Simulation of electron energy loss spectra of nanomaterials with linear-scaling density functional theory

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Atomic Scale Materials Microscopy: Theory Meets Experiment
York 27/6/17

Motivation - TiO_2

Functional

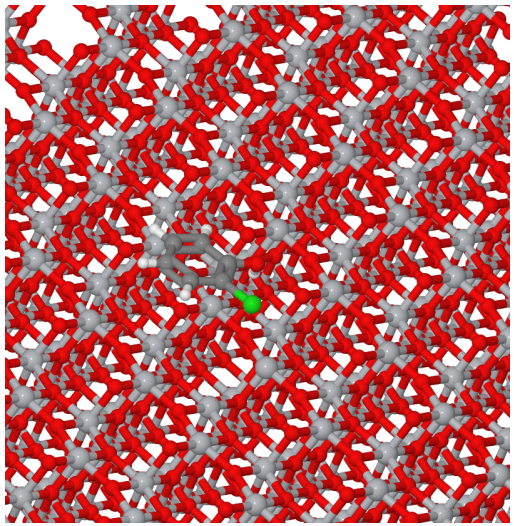
- Photocatalysis
- Photovoltaics

Economic

- Abundant
- Cheap
- Non-toxic

Defects

- What surface structures are present?
- Have we made what we intended to make?



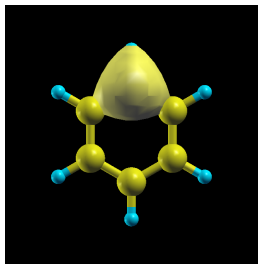
How Can Theory Help?

- Identify likely stable structures (AIRSS etc.)
- Predict experimentally measurable properties

Linear Scaling DFT - ONETEP

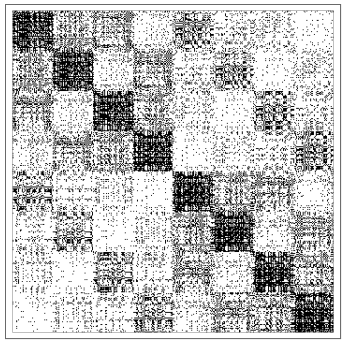
NGWF

Non-orthogonal Generalised Wanier Function - spatially localised basis function, itself expressed in terms of periodic sinc (PSinc) functions



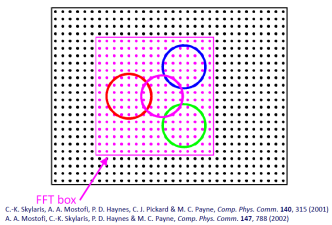
Density Kernel

Used to express the density matrix in terms of NGWFs $\rho(r, r') = \phi_\alpha(r) K^{\alpha\beta} \phi_\beta(r')$



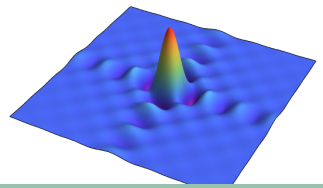
FFT Box

Segment of the cell containing an NGWF and all NGWFs which overlap it



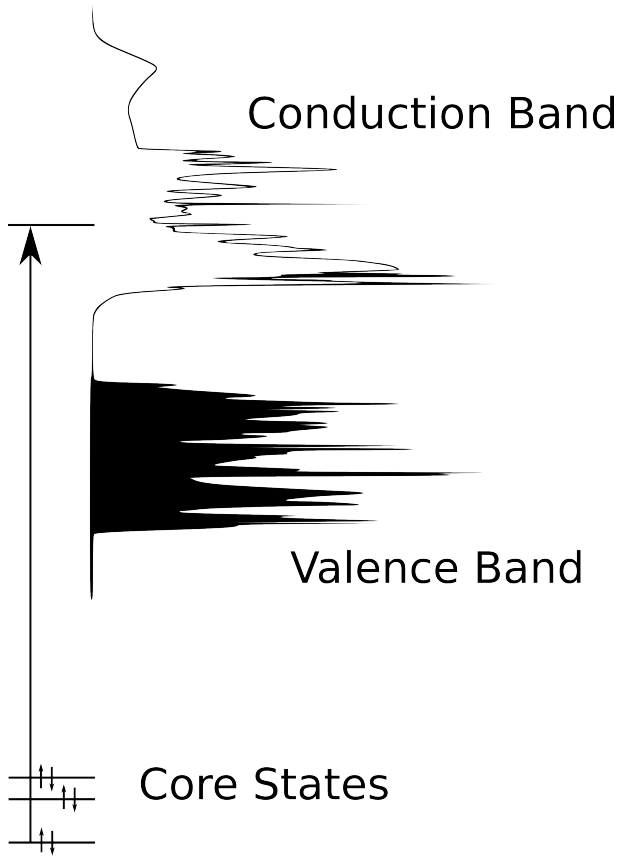
Cut off

The PSinc plane wave basis is truncated to waves with an energy less than the cut off energy



Modeling EELS

- Fermi's Golden Rule
- Dipole approximation
- $\epsilon_2(\omega) = \frac{1}{\Omega} \sum_c \sum_i |\langle \psi_i | \mathbf{r} | \psi_c \rangle|^2 \delta(E_i - E_c - \omega)$
- c runs over core states, i over conduction band states
- Compute matrix elements like $|\langle \psi_i | \mathbf{r} | \psi_c \rangle|$
- Focus on single core state
- Use OptaDoS to convert matrix elements into spectrum
- Various broadening schemes available



Conduction Band

- In ground state calculation NGWFs and Kernel optimised to represent valence manifold
- Valence NGWFs bad at representing the conduction manifold
- A separate kernel and NGWF set must be optimised
- $\rho_c(r, r') = \chi_\alpha(r) K_c^{\alpha\beta} \chi_\beta(r')$
- Optimisation non self consistent $\rightarrow$ faster

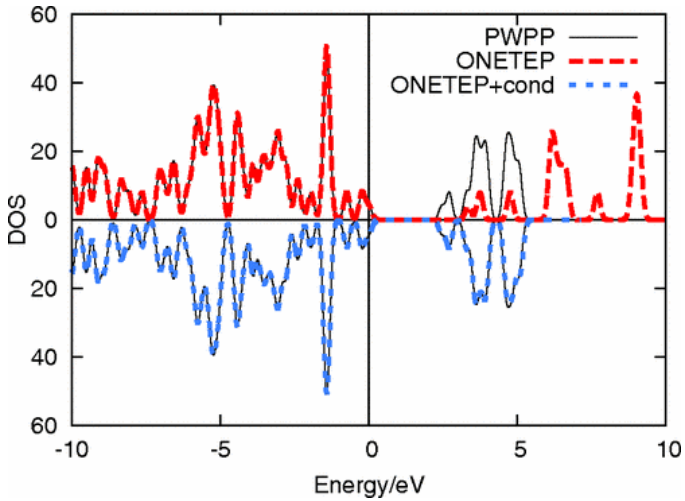
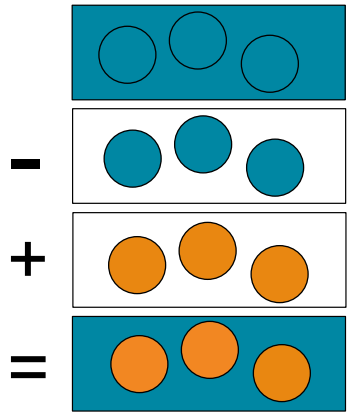


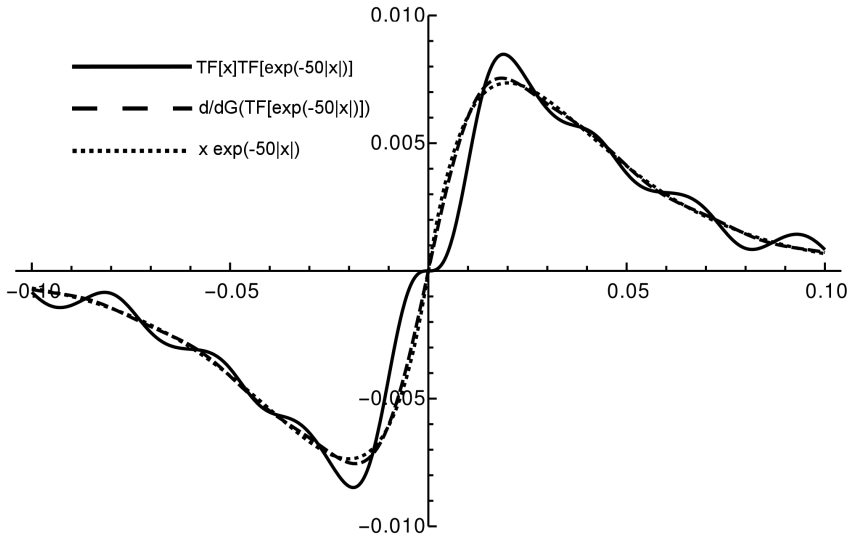
Figure: Improvement in accuracy of conduction DoS when a separate kernel and NGWF set are used. From[1]

[1] Ratcliff, Laura E., Nicholas DM Hine, and Peter D. Haynes. "Calculating optical absorption spectra for large systems using linear-scaling density functional theory." Physical Review B 84, no. 16 (2011): 165131.

Projector Augmented Wave

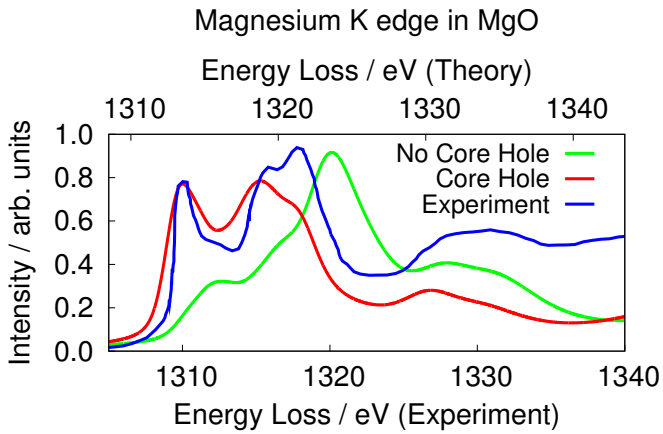
- Need correct wavefunction near the nucleus to do EELS calculations.
- PAW - Projector Augmented Wave, method due to Blöchl used to retrieve all electron properties from a pseudo potential calculation
- $|\psi^{\mathrm{KS}}\rangle = |\widetilde{\psi}^{\mathrm{KS}}\rangle + \sum_i \langle \widetilde{p}_i | \widetilde{\psi}^{\mathrm{KS}} \rangle (|\varphi_i\rangle - |\widetilde{\varphi}_i\rangle)$
- Form core-position kets $\mathbf{r}|\psi_c\rangle$ using Fourier space method





Core Holes

- Electron excited to the CB leaves hole
- Electron and hole interact, pronounced in insulators (reduced screening)
- Must account for this
- One solution is to modify PAW dataset used for excited atom
- This is only an approximation
- Can include fractional core holes
- Example configuration strings for carbon: $1s^2 2s^2 2p^4 \rightarrow 1s^1 2s^2 2p^5$ $1s^2 2s^2 2p^4 \rightarrow 1s^{1.5} 2s^2 2p^{4.5}$



Computing Edge Offset Energies

- We follow the approach of Mizoguchi[1]
- Compute ground state energy for system with and without core hole
- In the core hole case the excited electron is included
- Energy difference of these two calculations estimates correction to conduction band offset due to core hole
- Use results for dataset generation to include core orbital effects

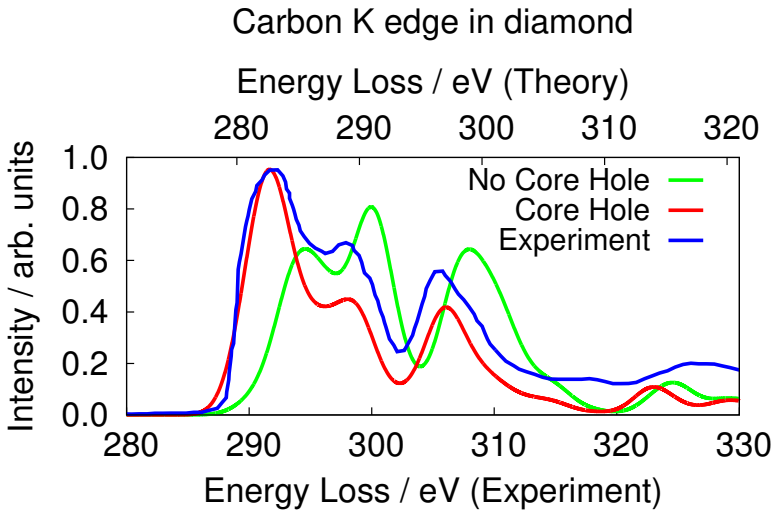
Edge Offset Energy

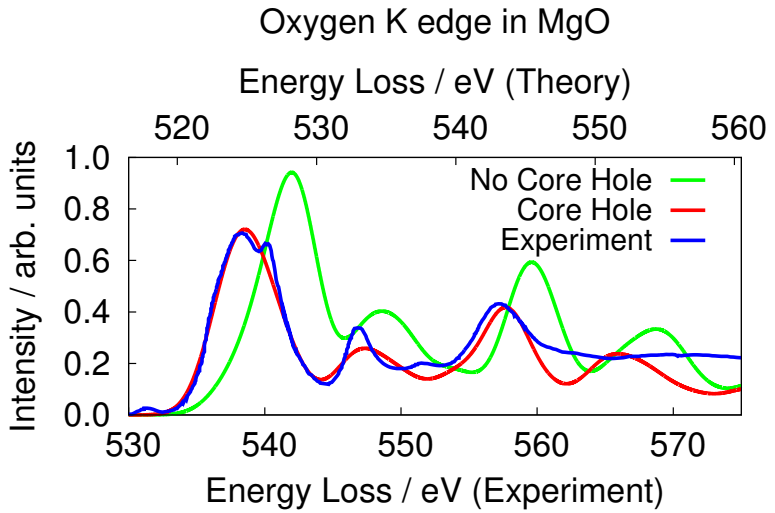
Compute Using:

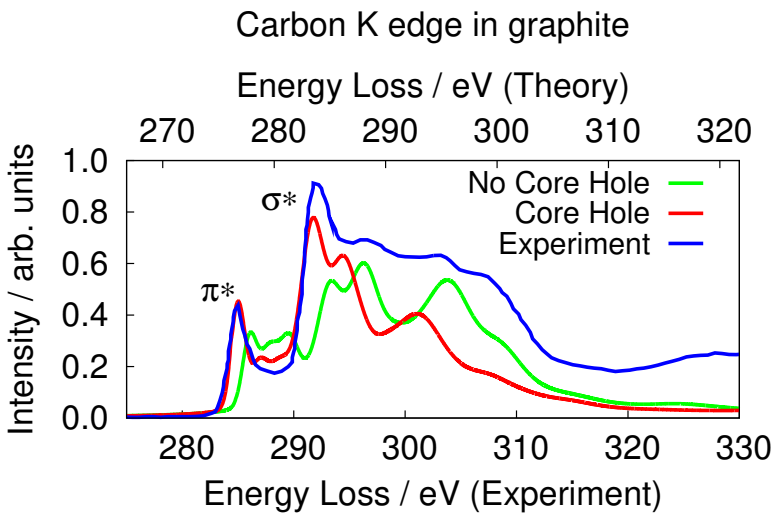
$$E_{\mathrm{edge}} = (E_{\mathrm{sys+ch+e}} - E_{\mathrm{sys,gs}}) + (E_{\mathrm{aeatom+ch+e}} - E_{\mathrm{aeatom,gs}}) - (E_{\mathrm{psatom+ch+e}} - E_{\mathrm{psatom,gs}})$$

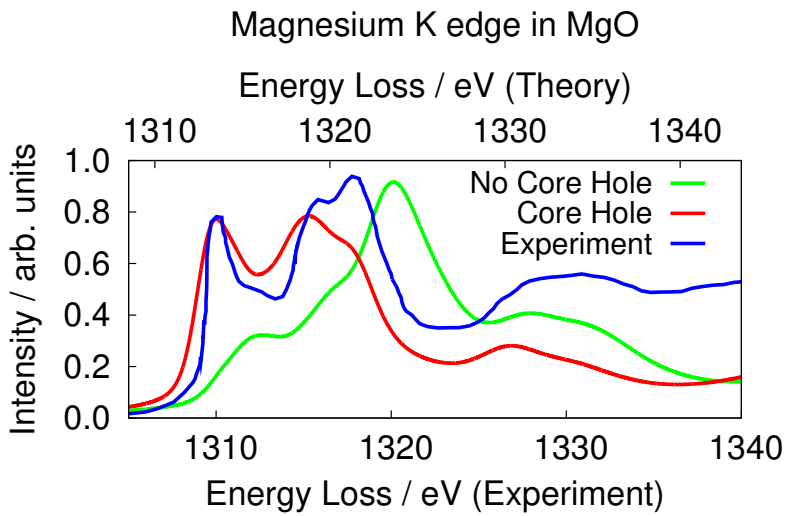
[1] Mizoguchi, Teruyasu, Isao Tanaka, Shang-Peng Gao, and Chris J. Pickard. "First-principles calculation of spectral features, chemical shift and absolute threshold of ELNES and XANES using a plane wave pseudopotential method." Journal of Physics: Condensed Matter 21, no. 10 (2009): 104204.

Some Simple Tests



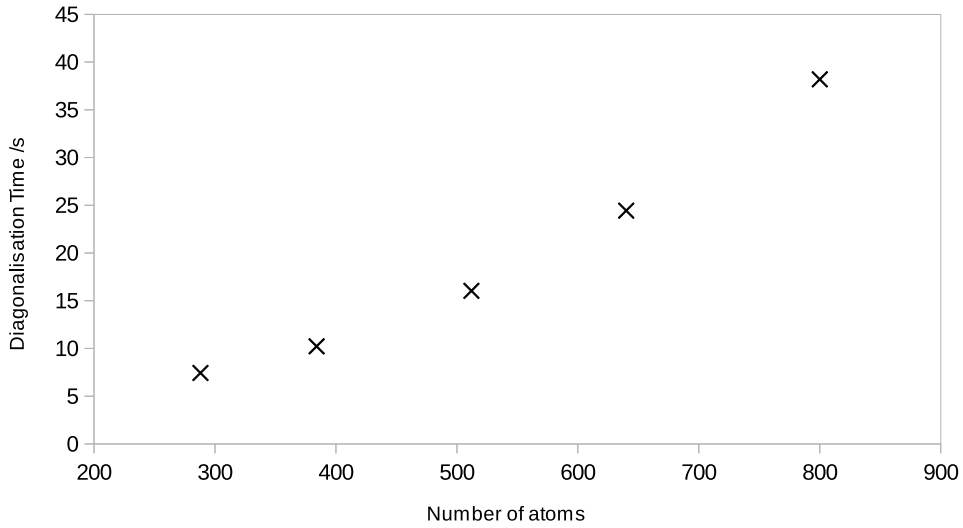


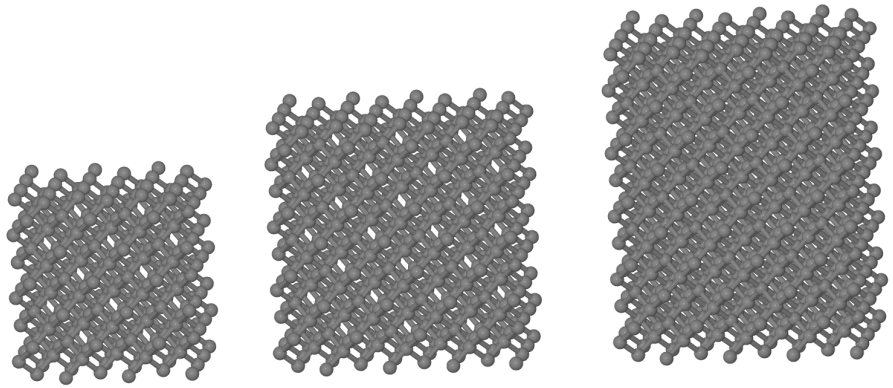




Effort Scaling

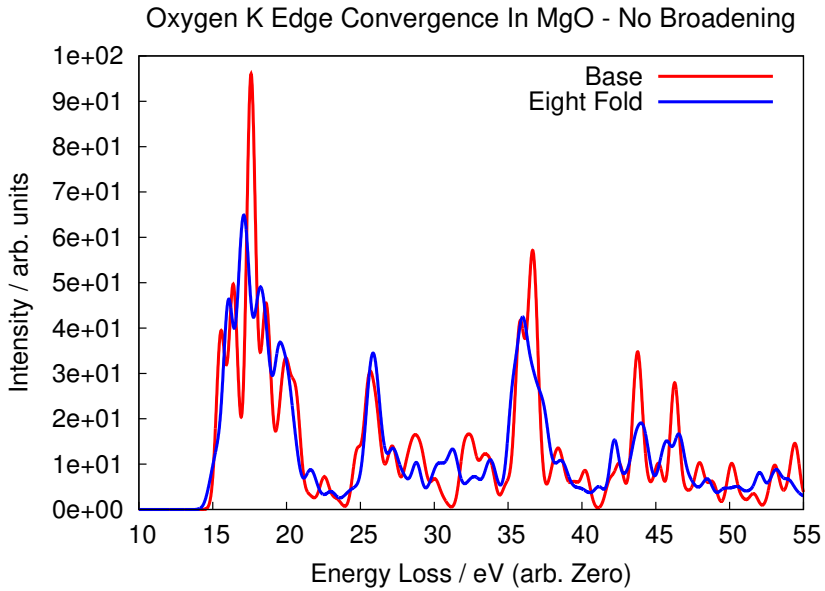
- Ground state calculation: $\mathcal{O}(n)$
- We need Kohn-Sham conduction wavefunctions
- Use plain diagonalisation: $\mathcal{O}(n^3)$
- ONETEP's minimal basis keeps the matrices manageable for systems with up to several thousand atoms.

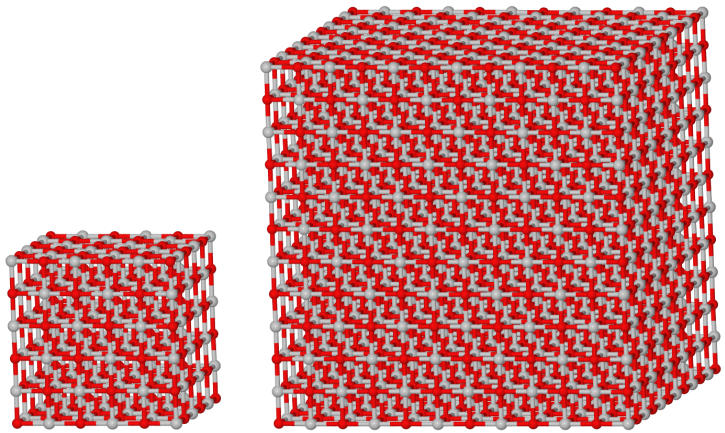




Size Convergence

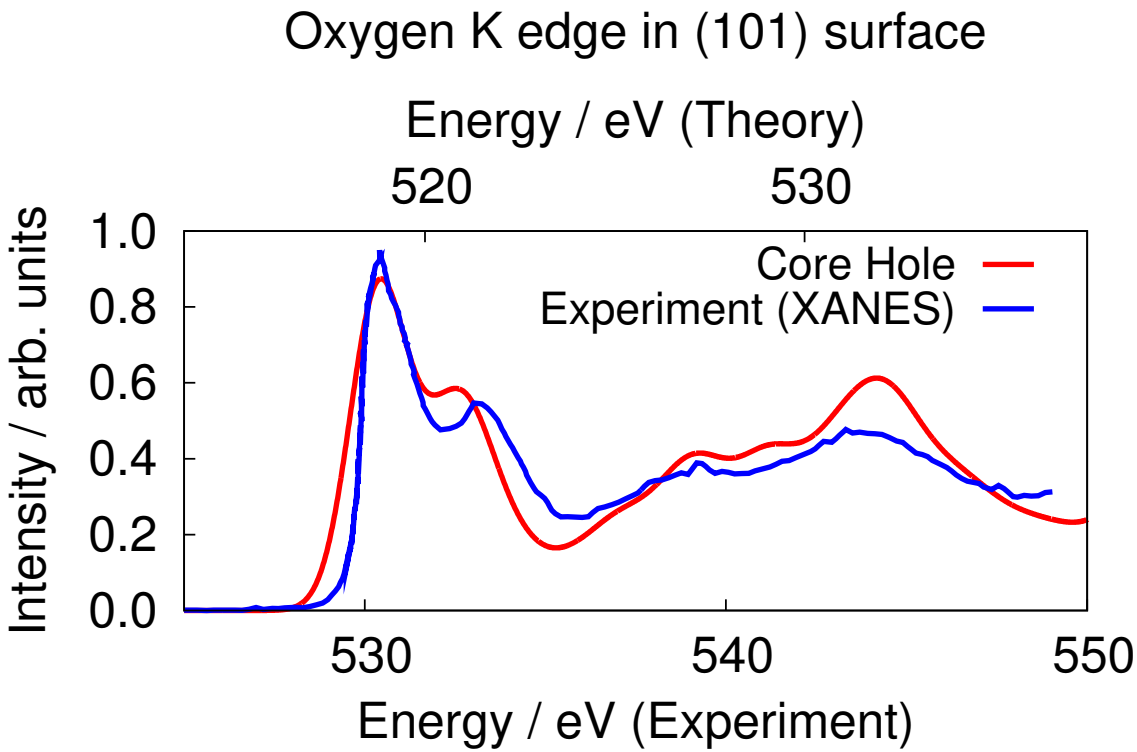
- Great advantage of ONETEP - large cells
- We can study the convergence of spectra with respect to simulation cell size
- We find that simulations at the 200 atom scale are well converged





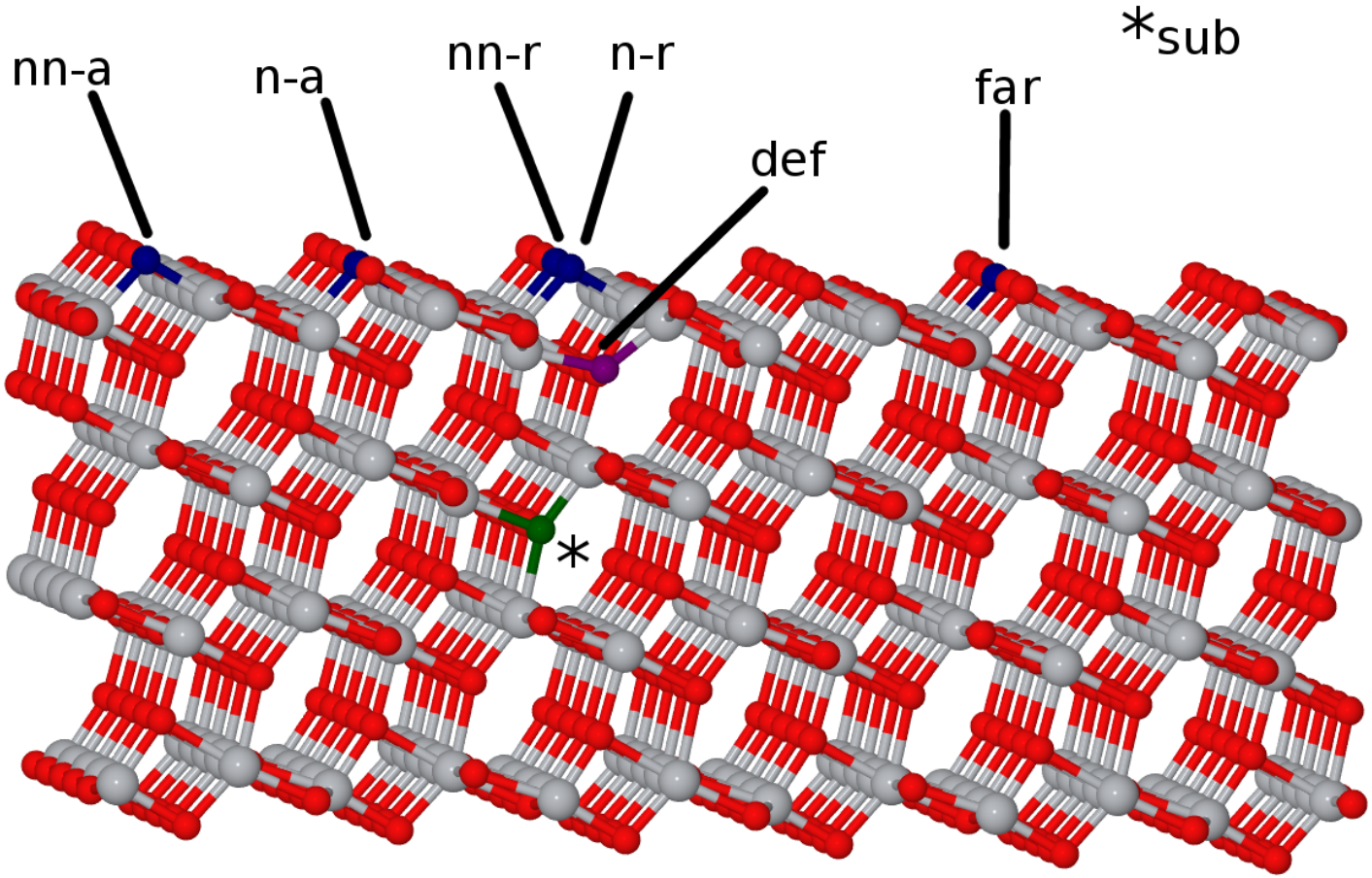
The Perfect Surface

Comparison to X-ray Absorption Near Edge Spectroscopy[1]

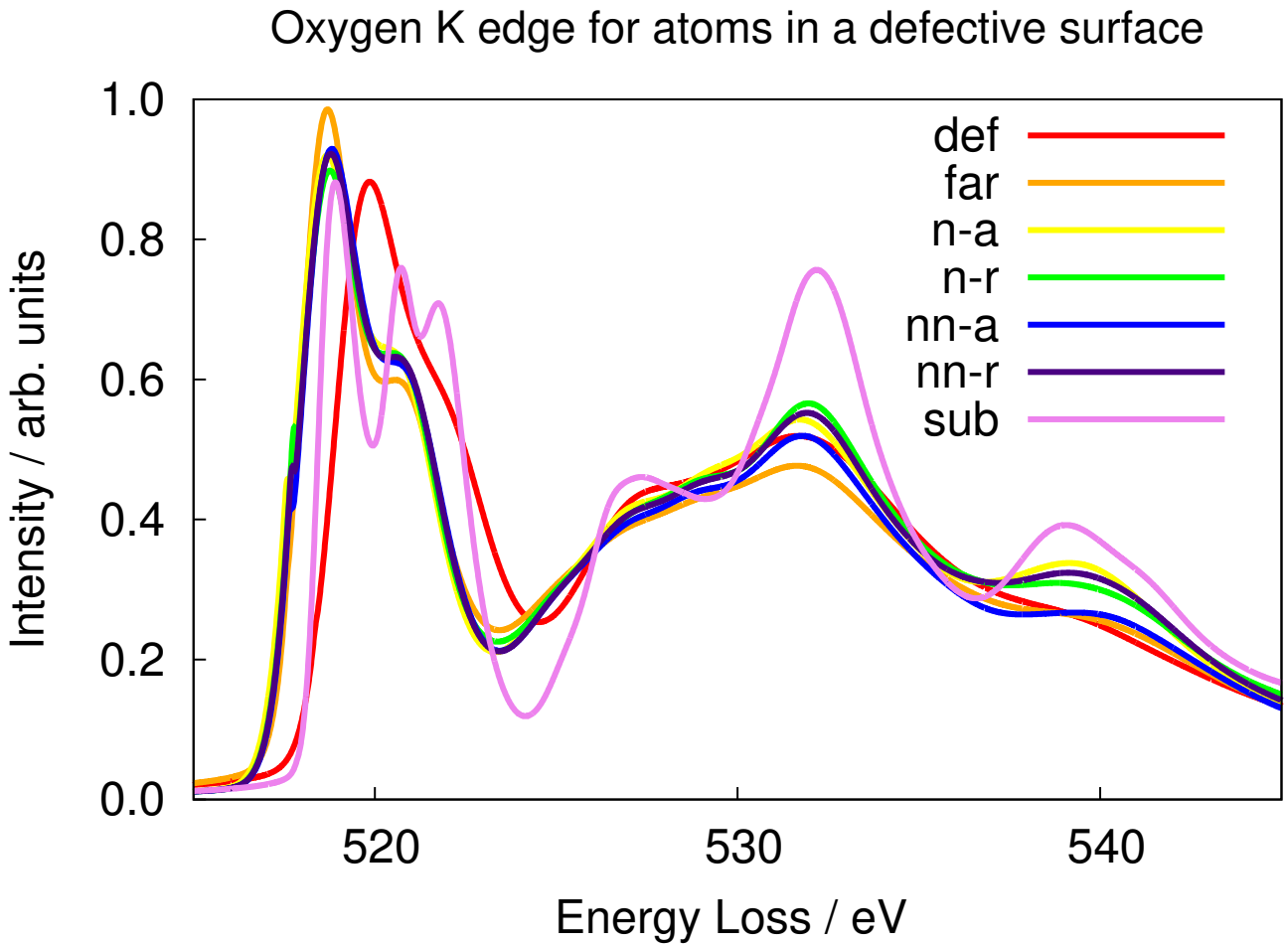


[1] Experimental data from: Thomas, A. G., W. R. Flavell, A. K. Mallick, A. R. Kumarasinghe, D. Tsoutsou, N. Khan, C. Chatwin et al. "Comparison of the electronic structure of anatase and rutile TiO 2 single-crystal surfaces using resonant photoemission and X-ray absorption spectroscopy." Physical Review B 75, no. 3 (2007): 035105.

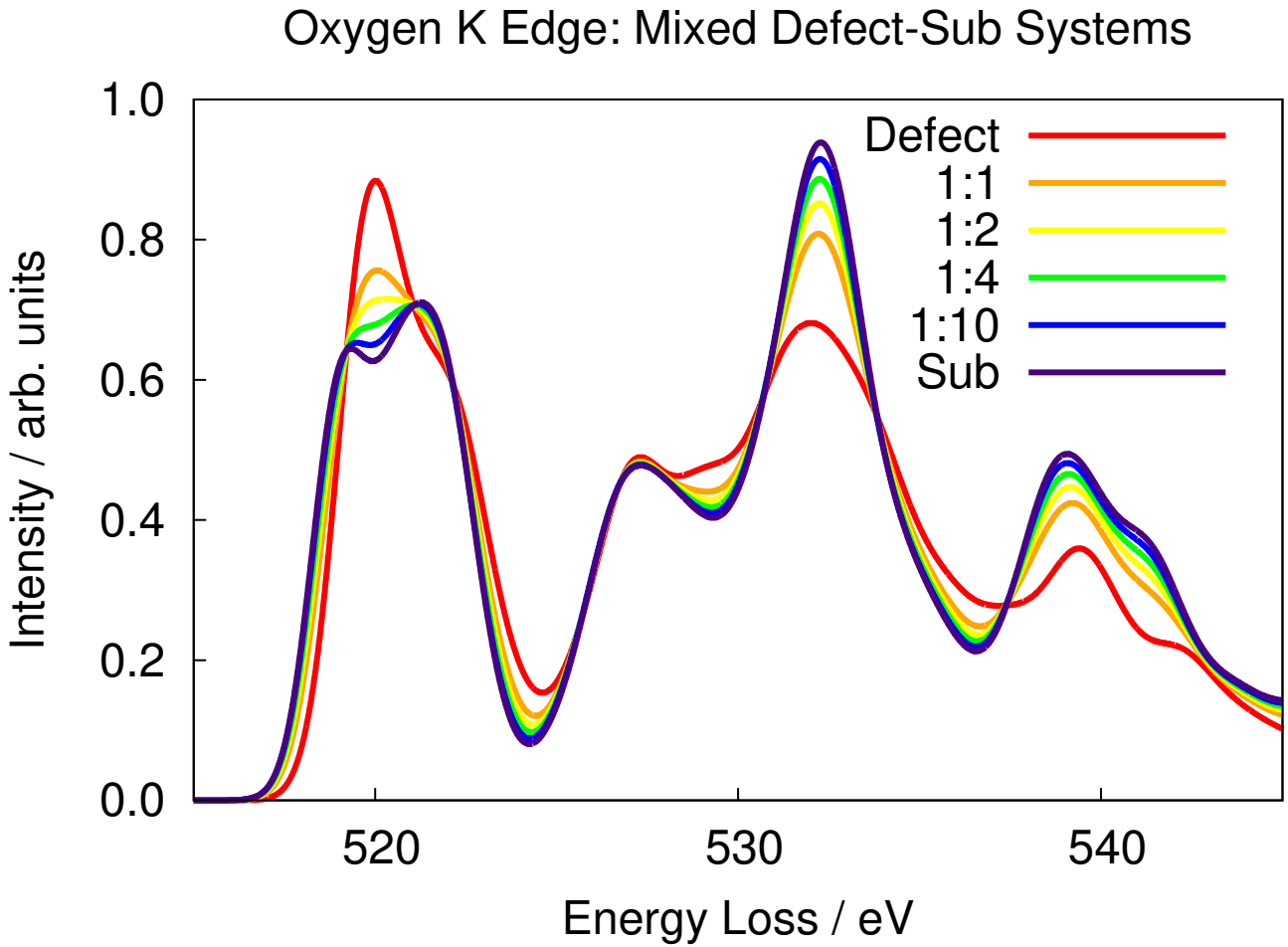
Adding Defects



Initial Results - Very Local?



Finite Thickness



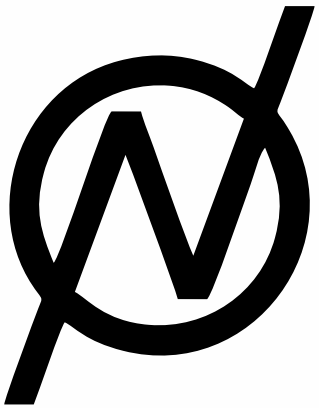
Directions

- Non native defects far easier as their edges will stand out
- EELS really is a very local method
- If we're hunting for defects we wont see anything unless:
  1. the beam strikes the size directly.
  2. Its helps a lot if the defect leads to split or greatly shifted
- Defects with radically different coordination
- Interstitials likely to be most distinctive intrinsic defect

Thanks

Nick Hine, Cate Ducati and the TCM group for their advice and support
Laura Ratcliff, who did a great deal of the ground work for this project
The NanoDTC, for funding my position
This work was performed using the Darwin Supercomputer of the University of Cambridge High Performance Computing Service.

TCM



And, of course, all of you for your attention.