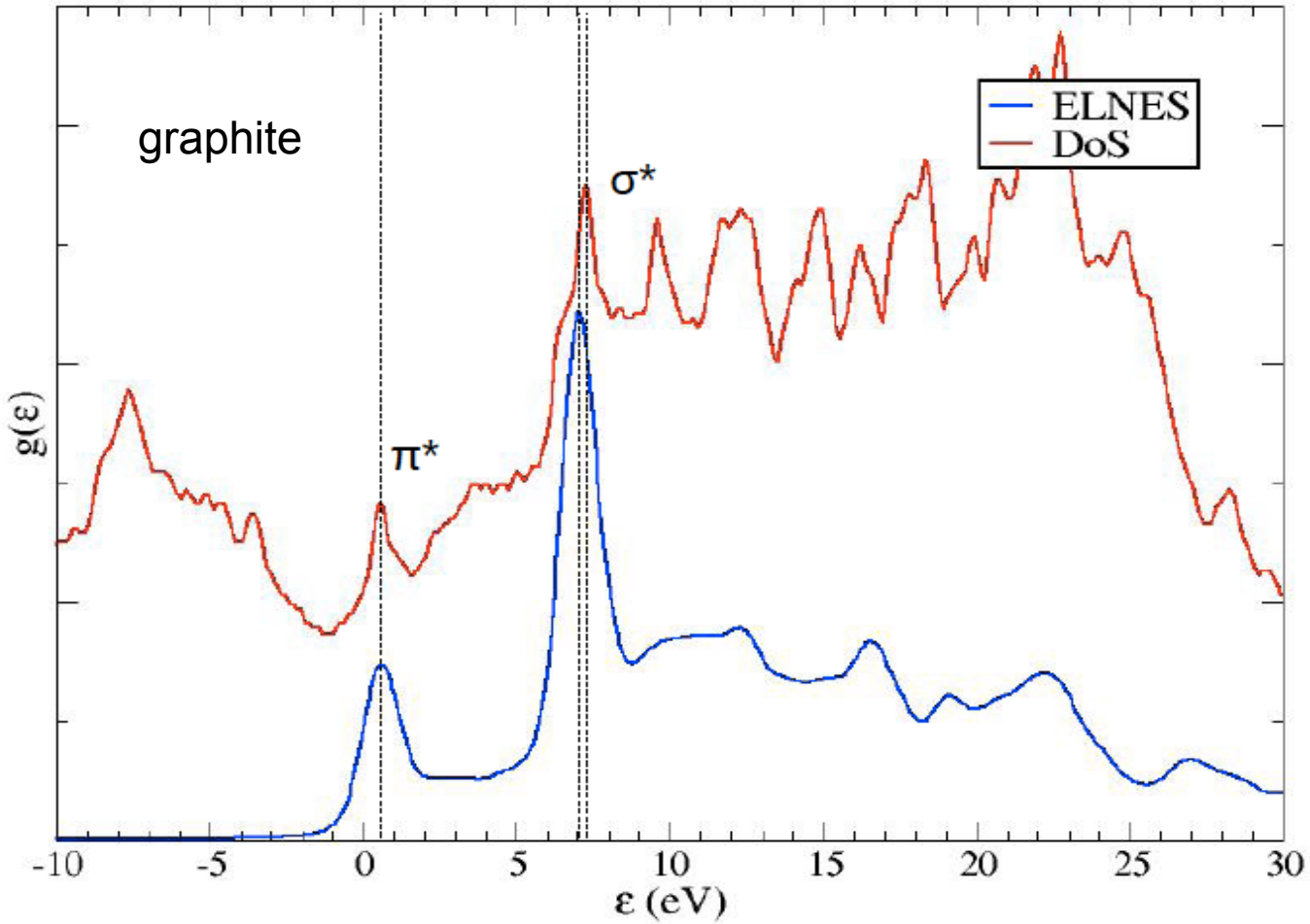
$$\langle f|e^{i\mathbf{q}.\mathbf{r}}|i\rangle = \langle f|i\rangle + i\langle f|\mathbf{q}.\mathbf{r}|i\rangle + \frac{1}{2}\langle f|(\mathbf{q}.\mathbf{r})^2|i\rangle - \frac{i}{6}\langle f|(\mathbf{q}.\mathbf{r})^3|i\rangle + \frac{1}{24}\langle f|(\mathbf{q}.\mathbf{r})^4|i\rangle + \cdots$$

Dipole term

$$\langle f\,|x|\,1s\rangle \approx \langle f|P_x\rangle$$

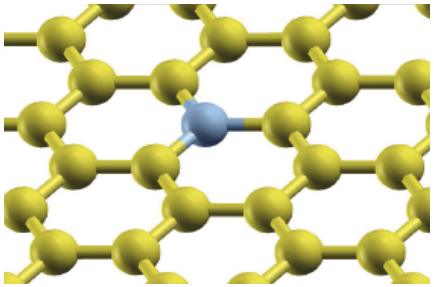
Core level spectra can be thought of as angular momentum projected density of states

EELS vs DOS

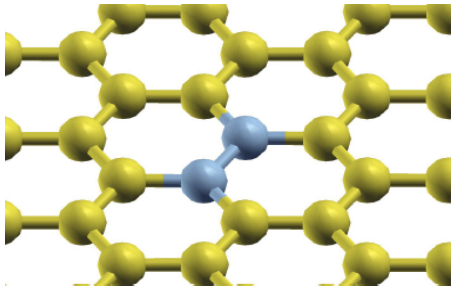


N-doping in graphene

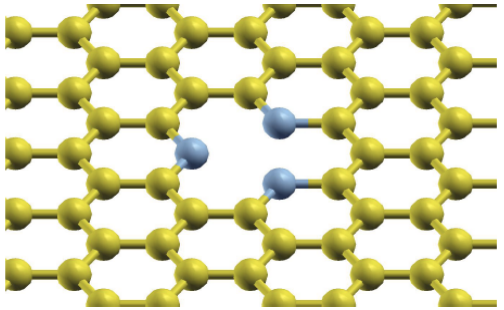
Josh Tsang - Masters Thesis



Substitutional



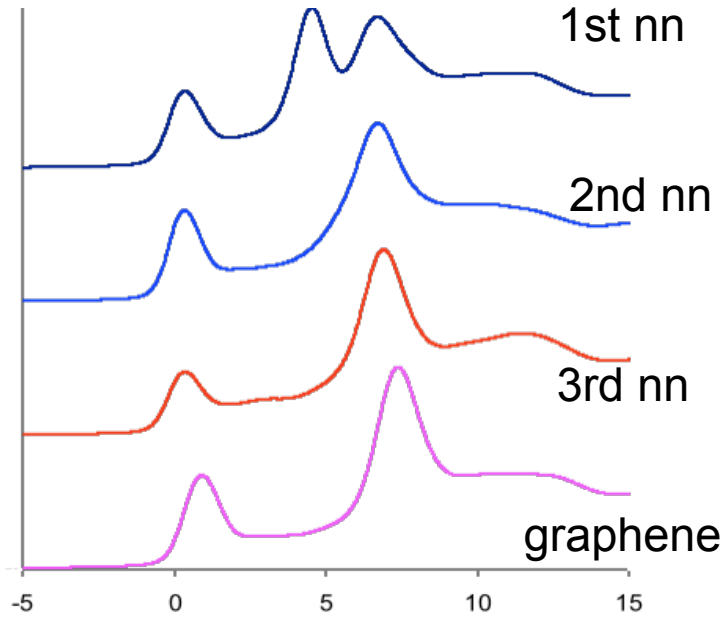
bi-nitrogen



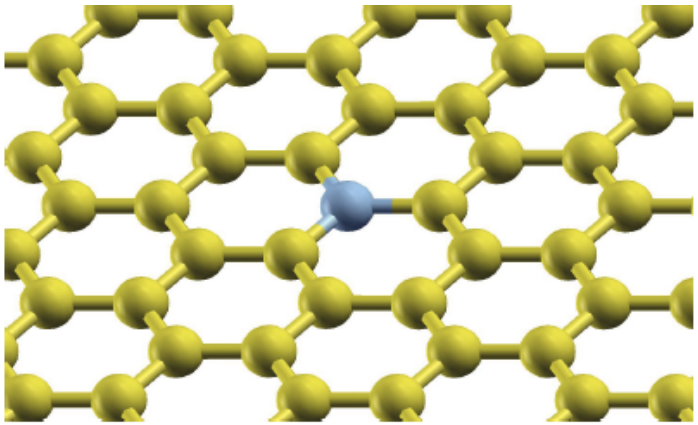
tri-pyridinic

… and many others. Growth conditions, curvature etc. affects defect stability

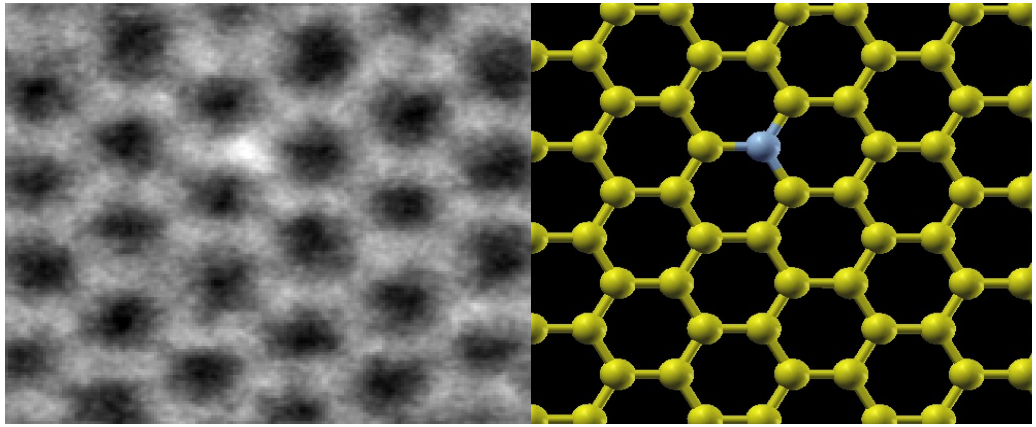
Substitutional Defect

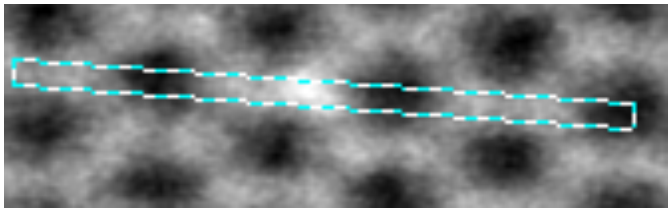


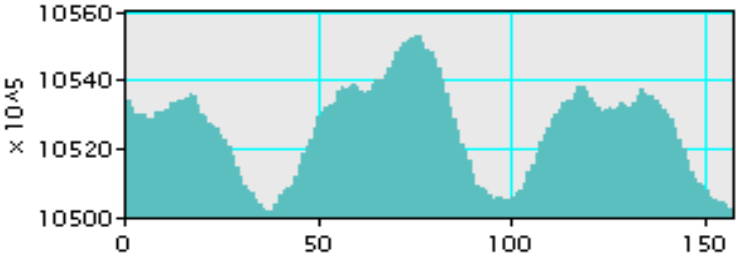
Carbon K-edge



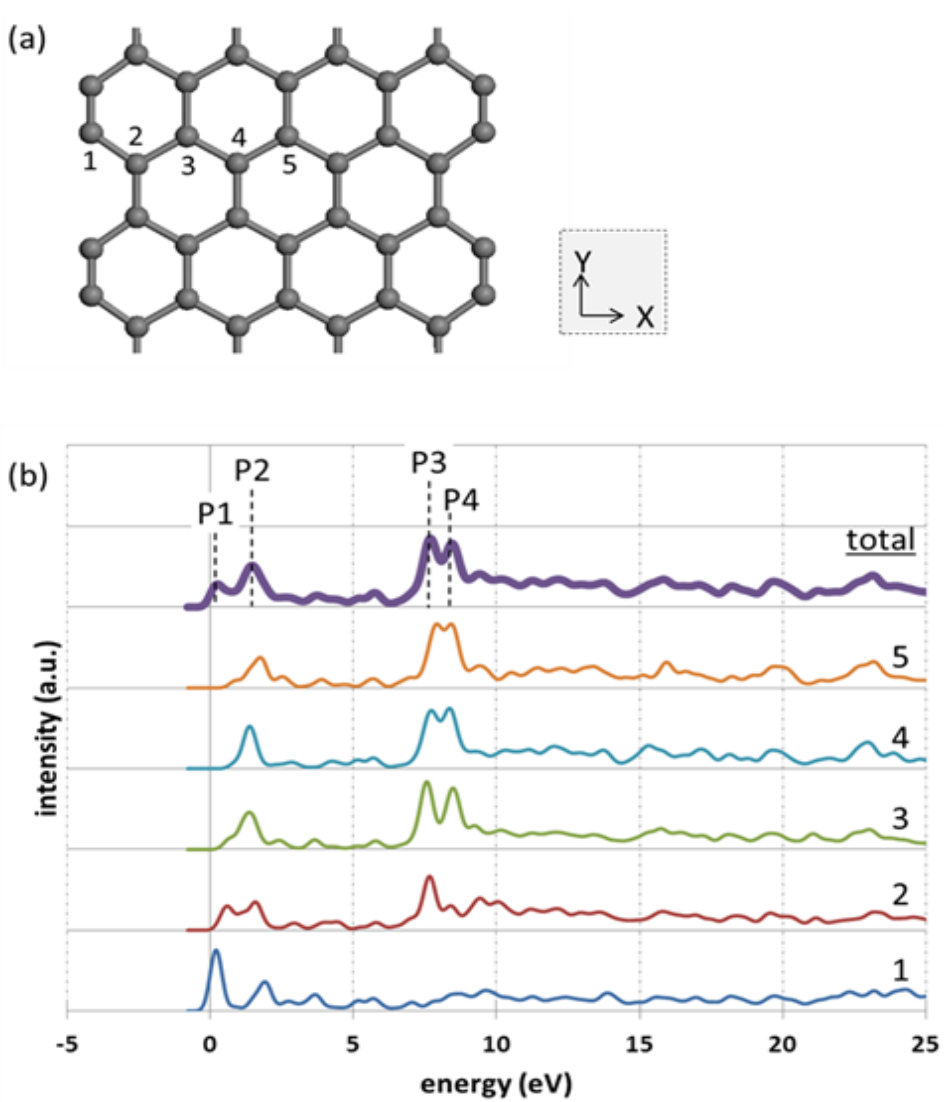
STEM Imaging

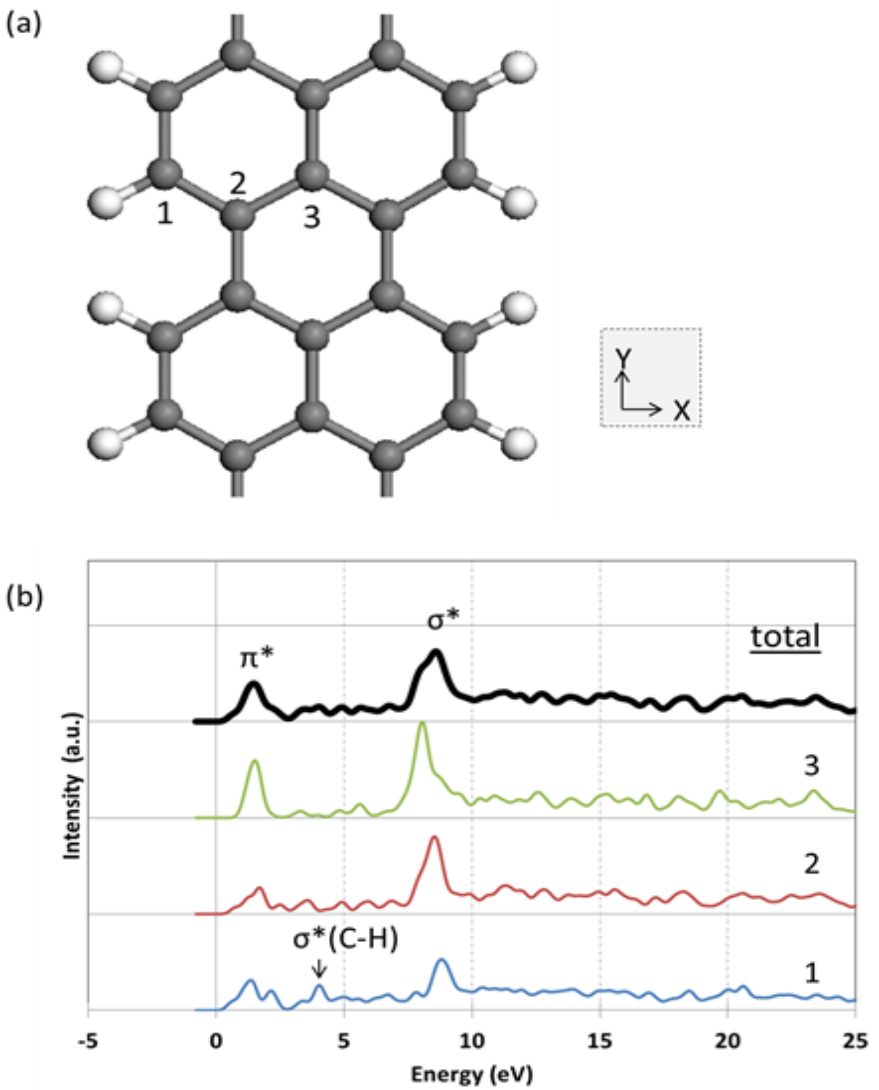




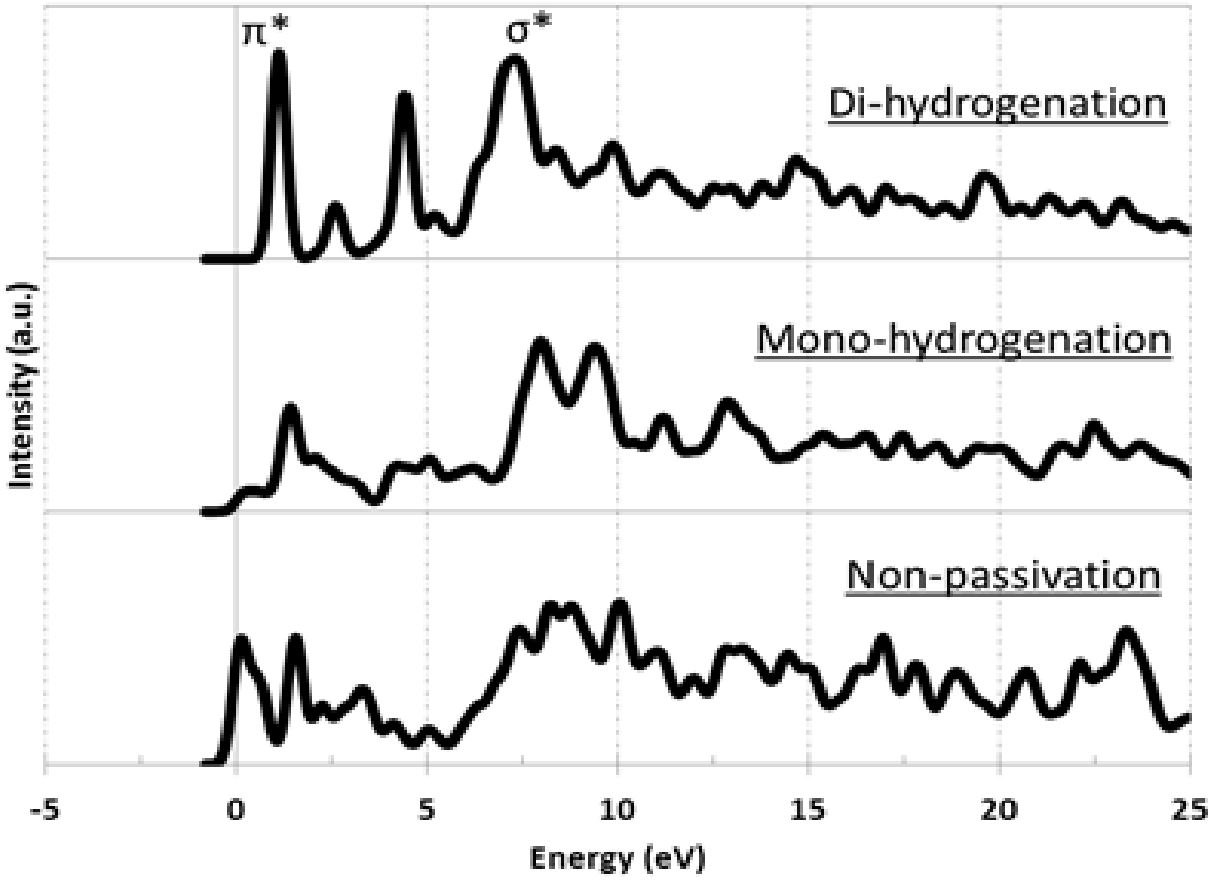


Nanoribbon: armchair termination





Nanoribbon: zigzag termination



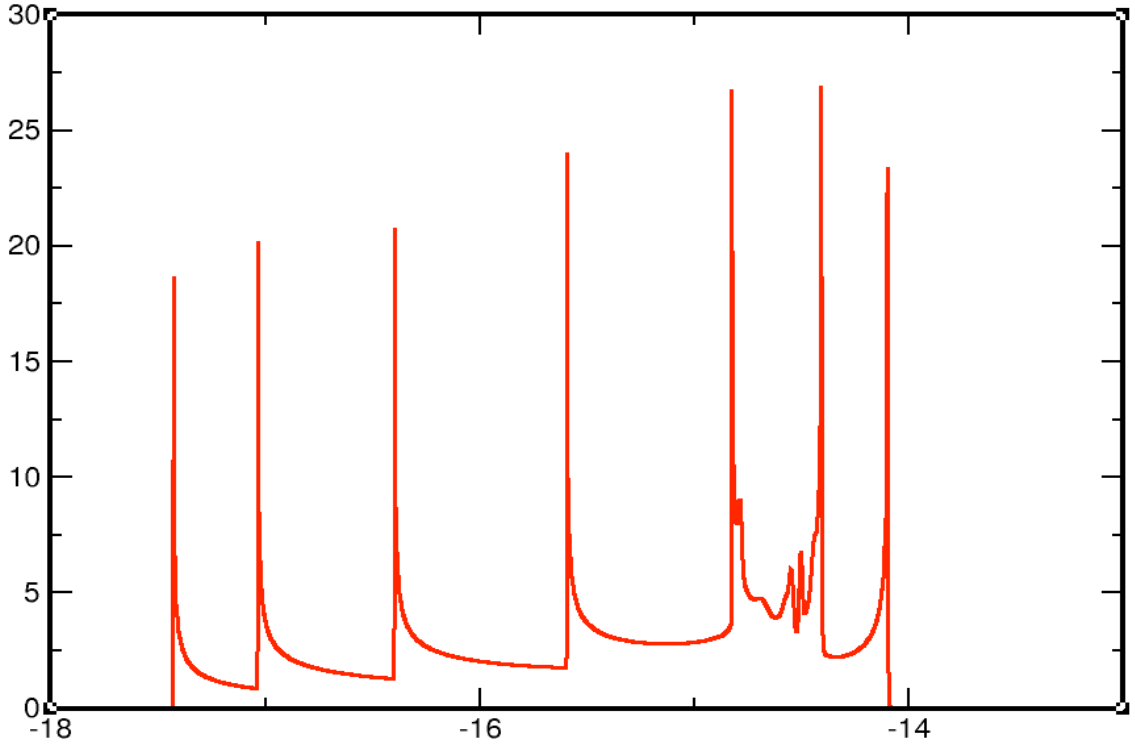
"Theoretical study of core-loss electron energy-loss spectroscopy at graphene nanoribbon edges",
Nobuyuki Fujita, Philip Hasnip, Matt Probert and Jun Yuan,
J. Phys. Condens. Matter 27, 305301 (2015).

Numerically Accurate Spectral Properties

www.optados.org

Andrew Morris (Cambridge), Rebecca Nicholls (Oxford), Chris Pickard (UCL), Jonathan Yates (Oxford)

DOS BN nanoribbon



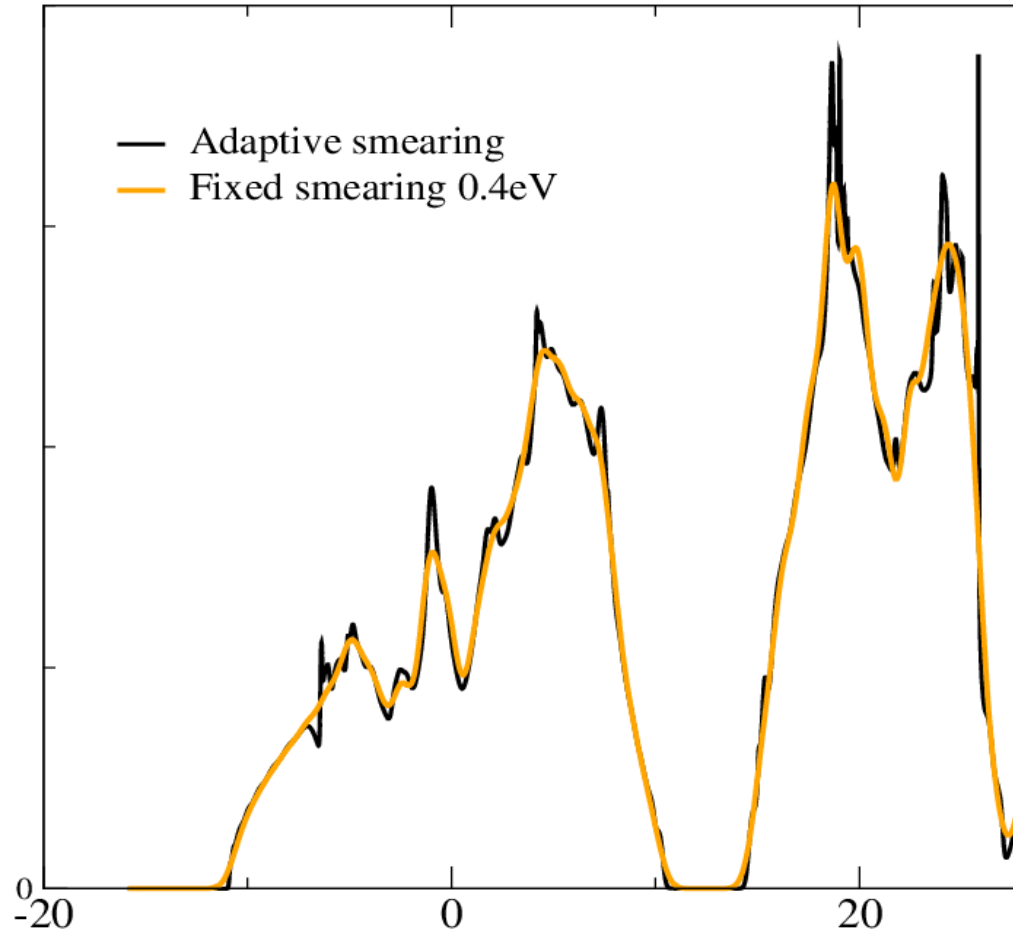
Adaptive broadening convolves each energy band with a Gaussian or Lorentzian whose width depends on the band-gradient (in reciprocal-space);
*from J.Yates, X.Wang, D.Vanderbilt and I.Souza, Phys. Rev. B, **75**, 195121 (2007)*

Optados

www.optados.org

Andrew Morris, Rebecca Nicholls,
Chris Pickard, Jonathan Yates

- Density of states (DOS)
- Projected DOS
- Joint-density of states (JDOS)
- Core-loss
  - Absorption and Emission
  - momentum (q) decomposition
  - Instrument and lifetime broadening
- Low loss
  - Metals & insulators



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*from J.Yates, X.Wang, D.Vanderbilt and I.Souza, Phys. Rev. B, **75**, 195121 (2007)*

Practical Details

CASTEP

- computes core and valence wavefunctions
- forms matrix elements

$$\langle \psi^n_{\mathbf{k}} | \mathbf{r} | c \rangle$$

Must use on-the-fly pseudo-potentials

Keywords:

```
task          : spectral
spectral_task : coreloss
```

OPTADOS www.optados.org

- Reads matrix elements
- Forms spectrum
- Can add instrument and lifetime broadening effects

more details in this afternoon's practical

Core-hole effects

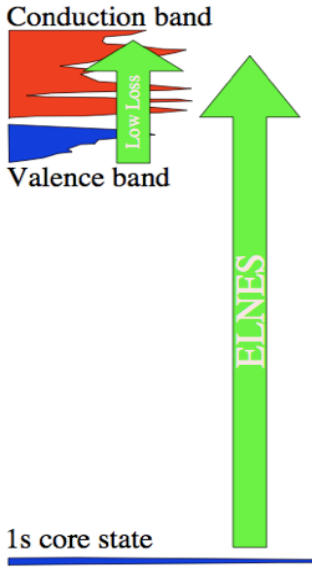
Single-particle approximation

Beyond the “sudden” approximation

1) Core electron ejected
2) Lattice remains fixed
3) Final states relax

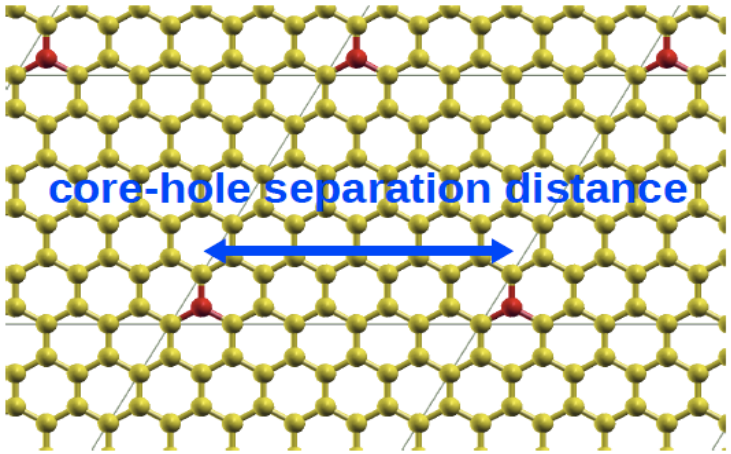
Initial core state from an atomic calculation

Final states from self consistent calculation with a single excited atom



Supercell approximation

- Core-hole atom breaks translational symmetry
- Create “supercell” of unit cell to reduce interaction between images
- Converge wrt supercell size



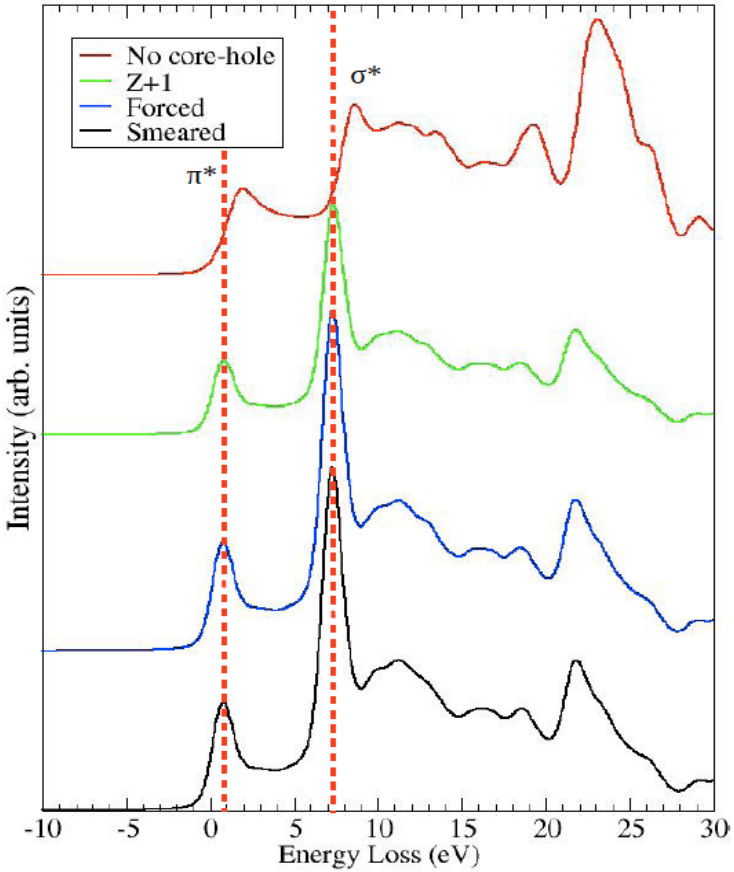
Excited Atom

Methods to include core-hole

- Z+1 approximation *(e.g. replace C with N)*
- Constrained calculation *(only possible with AE code)*
- Excited-state pseudopotentials

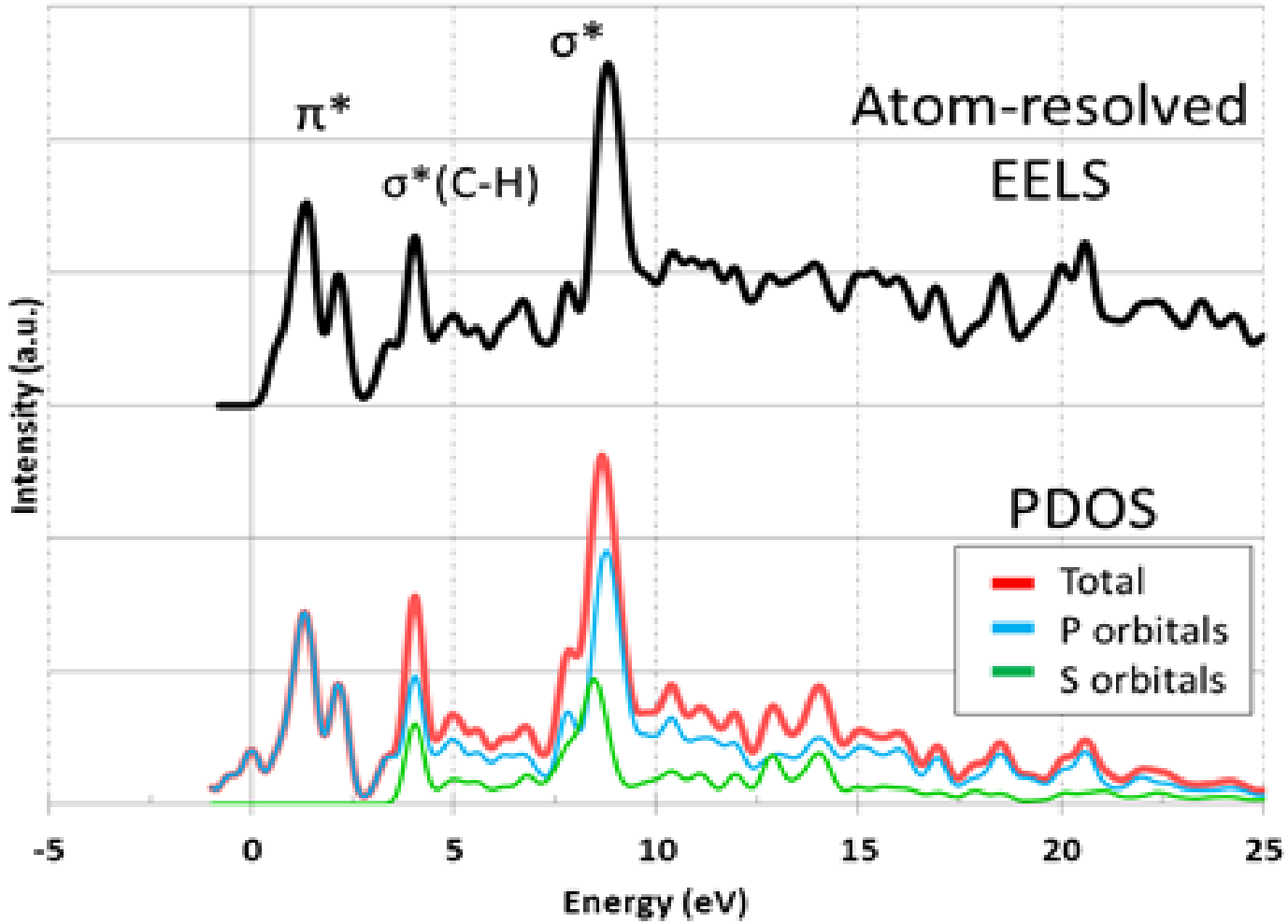
CASTEP's on-the-fly pseudopotential generator can create excited-state pseudopotentials (see practical)

Effect of core-hole depends on the material



Graphite

Angular Momentum Decomposition



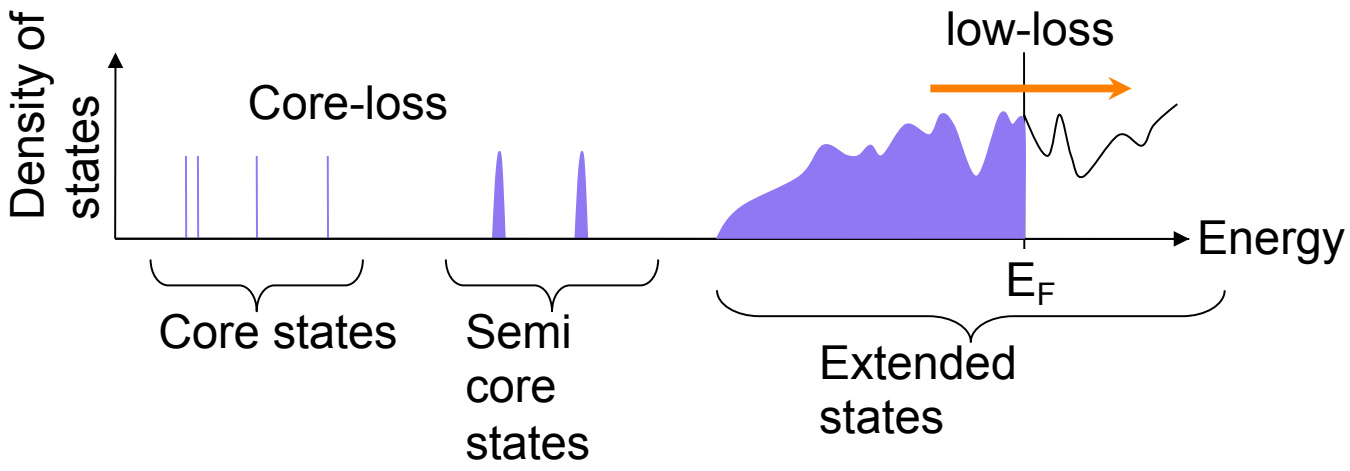
"Theoretical study of core-loss electron energy-loss spectroscopy at graphene nanoribbon edges",
Nobuyuki Fujita, Philip Hasnip, Matt Probert and Jun Yuan,
J. Phys. Condens. Matter 27, 305301 (2015).

Low Loss

$$\epsilon_2(E) = \frac{2\pi e^2}{\Omega \epsilon_0} \sum_{i,j,\mathbf{k}} | < \psi_{i\mathbf{k}} | \hat{\mathbf{u}}.\mathbf{r} | \psi_{j\mathbf{k}} > |^2 \delta(\epsilon_{i\mathbf{k}} - \epsilon_{j\mathbf{k}} - E)$$

The low-loss dielectric function is a weighted joint-density of states

$$jDOS(E) = \frac{1}{N_k} \sum_{i,j,\mathbf{k}} \delta(\epsilon_{i\mathbf{k}} - \epsilon_{j\mathbf{k}} - E)$$



Practical Details

CASTEP

- computes valence wavefunctions
- forms optical matrix elements

keywords

```
task : spectral
spectral_task : optics
```

OPTADOS www.optados.org

- Reads matrix elements
- Forms
- Uses Kramers-Kronig to obtain
- Computes loss function, conductivity, refractive index etc
- Can add broadening effects

more details in this afternoon's practical

Low loss

CASTEP

$$\varepsilon_2(\omega) = \frac{2\pi e^2}{\Omega \epsilon_0} \sum_{i,j,\mathbf{k}} | < \psi_{i\mathbf{k}} | \hat{\mathbf{u}}.\mathbf{r} | \psi_{j\mathbf{k}} > |^2 \delta(\epsilon_{i\mathbf{k}} - \epsilon_{j\mathbf{k}} - E)$$

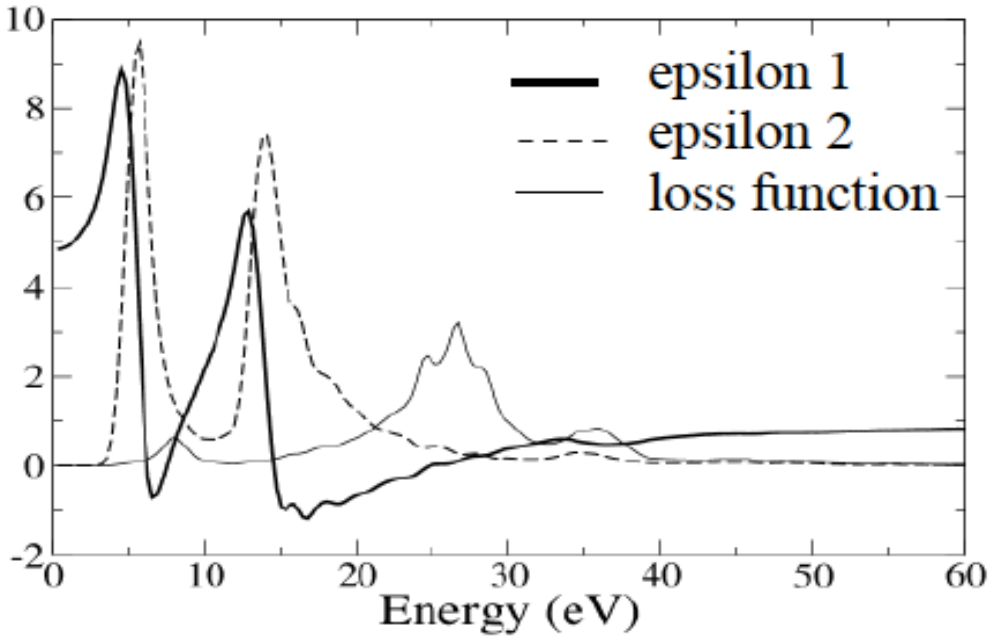
Kramers Kronig

OPTADOS

$$\varepsilon_1(\omega)$$

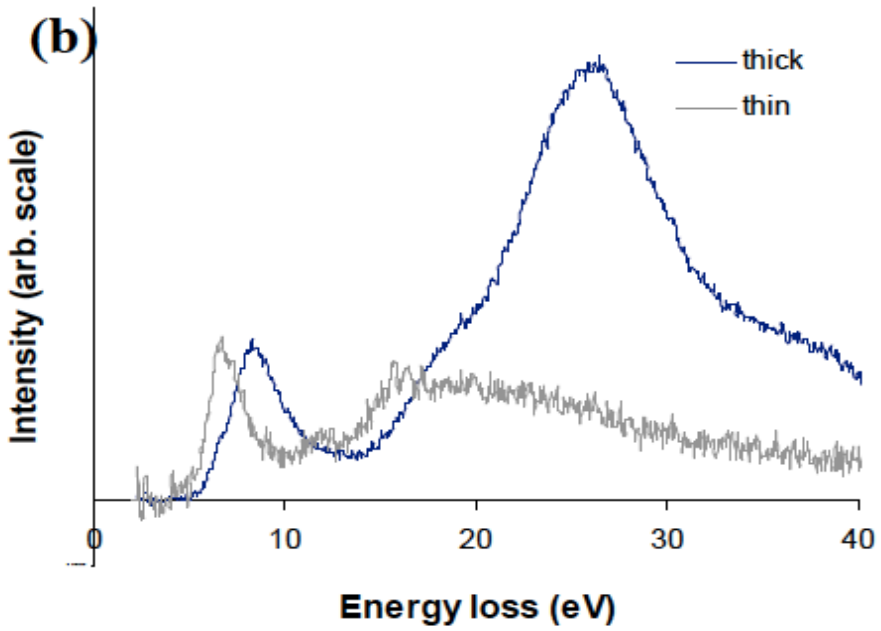
OPTADOS

$$Im\left\{\frac{-1}{\varepsilon(\omega)}\right\}$$

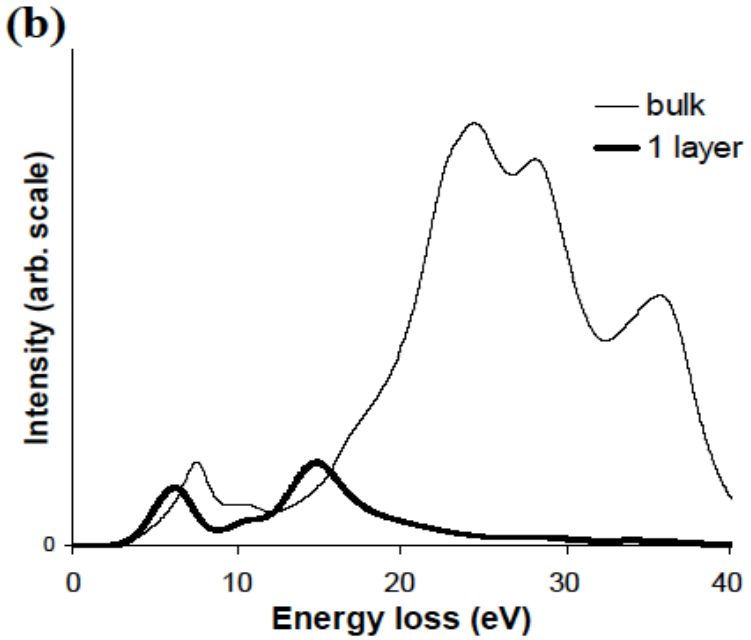


BN sheets

Experiment



Calculation



Beyond the ground state?

Many-body perturbation theory

Start with DFT
Use GW to get corrected excited states
Use Bethe-Salpeter Equation (BSE) to include electron-hole interactions (exciton)

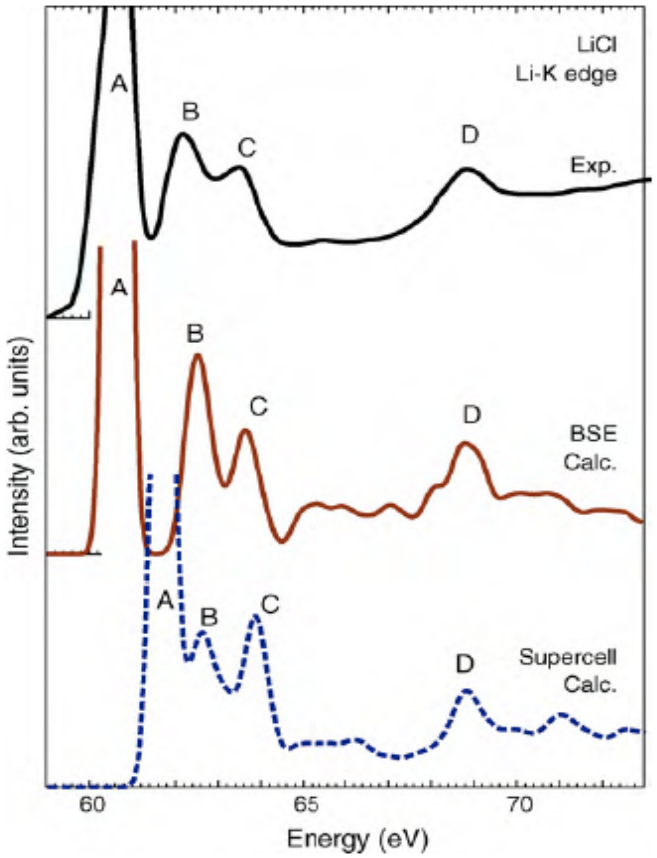
Time-Dependent DFT

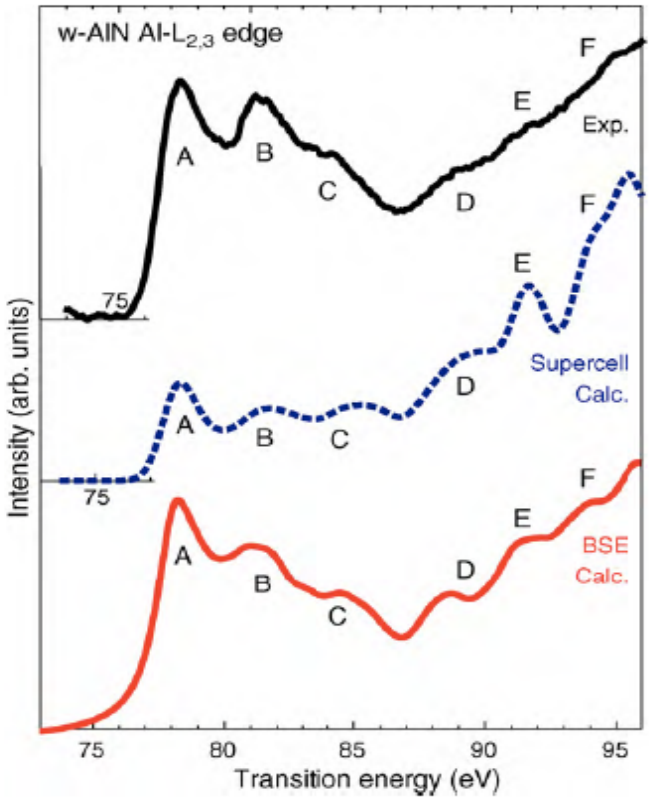
Exact solution of time-dependent QM
Need to devise time/frequency-dependent exchange-correlation kernel (see TDDFT lecture); may be useful for low-loss EELS

Multiplet Effects

For edges such as the $L_{2,3}$ there can be strong overlap between the core and valence wavefunctions

Li-K edges of LiCl





T. Mizoguchi et al. / Micron 41 (2010) 695–709

Things to remember

Standard electronic structure tools can provide qualitative interpretation of core and low-loss EELS

Care must be taken in interpreting unoccupied states in DFT; recall Hohenberg-Kohn theorem is only for *ground state* properties.

Many-body approaches such as GW (see next lecture) provide a route to *quantitative s*imulations, but at a v. high computational cost.

For core states with l>0 there can be strong core-valence overlap, which is often not well captured; i.e. K-edge EELS simulated much more reliably than L- or M-edge EELS.

Can TD-DFT (see previous lecture) provide a useful balance of speed and accuracy?

Getting more information

OptaDOS manual
http://www.optados.org

Chris Pickard's PhD thesis:
http://www.tcm.phy.cam.ac.uk/~cjp20/old/thesis.ps.gz

Summary paper of Castep's spectroscopic capabilities:
"Electron and vibrational spectroscopies using DFT, plane waves and pseudopotentials: CASTEP implementation"
V. Milman, K. Refson, S.J. Clark, C.J. Pickard, J.R. Yates, S.P. Gao, P.J. Hasnip, M.I.J. Probert, A. Perlov, M.D. Segall
Journal of Molecular Structure: THEOCHEM 954 (1-3) 22-35 (2010)