Title: Density Functional Theory: A New Computational Approach for XAS of Solids

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Abstract:

Density Functional Theory: A New Computational Approach for XAS of Solids

Looking for Rydberg transitions using GPAW

Mercedes Martinson under Dr. Stephen Urquhart

Women in Physics Canada
IQC – July 20th, 2011

UNIVERSITY OF SASKATCHEWAN

- Rydberg Transitions
- GPAW
  - Grid-based projector-augmented wave method
- FD mode
  - Finite Difference
- LCAO mode
  - Linear Combinations of Atomic-like Orbitals
- Results
- Future work

Rydberg Orbitals and Transitions

- For an atom, an orbital with principal quantum number greater than that of any occupied orbital of the ground state.
- For a molecular entity, a molecular orbital which correlates with a Rydberg atomic orbital in an atomic fragment produced by dissociation.
- In spectra, Rydberg transitions appear as lower intensity near-edge peaks

- GPAW is a density-functional theory (DFT) Python code based on the projector-augmented wave (PAW) method. It uses real-space uniform grids and multigrid methods or atom-centered basis-functions.
- It's freely available!
- Finite Difference (FD) mode
- Linear Combination of Atomic-like Orbitals (LCAO) mode

https://wiki.fysik.dtu.dk/gpaw/

How to calculate a spectrum in GPAW

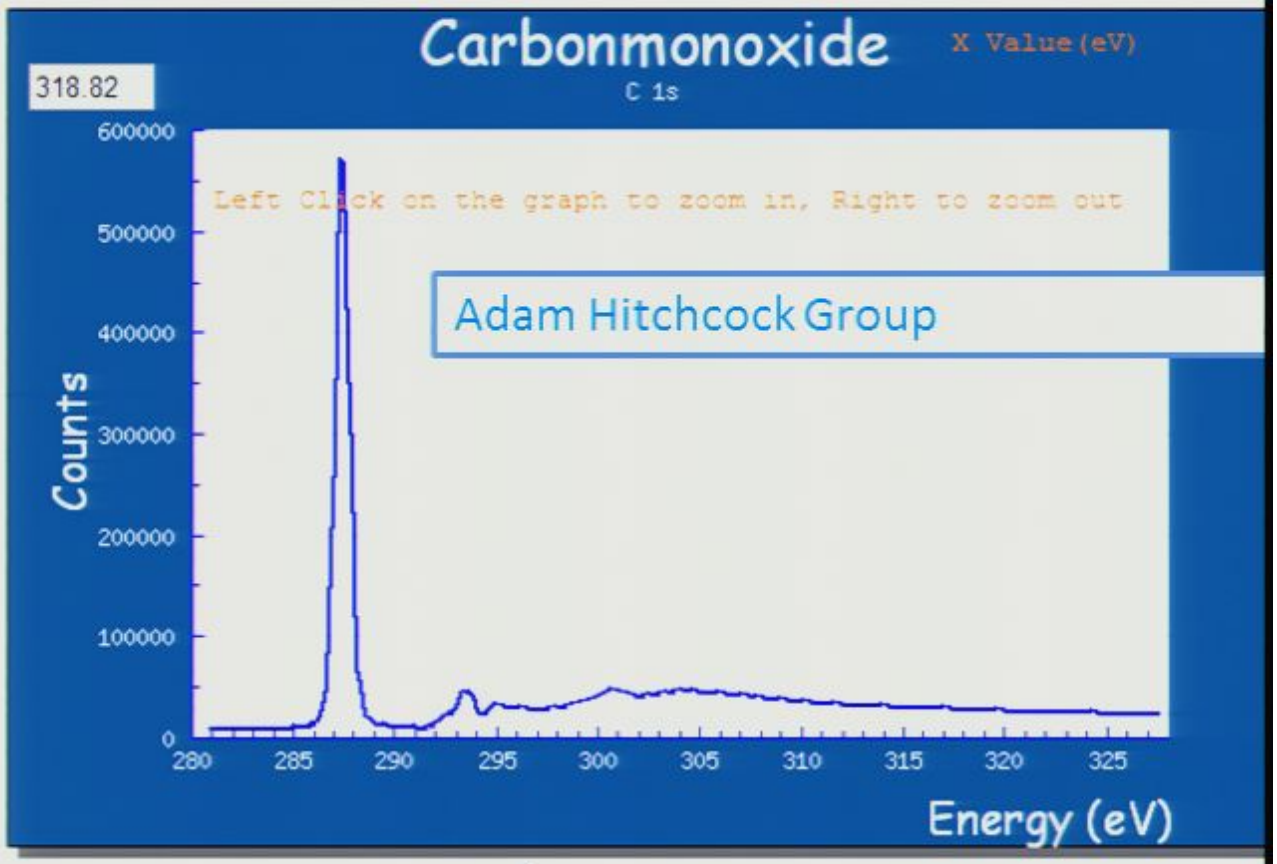
1. "ground state" calculation with a core hole
   - Produces the spectrum
2. Ground state energy
3. Energy of a half core hole
   - Spectrum is shifted by the difference of these (core hole – ground state), which

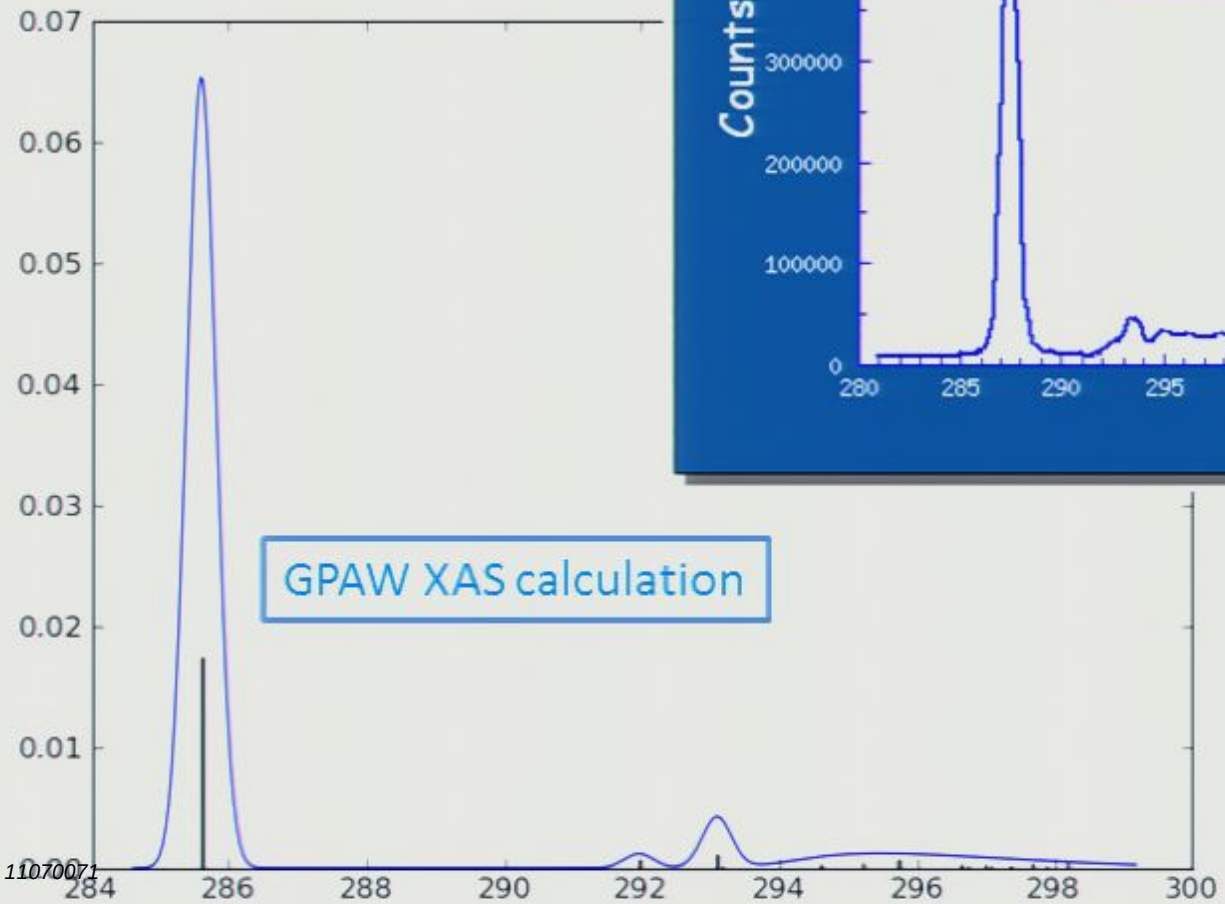
- Each step can be done with either LD or LCAO

FD mode

- A popular numerical algorithm
- Accurate
- Doesn’t pick up NEXAFS features
- Convergence problems
- Inflexible

Carbonmonoxide (CO)





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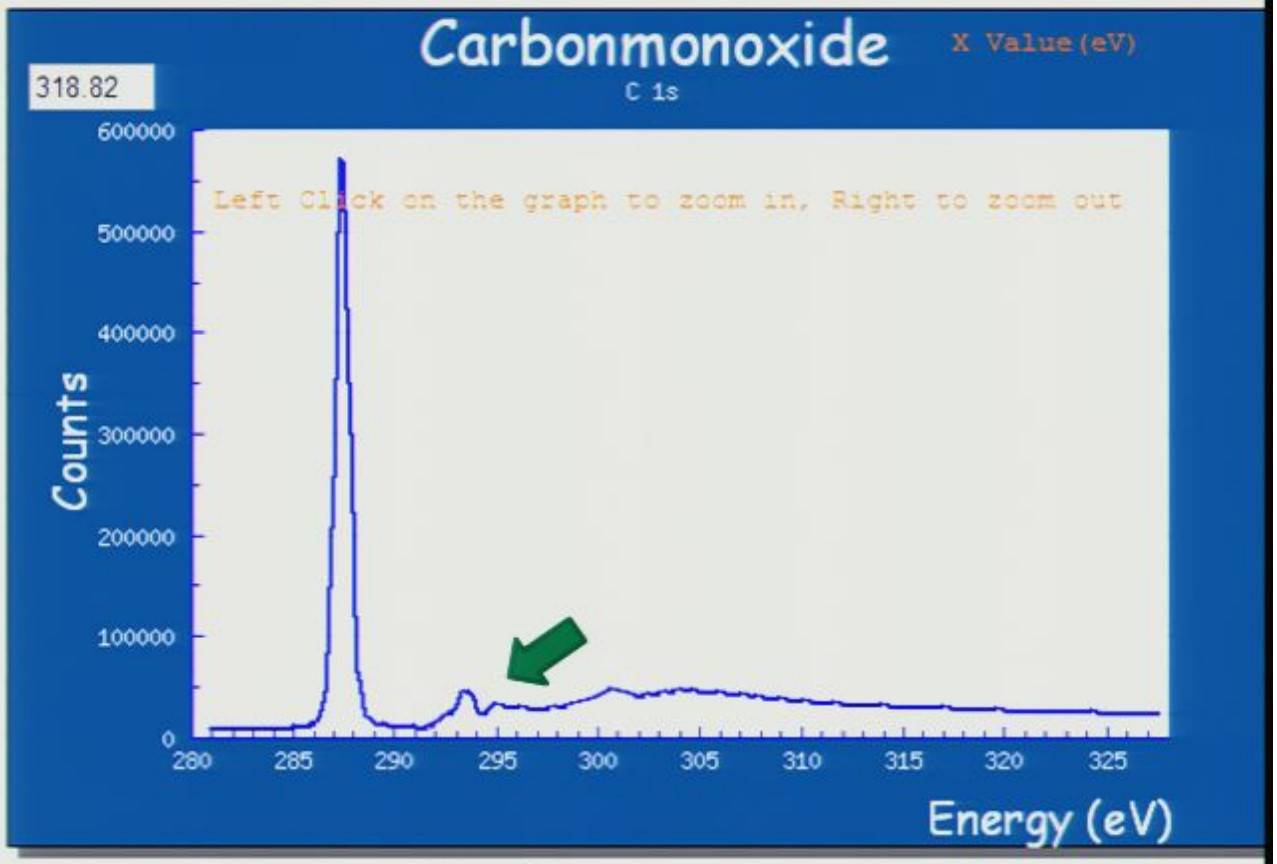
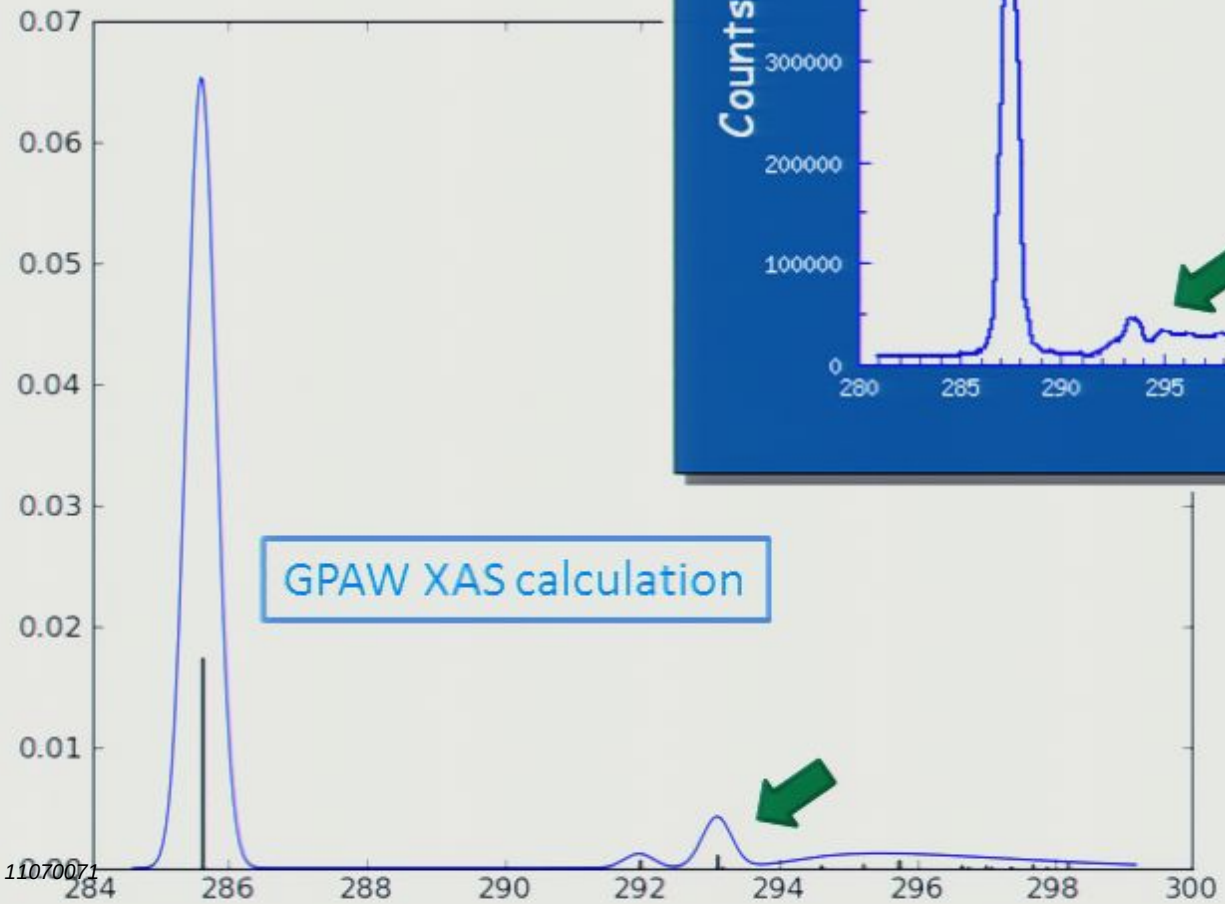
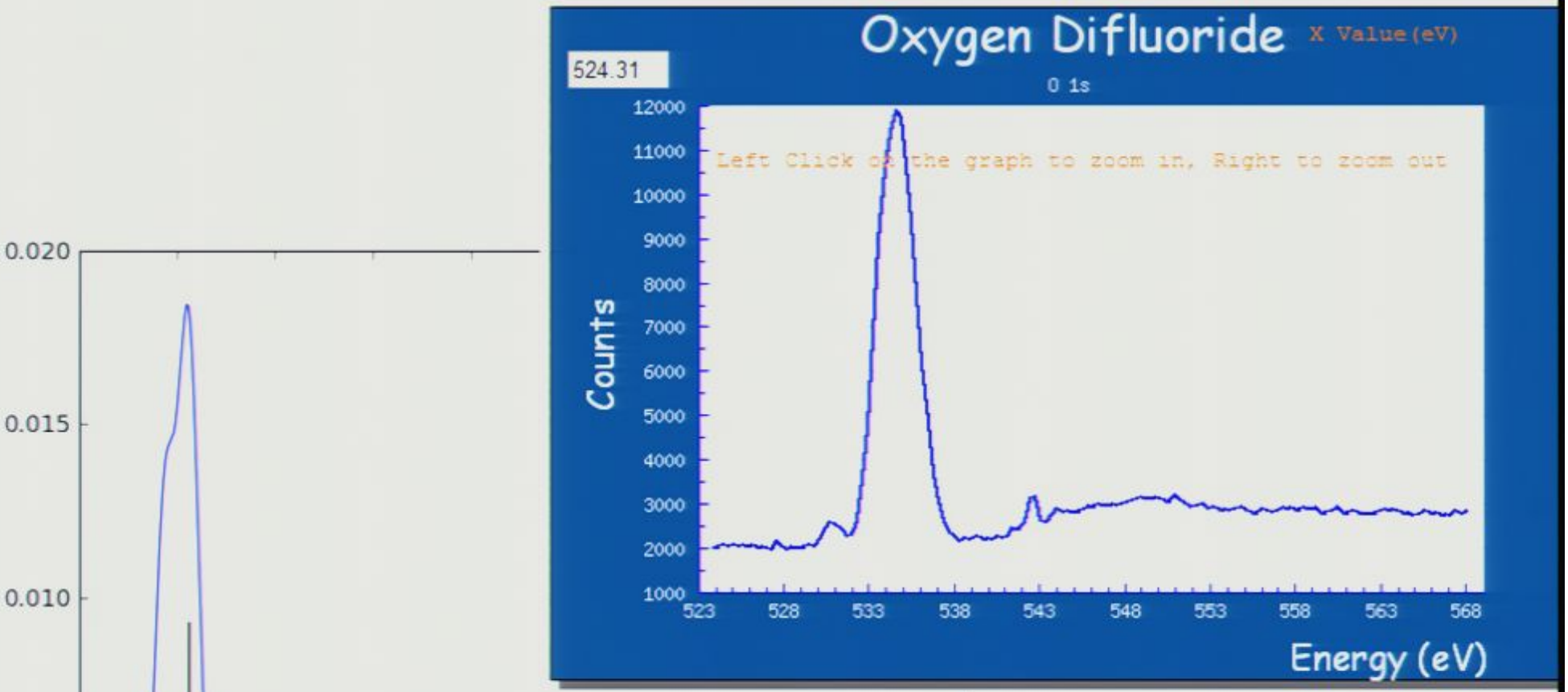


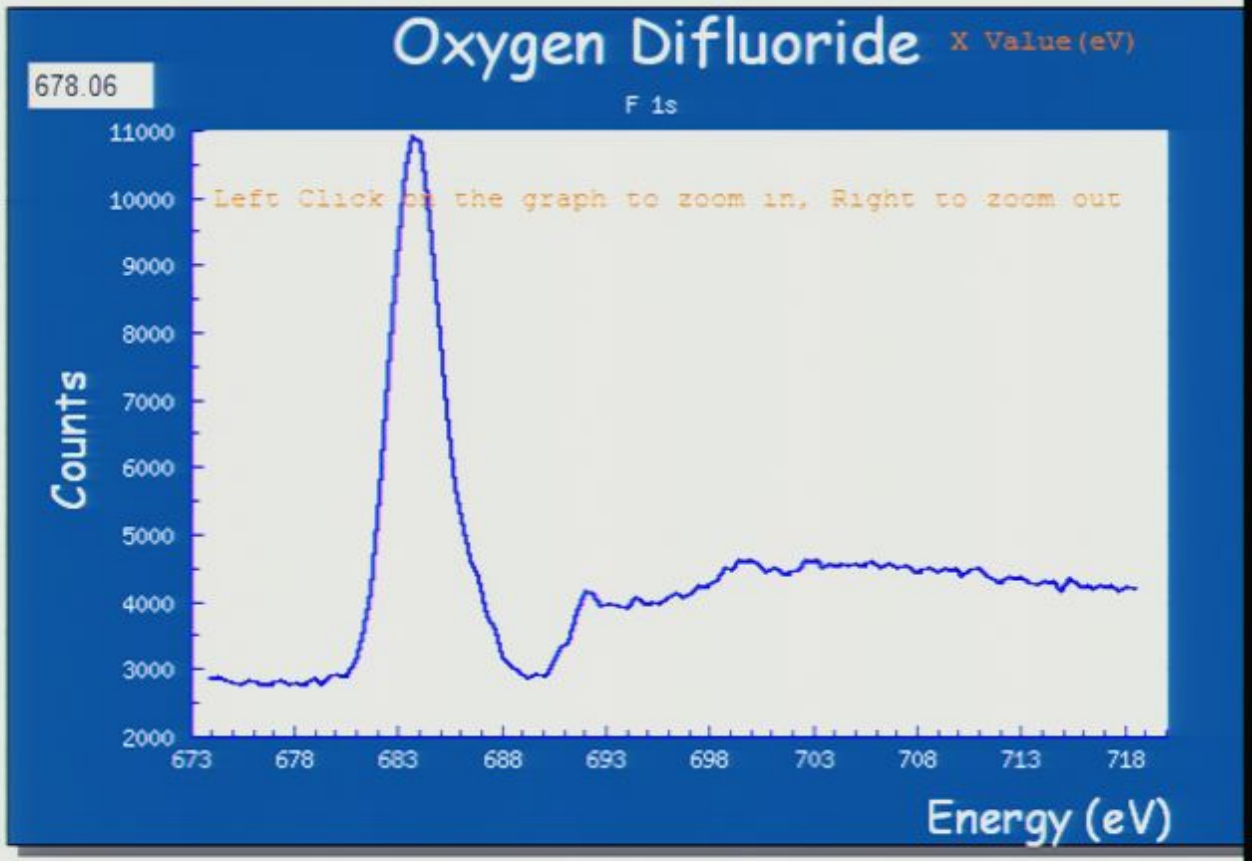


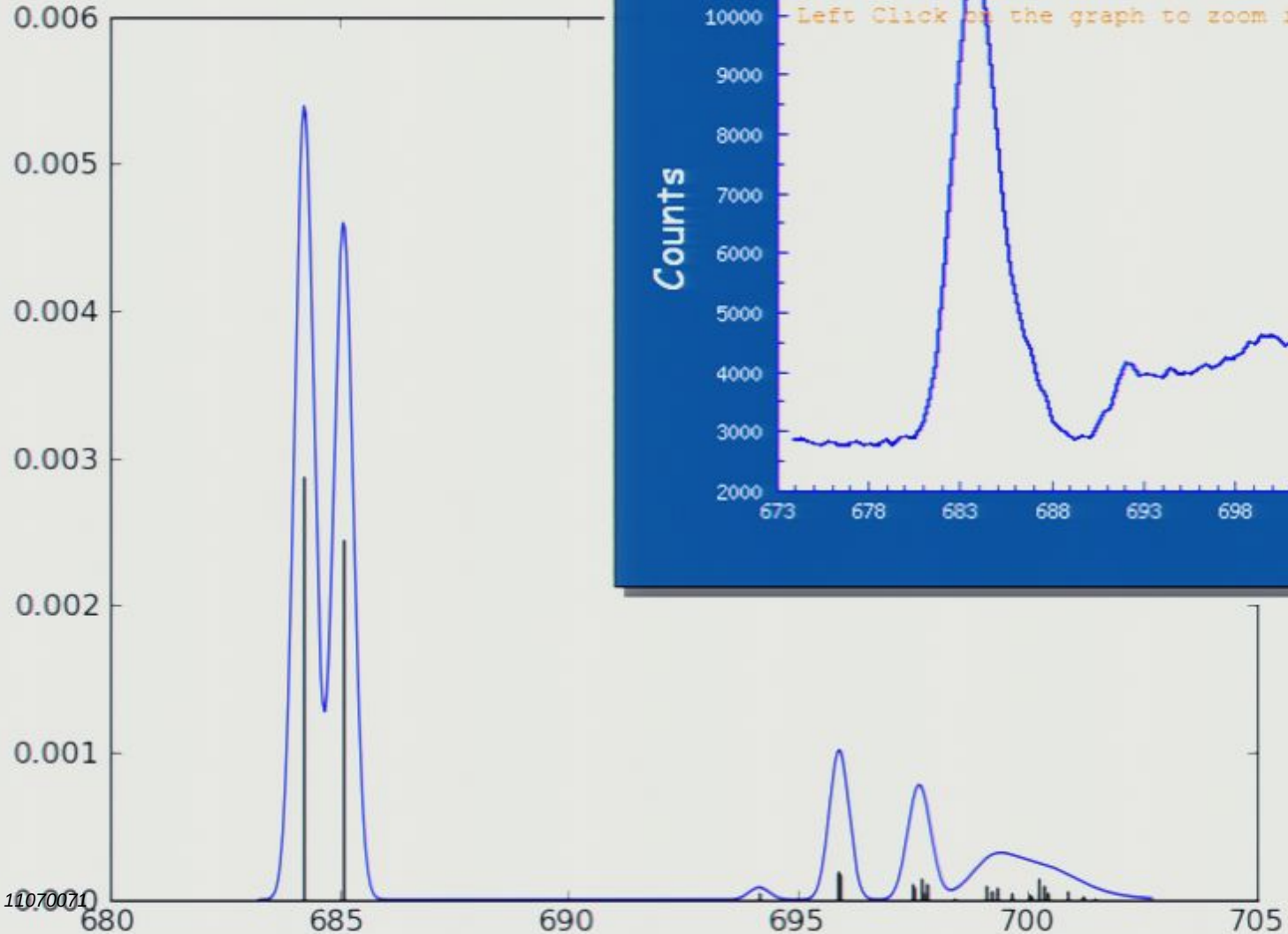
GPAW XAS calculation

Oxygen Difluoride (F2O)
O 1s

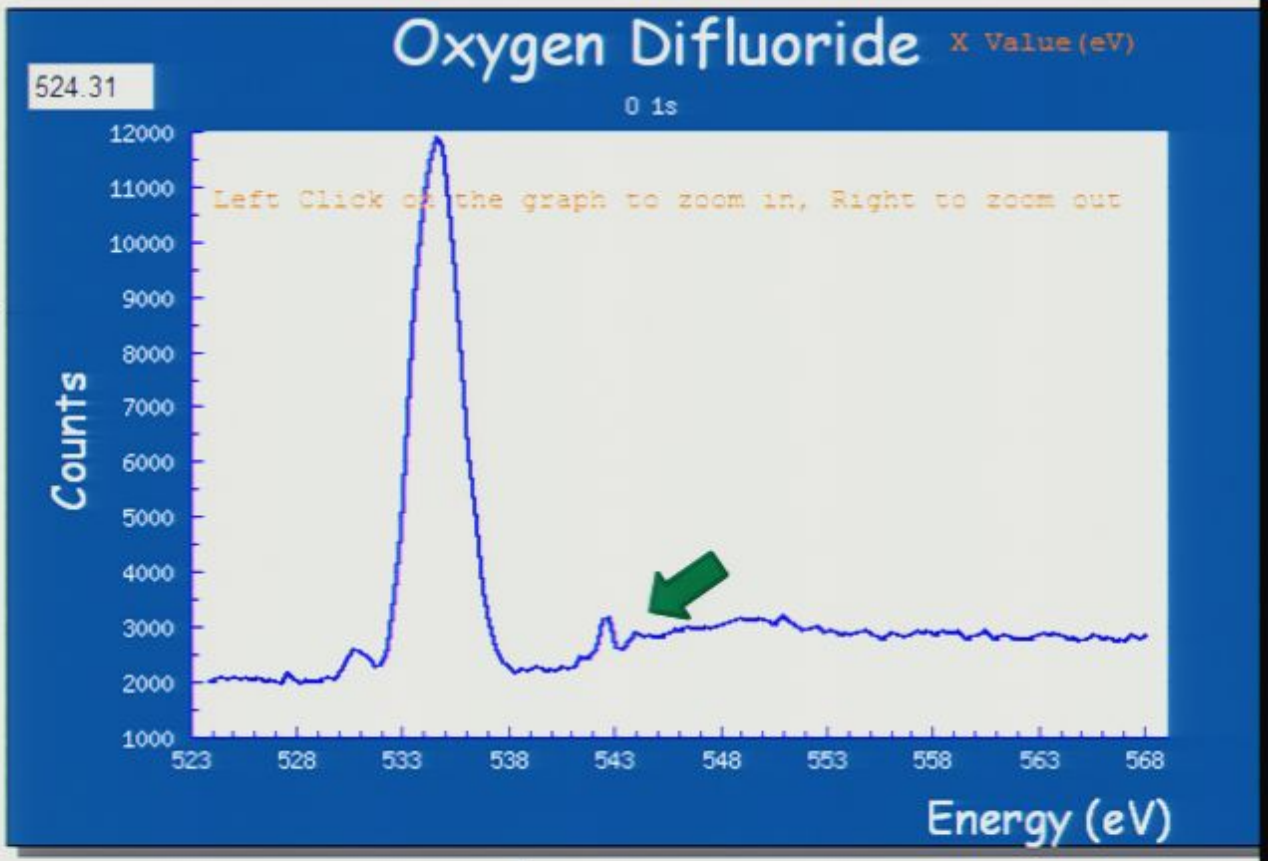


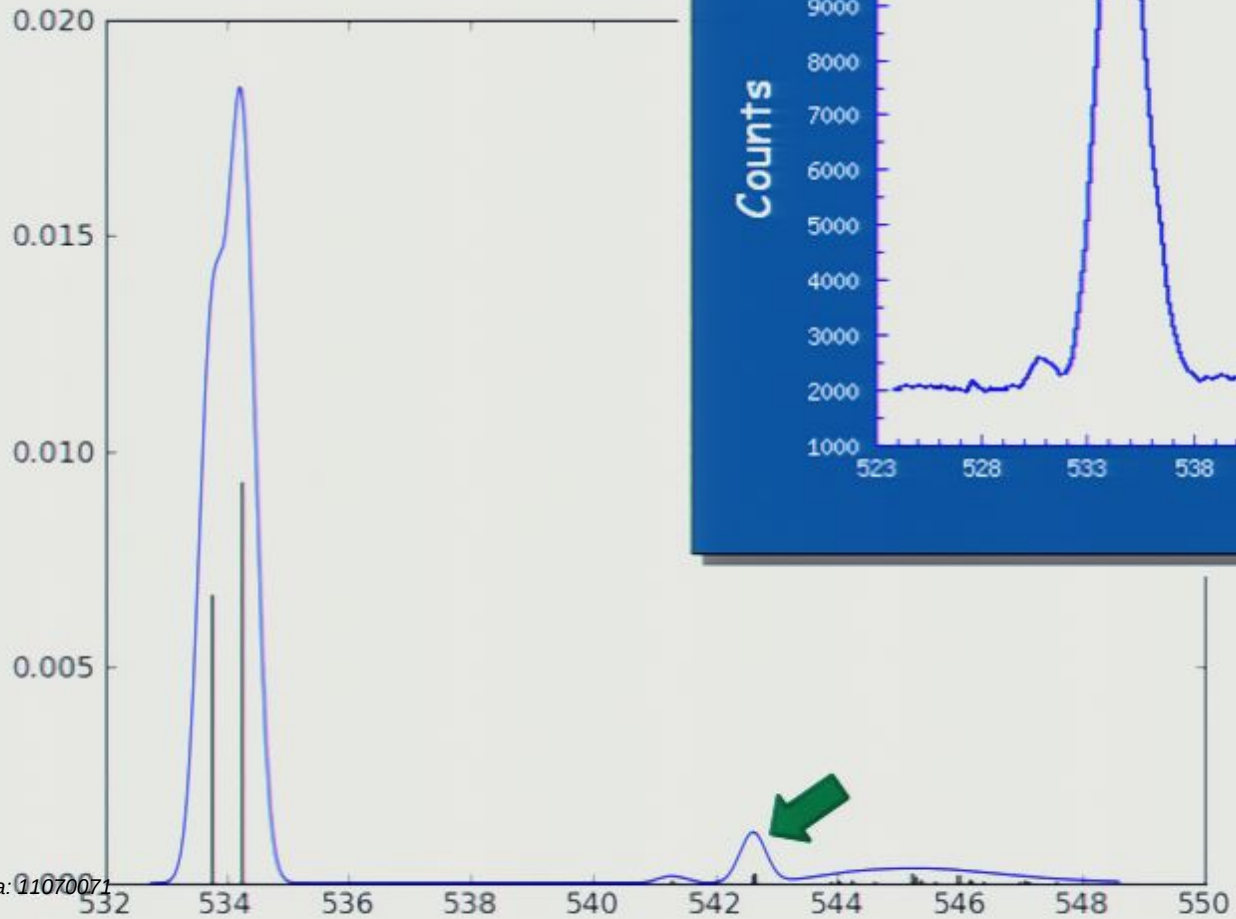
Oxygen Difluoride (F2O)
F 1s



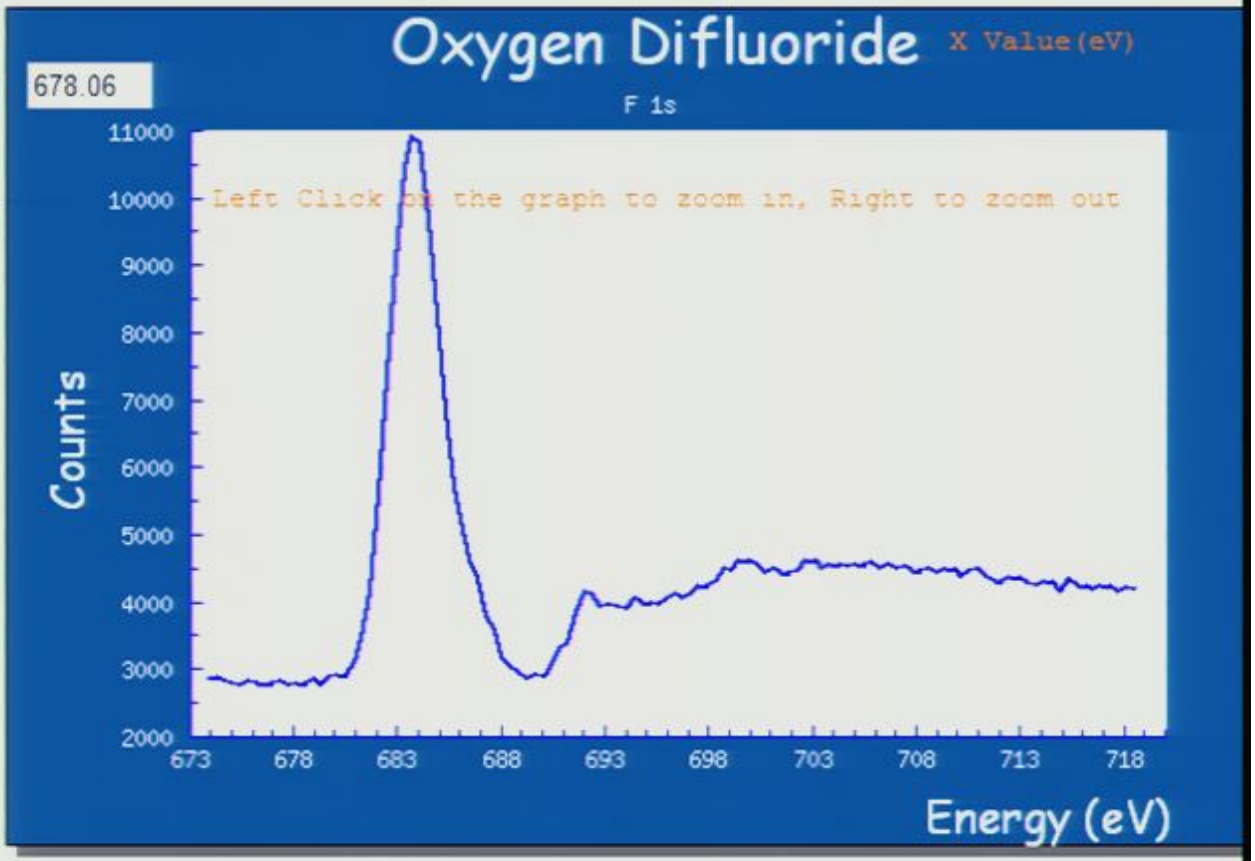


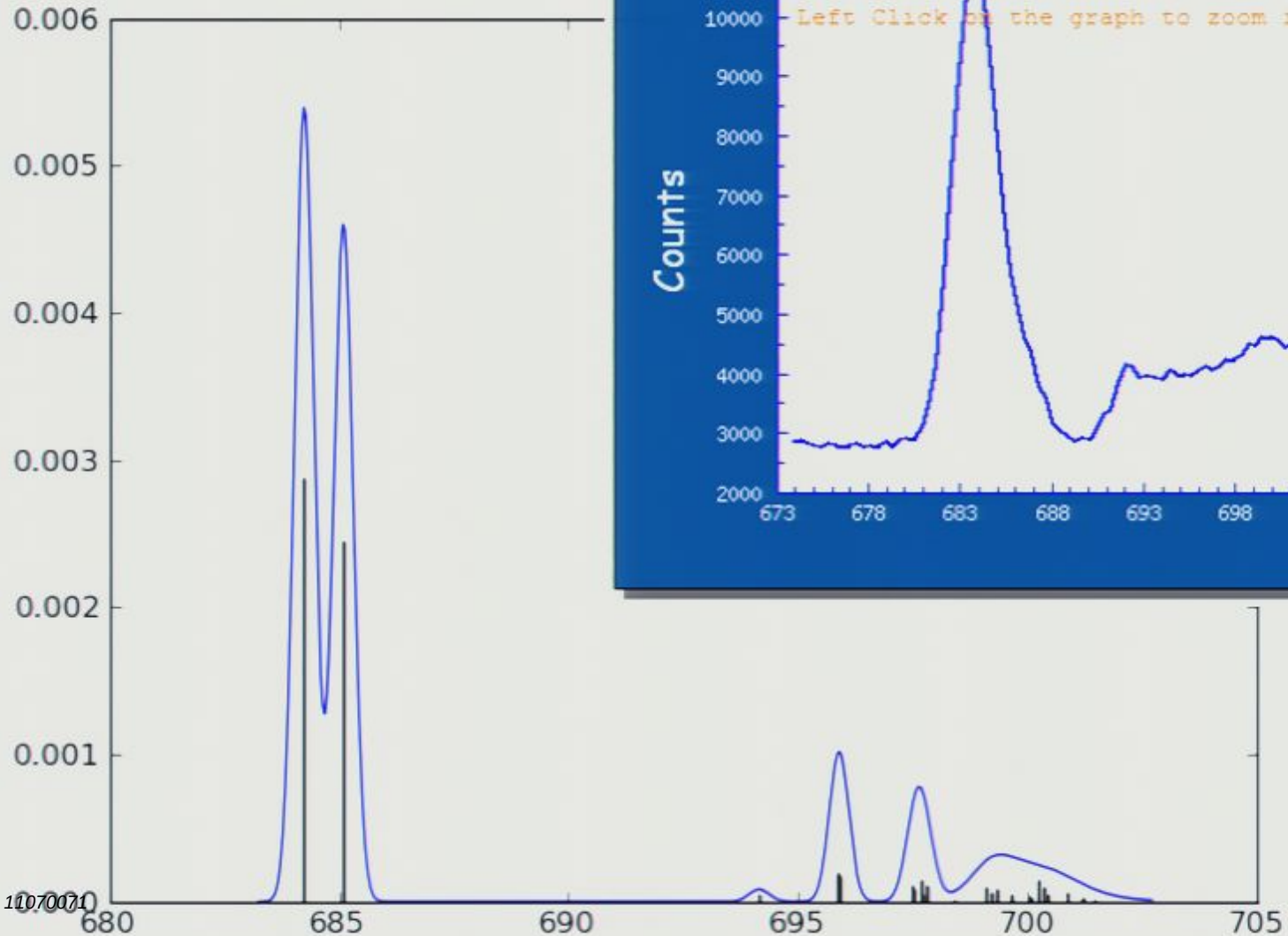
Oxygen Difluoride (F2O)
O 1s





Oxygen Difluoride (F2O)
F 1s



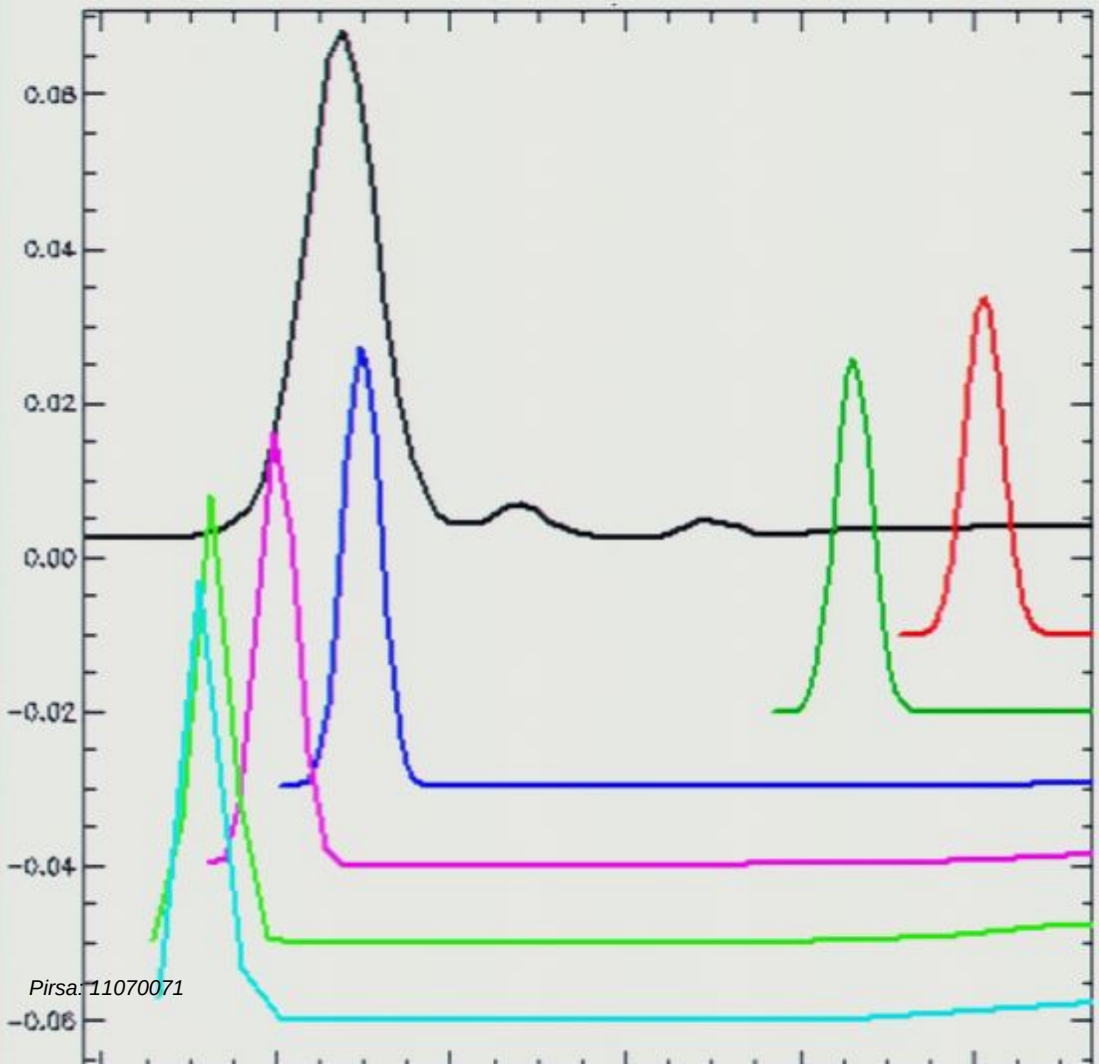


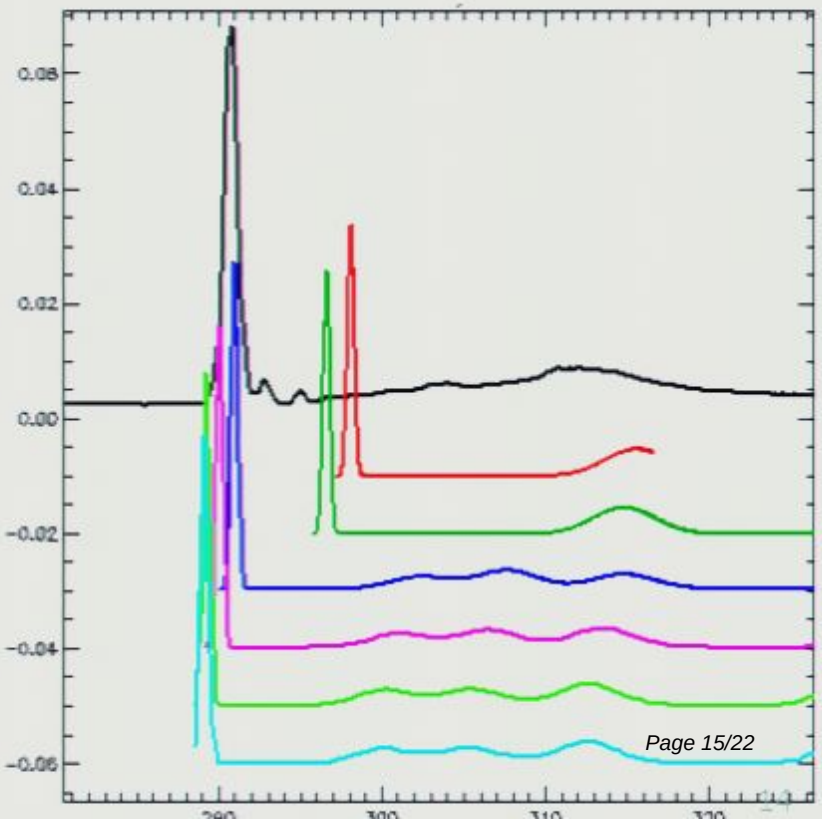
LCAO mode

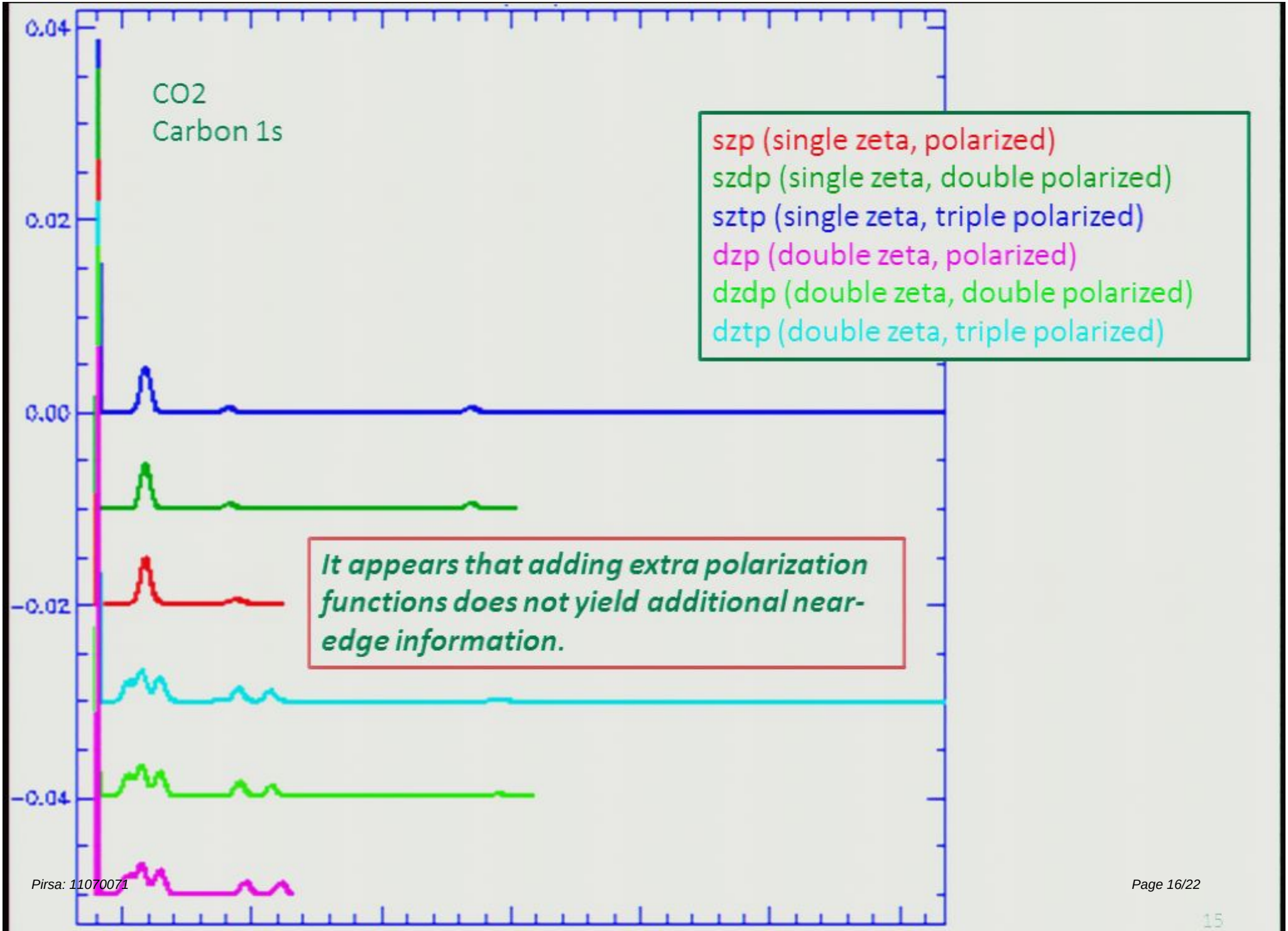
- Popular method to model molecules as collections of interacting atoms
- Faster calculations
- Sacrifices accuracy
- Flexibility: different basis sets
- Avoids convergence issues

CO2
Carbon 1s

Experimental, Hitchcock et al.
sz (single zeta)
szp (single zeta, polarized)
dzp (double zeta, polarized)
tzp (triple zeta, poarized)
qzp (quad zeta, polarized)
qztp (quad zeta, trip pol)






0.04
0.02
0.00
-0.02
-0.04
CO2
Carbon 1s
szp (single zeta, polarized)
szdp (single zeta, double polarized)
sztp (single zeta, triple polarized)
dzp (double zeta, polarized)
dzdp (double zeta, double polarized)
dztp (double zeta, triple polarized)
It appears that adding extra polarization functions does not yield additional near-edge information.

Results

- Weren't able to accurately and reliably produce the near-edge features
- FD mode was much more accurate, but refused to converge on many common molecules (e.g. CO2)
- LCAO always converged, but not always to the right place

Future Work

- Looking for more flexible basis sets
- Improving convergence in FD mode

References

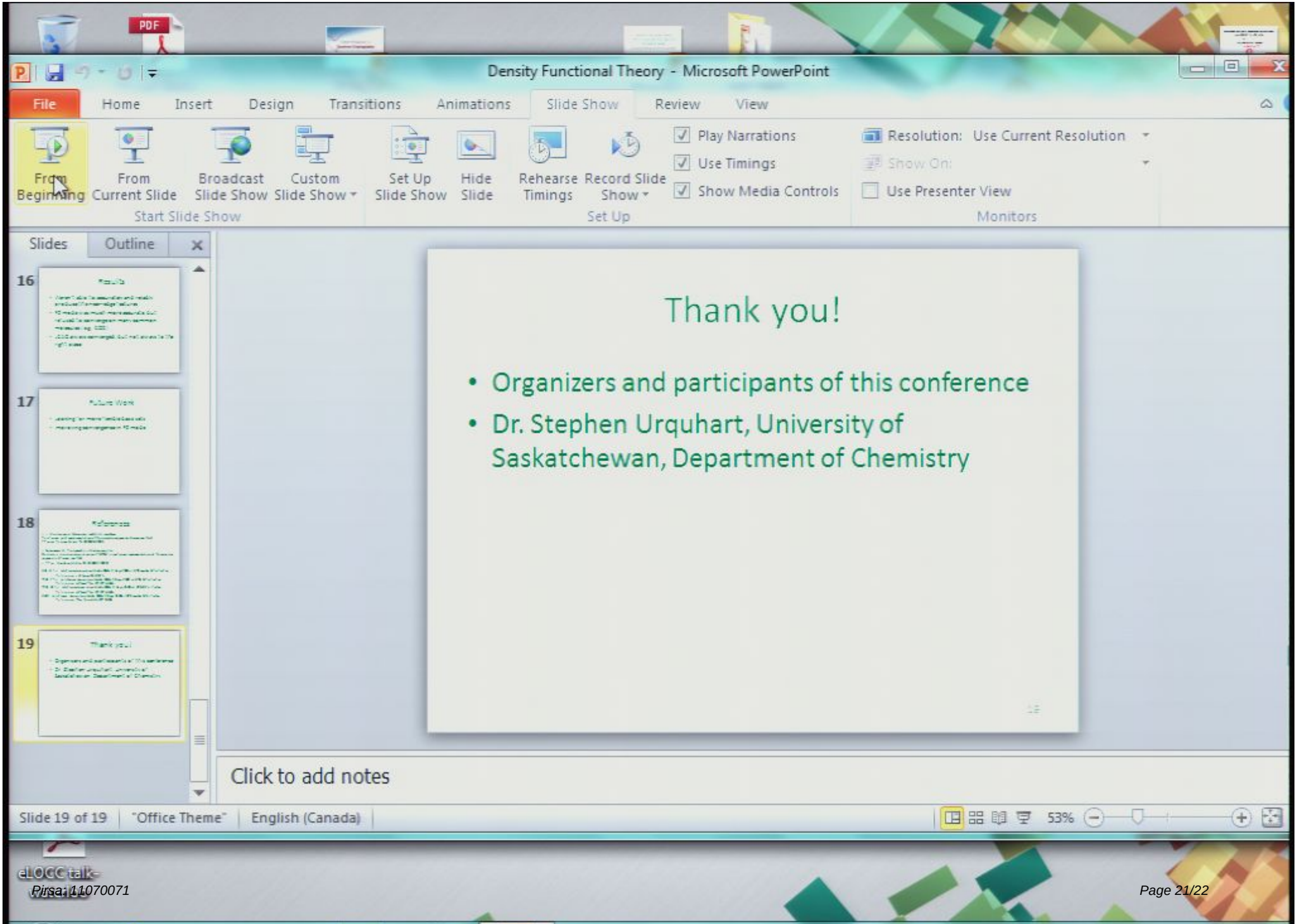
J. J. Mortensen, L. B. Hansen , and K. W. Jacobsen
Real-space grid implementation of the projector augmented wave method
Physical Review B, Vol. 71, 035109, 2005

J. Enkovaara, C. Rostgaard, J. J. Mortensen et al.
Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method
J. Phys.: Condens. Matter 22, 253202 (2010)

CO (C 1s): Hitchcock, Acquisition Mode: EELS, 2 deg, 2500 eV CRE mode, 0.7 eV fwhm
Reference: J. El. Spec.18 (80) 1.
F2O (F 1s): Hitchcock, Acquisition Mode: EELS, 2 deg., 2500 eV CRE, 0.7 eV fwhm
Reference: J.Chem.Phys. 87 (87) 4344.
F2O (O 1s): Hitchcock, Acquisition Mode: EELS, 2 deg., 2500 eV CRE, 0.7 eV fwhm
Reference: J.Chem.Phys. 87 (87) 4344.
CO2: Hitchcock, Acquisition Mode: EELS, 2 deg, 2500eV CRE mode, 0.7eV fwhm
Reference: Phys. Rev. A 36 (87) 1683.

Thank you!

- Organizers and participants of this conference
- Dr. Stephen Urquhart, University of Saskatchewan, Department of Chemistry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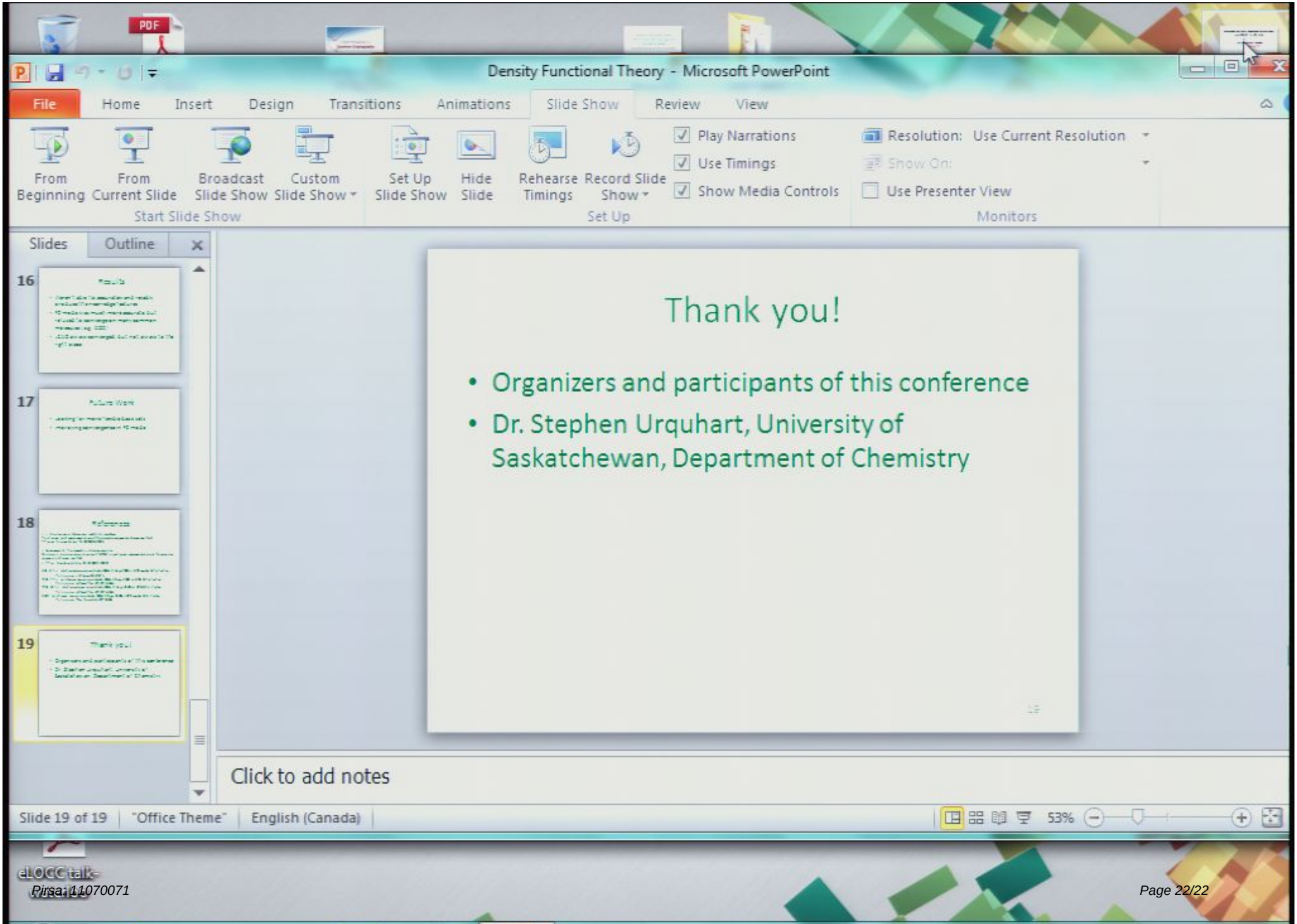
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