Simulating X-ray Absorption Spectra from First Principles
and
Developing Intuitive Interfaces to High-Performance Computing

David Prendergast
Theory of Nanostructured Materials Facility
Molecular Foundry,
Lawrence Berkeley National Laboratory

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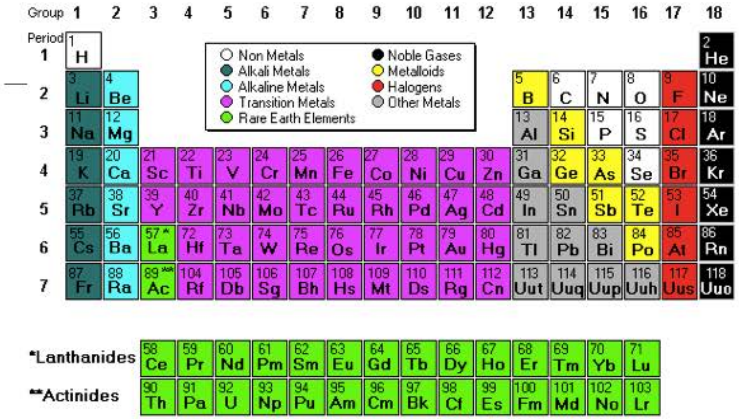
X-ray Absorption and Core-level excitations

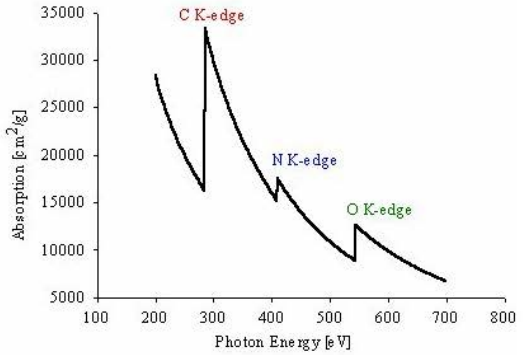
Notation:

K	1s	L_1	2s	M_1	3s	...
		L_2	$2p_{1/2}$	...		
		L_3	$2p_{3/2}$	...		
				...		



Electron binding energies in eV
http://xdb.lbl.gov

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$
1 H	13.6						
2 He	24.6*						
3 Li	54.7*						
4 Be	111.5*						
5 B	188*						
6 C	284.2*						
7 N	409.9*	37.3*					
8 O	543.1*	41.6*					
9 F	696.7*						
10 Ne	870.2*	48.5*	21.7*	21.6*			
11 Na	1070.8†	63.5†	30.65	30.81			
12 Mg	1303.0†	88.7	49.78	49.50			
13 Al	1559.6	117.8	72.95	72.55			
14 Si	1839	149.7*b	99.82	99.42			
15 P	2145.5	189*	136*	135*			
16 S	2472	230.9	163.6*	162.5*			
17 Cl	2822.4	270*	202*	200*			
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†



Elements easily resolvable as isolated steps or **edges** in absorption or energy loss

Focus on Near-Edge Fine Structure

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Core-level spectroscopy

Advanced Light Source, LBNL

NEXAFS

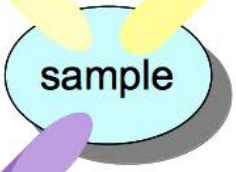
OR

Electron energy loss (EELS)

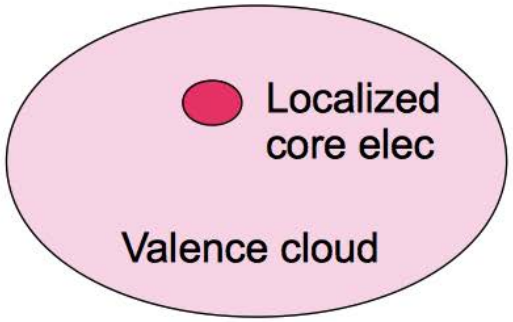
National Center for Electron Microscopy, LBNL

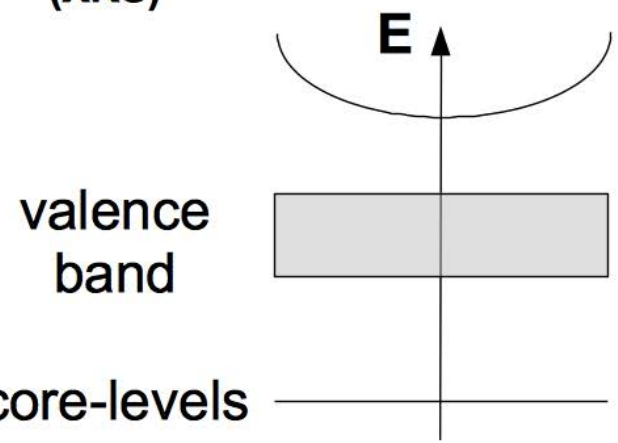
SSRL/SLAC

X-ray Raman Spectroscopy (XRS)



r-space





k-space

Explores the (projected) unoccupied density of states of materials

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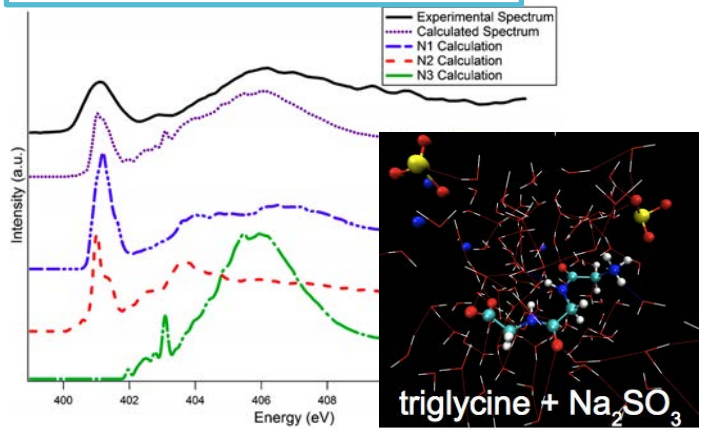
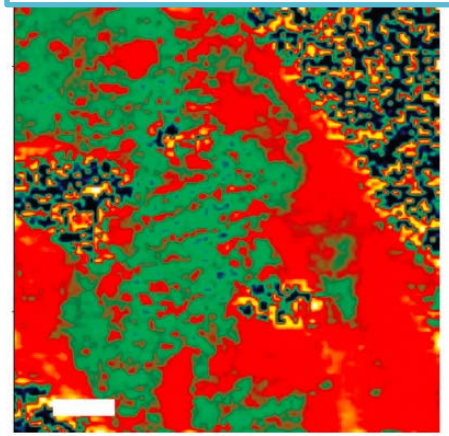
What can one learn* from X-ray spectra?

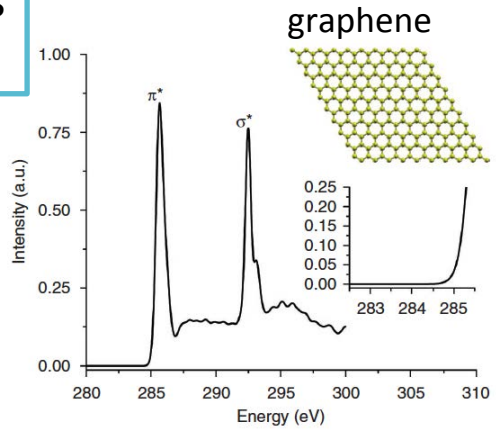
molecular conformation and solvent interactions



Schwartz, Prendergast, et al., PNAS (2010)

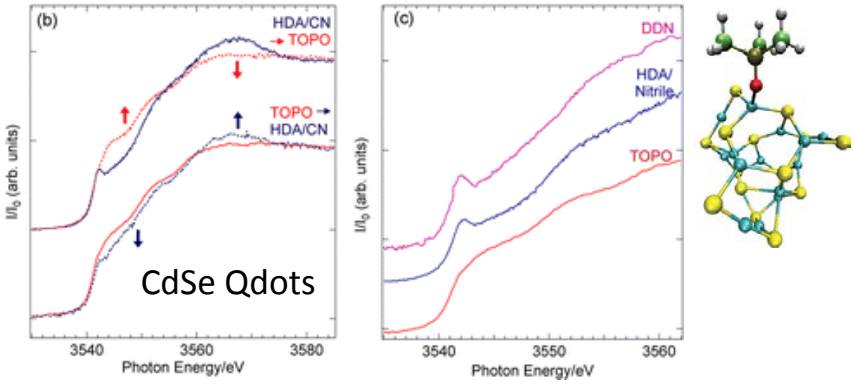
electronic interactions and charge transfer





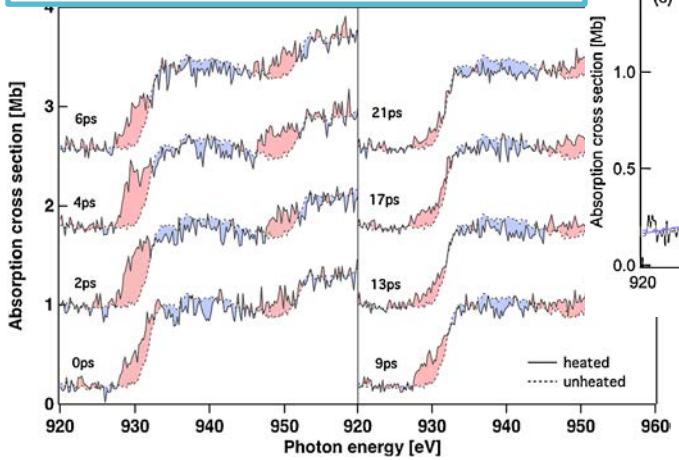
Schultz, Prendergast, et al., Nature Comms (2011)

nanocrystal surface chemistry



Lee, Whitley, Prendergast, et al., Nano Lett (2012)

ultrafast electron dynamics



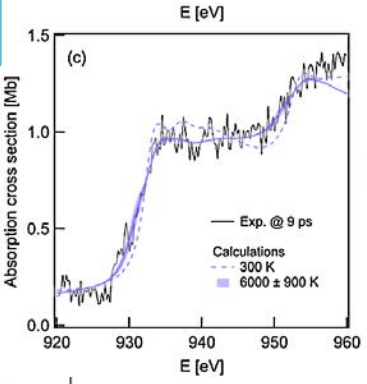


photo-pumped copper

Cho, Ogitsu, Prendergast, et al., Phys Rev Lett (2011)

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*Requires first-principles (dynamics) simulations…

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Synchrotron Light Sources worldwide

Present and future…

LCLS

NGLS
Next Generation Light Source

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U.S. Department of Energy Nanoscale Science Research Centers

Molecular Foundry

at:
Lawrence Berkeley National Laboratory
Berkeley, CA

access to:
Advanced Light Source
National Center for Electron Microscopy
National Energy Research Scientific Computing Center

Center for Integrated Nanotechnologies

at:
Sandia National Laboratories/ Los Alamos National Laboratory
Albuquerque/Los Alamos, NM

access to:
Los Alamos Neutron Science Center
National High Magnetic Field Laboratory

Center for Nanoscale Materials

at:
Argonne National Laboratory
Argonne, IL

access to:
Advanced Photon Source
Intense Pulsed Neutron Source
Electron Microscopy Center

Center for Nanophase Materials Sciences

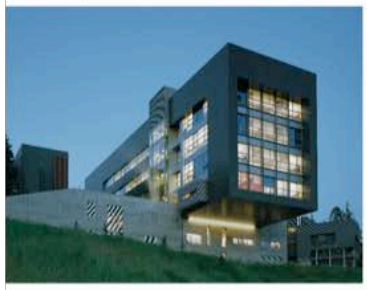
at:
Oak Ridge National Laboratory
Oak Ridge, TN

access to:
Center for Neutron Scattering
National Center for Computational Sciences
Shared Research Equipment Collaborative Research Center

Center for Functional Nanomaterials

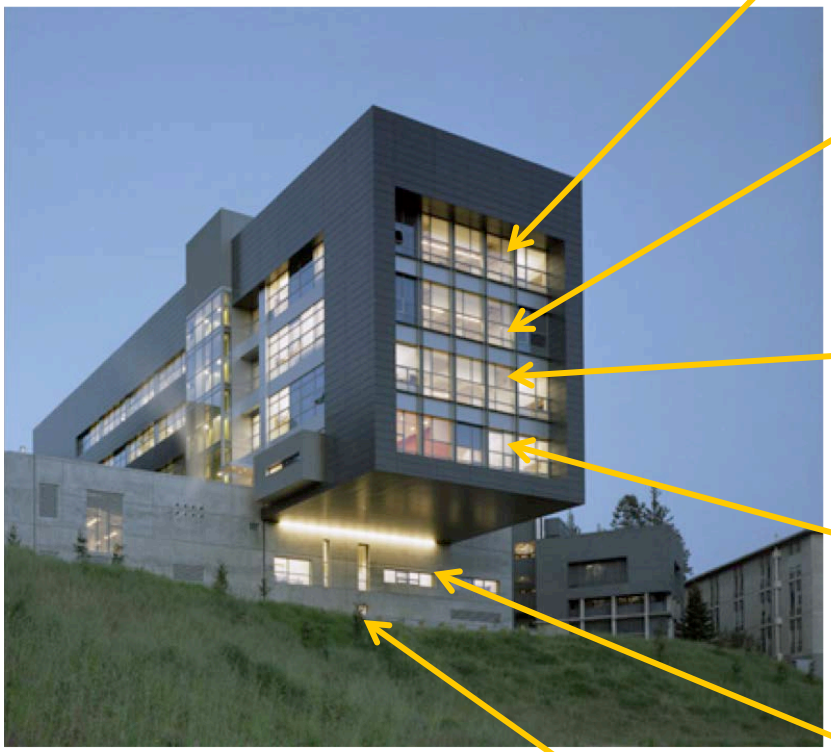
at:
Brookhaven National Laboratory
Upton, NY

access to:
National Synchrotron Light Source
Laser Electron Accelerator Facility





6 User facilities focused on interdisciplinary research



Foundry partners with LBNL national facilities:

- Advanced Light Source (ALS)
- National Energy Research Scientific Computing Center (NERSC)
- National Center for Electron Microscopy (NCEM)

- **Organic and Macromolecular Synthesis**
  Soft materials: organics, macromolecules, polymers and their assemblies
- **Biological Nanostructures**
  New bio-materials; new probes for bio-imaging; synthetic biology techniques
- **Inorganic Nanostructures**
  Science of semiconductor, carbon and hybrid nanostructures
- **Theory of Nanostructured Materials**
  Studies to guide understanding of new principles, behavior and experiments
- **Nanofabrication**
  Advanced lithographic and thin-film processing techniques
- **Imaging and Manipulation of Nanostructures**
  Characterization and manipulation of nanostructures

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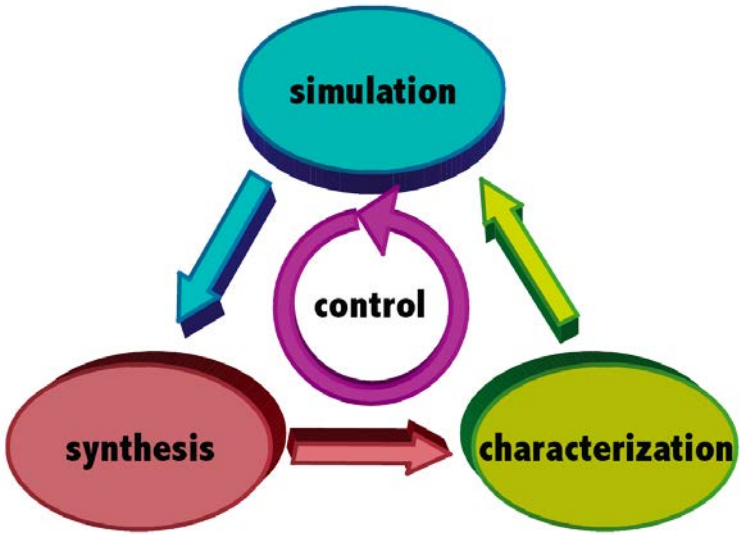
Joint Center for Energy Storage Research
(DOE Innovation Hub for Batteries)



Goal:

To make validated connections between atomistic chemical intuition and measurements on working electrochemical systems…

… using combined molecular dynamics and electronic structure calculations with simulated spectroscopy

Spectroscopy → Theory → Atomic Structure

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Argonne NATIONAL LABORATORY

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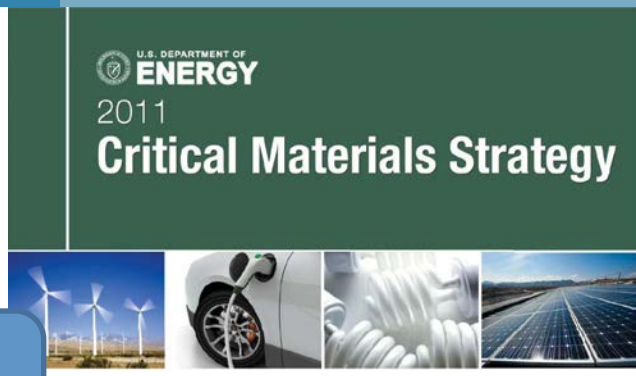
Revealing the Underlying Electronic Structure and Working Principles of Functional Materials



Desired Material Function
- Catalyst
- Lighting
- Radiation resistance
- Selectivity Separations

Working *f*-electron and/or Critical Material

X-ray Characterization (NEXAFS/XES/STXM)

Materials by Design
New material with similar electronic/ physical properties

Simulated Spectra Interpretation Electronic Properties

Improved Theory of Electronic State

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CHEMICAL SCIENCES DIVISION

LDRD: David Shuh, Andrew Canning, David Prendergast
Das Pemmaraju, Shuao Wang

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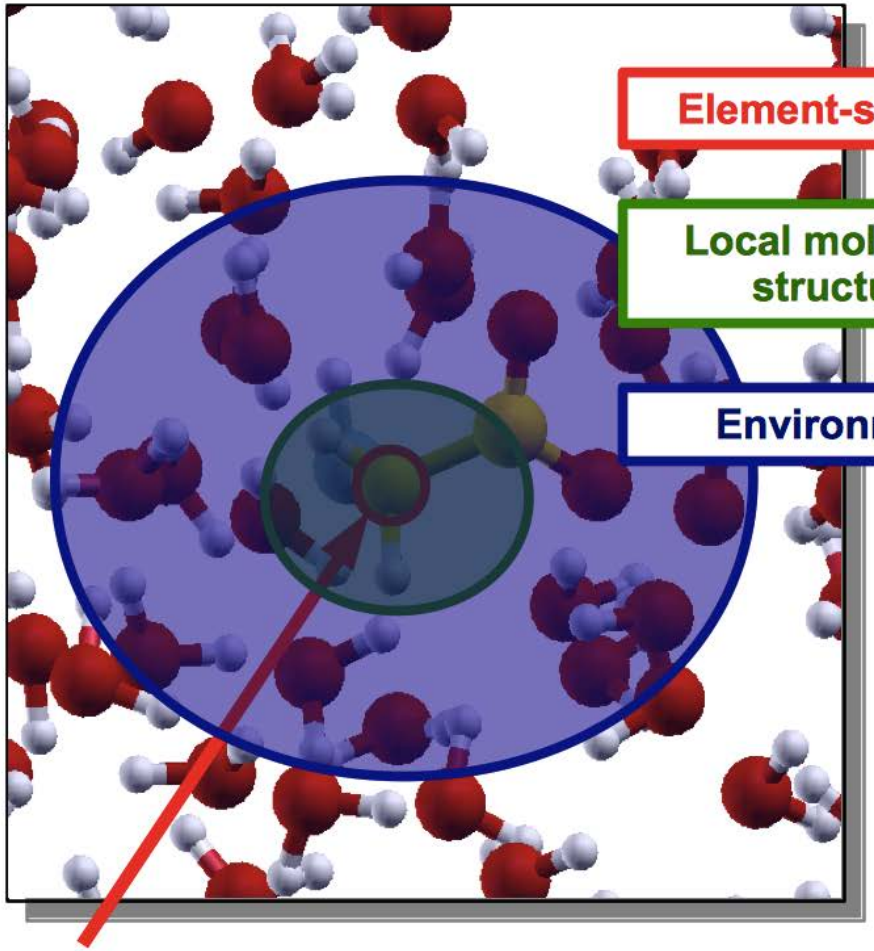
Core-level spectroscopy



Element-specific

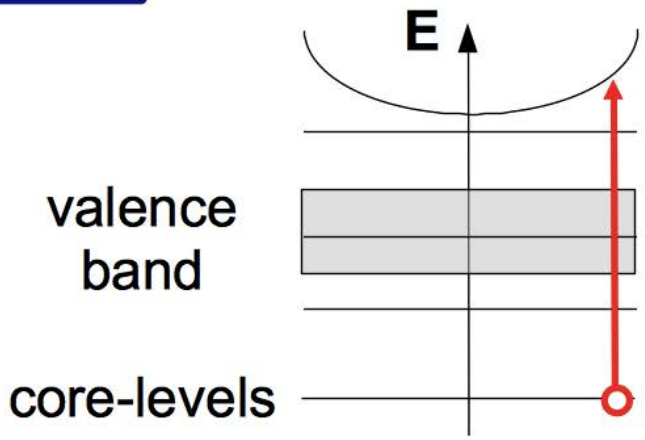
Local molecular structure

Environment

Localized core hole

r-space

Delocalized excited elec



k-space

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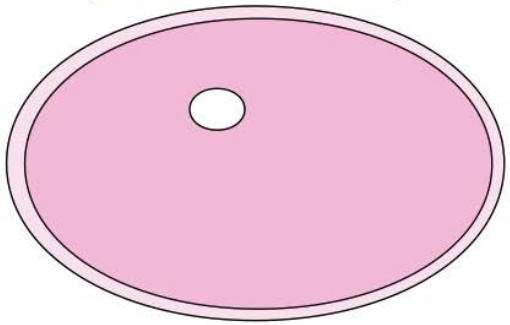
The XCH approach to simulating X-ray Absorption

Core-level spectra via Fermi's Golden Rule

$$\sigma(\omega) = 4\pi^2 \alpha_0 \hbar\omega \sum_f |\langle \Psi_f | \Delta H | \Psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

r-space

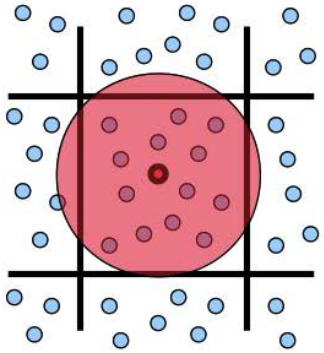


Single-particle approximation:

$$\langle \Psi_f | \Delta H | \Psi_i \rangle \approx S \langle \psi_f | \epsilon \cdot r | \psi_i \rangle$$

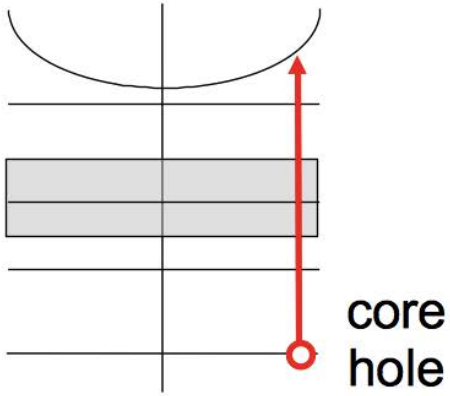
Final State Approximation

- Include e**X**cited electron and **C**ore **H**ole (**XCH**)
  i.e. *Constrained Density Functional Theory*



applied under periodic boundary conditions

k-space



Pl

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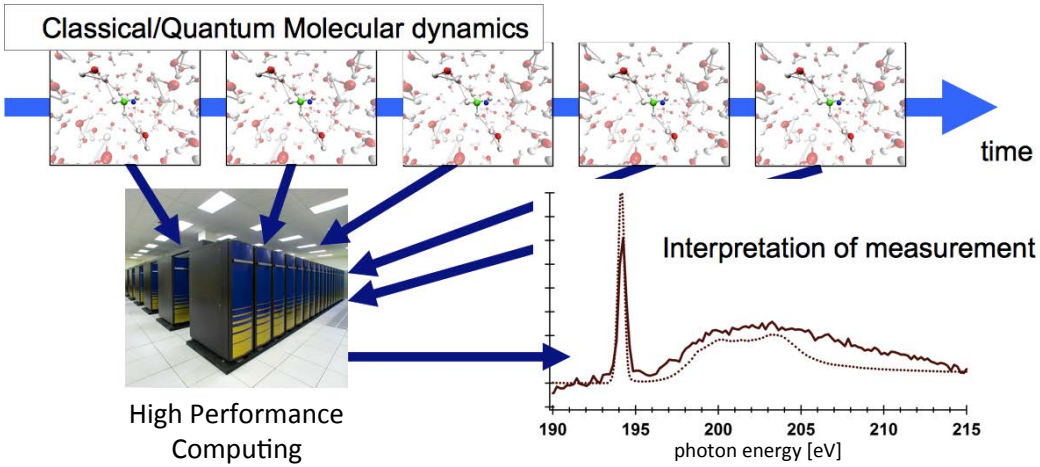
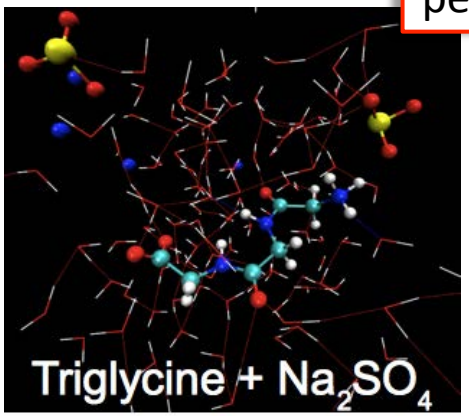
Molecular Dynamics to explore configuration space

~100x more effort per atom



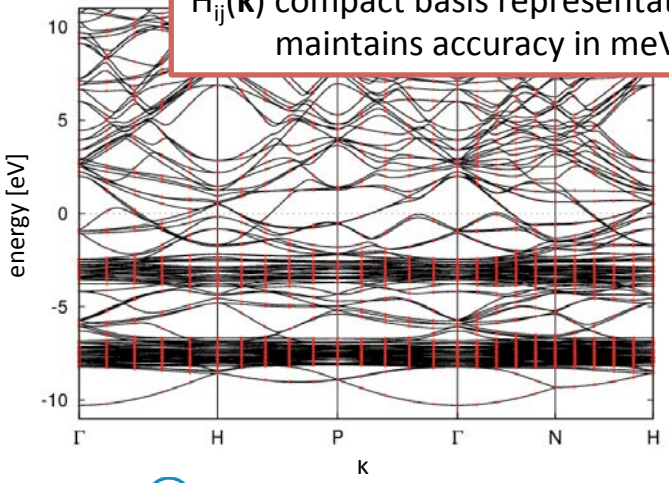
High Performance Computing

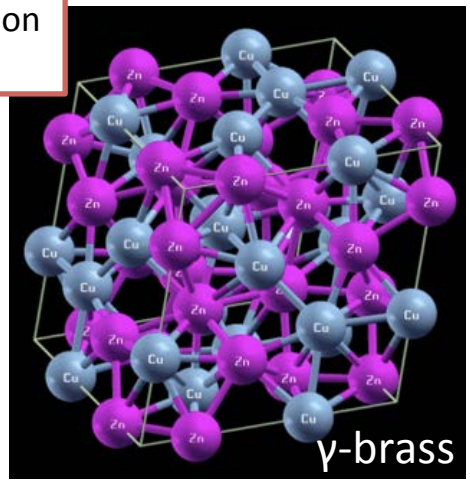


England, Prendergast, Saykally, et al., CPL 2011
Duffin, Prendergast, Saykally, et al., PCCP 2011
Schwartz, Saykally, Prendergast et al., PRL 2010
Schwartz, Prendergast, Saykally, et al., PNAS 2010

Efficient electronic structure calculations

$H_{ij}(\mathbf{k})$ compact basis representation maintains accuracy in meV





~100x faster

QUANTUMESPRESSO

Prendergast, Louie, PRB 2009
Shirley, PRB 1996

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... recently adapted to accelerate self-consistent field calculations

Hutchinson and Prendergast (in preparation)

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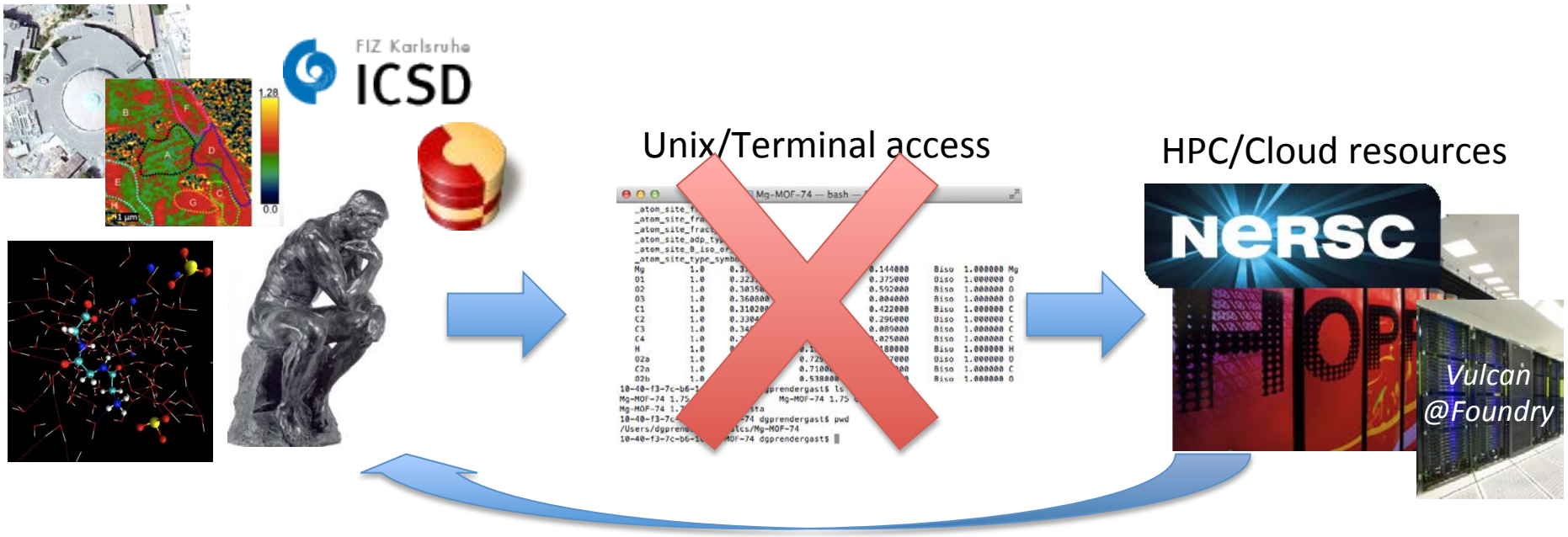
Web-based tools

Goal: To enhance User experience and throughput by providing access to unique computational tools running on high performance computing (HPC) resources

Specific Tool: ShirleyXAS – interpretation of X-ray absorption spectra



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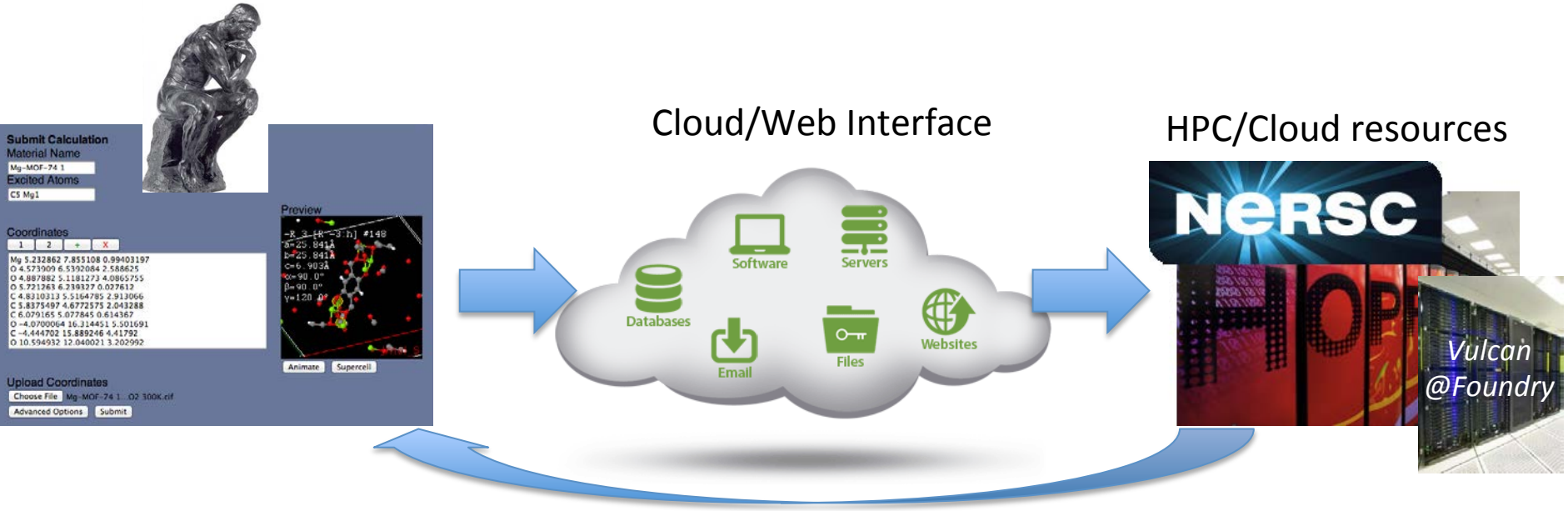

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X-ray Spectroscopy On-line

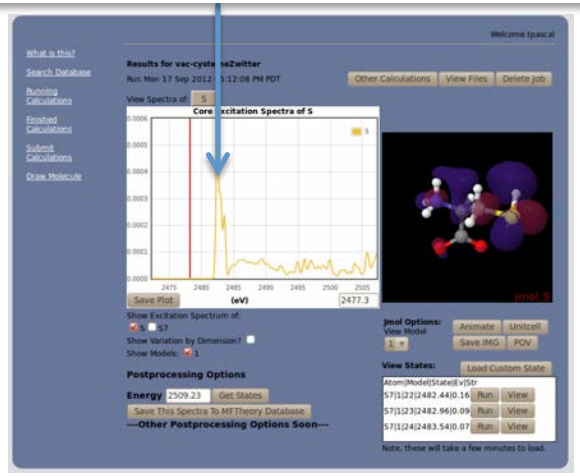
WebXS
X-ray Spectra Analysis

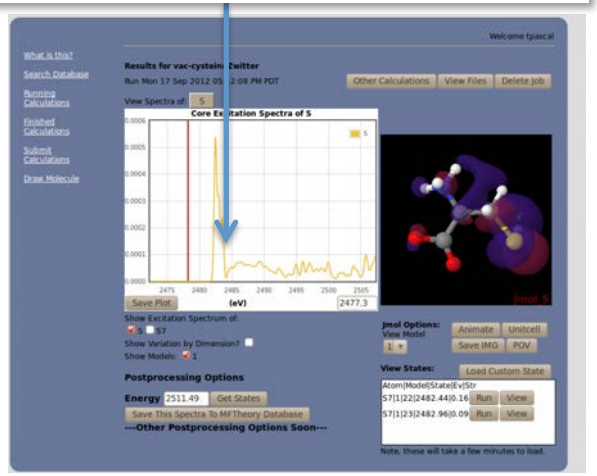
Jmol

newt

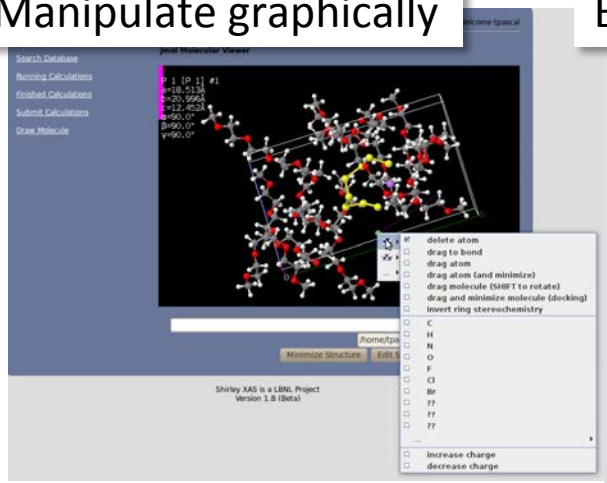
NERSC
National Energy Research Scientific Computing Center

Selectively interpret spectral features via electronic structure

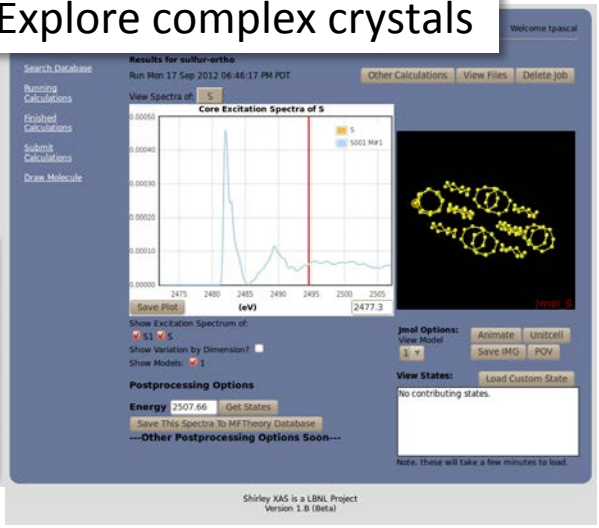




Manipulate graphically



Explore complex crystals



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https://portal.nersc.gov/project/mftheory/WebXS/

James Wonsever, Jack Deslippe, and David Prendergast

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Workflow for WebXS

- Measured Data (XAS, …) or Proposed Measurement
- State Hypothesis: structural, electronic, thermodynamic
- Loop over ensemble(snapshots, atoms):
  - First-principles simulation (GS, XCH, …)
  - spectrum of snapshot N, atom I
- Ensemble average
- Hypothesis test: comparison with measurement; possible iteration
- Spectral features – Analysis, Interpretation, Data-mining
- Outcome
  - Improved understanding for measurement/theory
  - Connection between atomic structure and electronic structure
  - Design of future (useful) experiments in silico

Challenges and Outlook for this Use Case

Inside Black box:

- Accuracy of electronic structure tools – new methods (DFT, GW, BSE, …)
- Efficiency of algorithms – adaptation to new architectures (multi-GPU)
- Open source development, shared databases
- Improved portability (common HDF5 I/O)

Data Analysis/Interpretation

- 100 MB x 100 excited atoms x 100 snapshots = 1 TB per point (P,T)
- How do we reduce without need to regenerate?
- Easy navigation of this data – GUI

Building workflows

- Easy interaction with HPC (w/o UNIX, e.g. NEWT API)
- Multiple calculations managed on HPC – parallel scripting (e.g. Swift)
- Simple, intuitive interface development

Tool for User-Based Science at National Facilities

- enable more users to be scientifically self-sufficient (remotely)