Berkeley XAS

https://nanohub.org/tools/xas

Benjamin Han

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1 X-ray Absorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy is an experimental technique for investigating local surface interactions of molecules. XAS can be used to infer the presence of specific bonds, the lengths of these bonds, and the orientation of molecules and functional groups on surfaces or in solids. The technique is particularly useful for examining systems comprised of low Z atoms, such as organic molecules.

XAS examines a structure’s localized rate of x-ray absorption across a spectrum of wavelengths or energies. X-rays tuned to the energy of a structure’s chemically inert core electrons have a high probability of absorption and excitation when shined on the system. An excited electron will be lifted from the ground state, leaving an electron hole in its wake. The excited state is highly unstable and the vacancy will immediately be filled by another electron. The difference in energy from the excited state is compensated by the emission of either a photon or another electron. These processes can be simultaneously measured (Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy, respectively) while conducting an XAS measurement.

The magnitude of the spectrum is given by the probability of transition, which we approximate within Fermi’s golden rule:

\[ P_{if} = \frac{2\pi}{\hbar} |H'_{if}|^2 \rho_f \]  

(1)

Where the matrix element \( H'_{kn} = \langle \Psi_k | H' | \Psi_n \rangle \) (see Dirac/Bra-ket notation) and \( \rho_f \) describes the density of final energy states. In a static electric field, the perturbed Hamiltonian can be approximated by \( H' = -\hat{\epsilon} \cdot R \), where \( \hat{\epsilon} \) is the polarization direction of the electromagnetic vector potential and \( R \) is the position operator.

X-ray Absorption Spectroscopy measures the local rate of photon absorption due to core electron excitation across an energy spectrum (typically on the order of 100-1000 eV). The absorption edges for low-Z atoms are well spread across
the spectrum, making their characteristic absorption lines easily distinguishable. The energies of absorption edges reveal detailed information regarding the atomic composition of the system. Small shifts in these lines provide further information regarding the presence of specific bonds, as well as their lengths and orientations. These shifts can also be probed by altering the beam’s polarization and orientation.

The rate of absorption scales with the density of possible final states, \( \rho_f \). Transitions to some states are forbidden by dipole selection rules, which indicate that transition probability is nonzero if and only if the matrix element

\[
\langle \Psi_i | H' | \Psi_f \rangle = \int_{-\infty}^{+\infty} \Psi_i^* H \Psi_f \, d\tau
\]

(2)
does not have odd parity (ungerade symmetry).

For example, an excitation in a copper (4s1, 3d10) core electron can only transition to the 3d orbital since the lower orbitals are already occupied. Because copper has few vacancies in the "d" orbital, it produces a relatively weak absorption spectrum. Conversely, iron (4s2, 3d6) has a greater number of possible transitions and demonstrates a much stronger absorption response. Spectrum peak heights can be used to determine the partial density of states.

2 Berkeley XAS

Berkeley XAS was developed by David Prendergast and Eric L. Shirley on top of the open source Quantum Espresso package. Berkeley XAS examines the absorption spectrum due to a 1s electron core hole (K-edge) using density functional theory.

By calculating the 1s electron bond energy, the tool determines the relative energy shift of the K-edge with respect to an isolated atom.

\[
\text{EnergyShift} = (E_{\text{system},x} - E_{\text{system,gs}}) - (E_{\text{atom},x} - E_{\text{atom,gs}}) - E_{\text{LUMO}}
\]

(3)

Where \( x \) indicates an excited state, \( gs \) refers to the energy of the ground-state, and \( LUMO \) is the lowest unoccupied molecular orbital.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Final Energy Shift (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>+285.44</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>+396.23</td>
</tr>
<tr>
<td>Oxygen</td>
<td>+527.73</td>
</tr>
</tbody>
</table>

Berkeley XAS then applies a final shift on top of the calculated shift in equation (3). The final shift is independent of molecular structure and was approximated by fitting peak energy with experimental data from the Hitchcock Group at McMaster University. The spectra used for peak fitting were carbon dioxide, ethanol, and pyridine, which are all available from the drop down on the
Molecule Structure input page. Berkeley XAS spectra are also renormalized to a maximum height of 1, however the calculated absolute values of the peak heights are unimportant and only their relative heights should be examined.

Because bonding is mostly dependent on the valence electrons, the nucleus and remaining electrons (core electrons) are simplified into a single effective potential, called a pseudopotential. Using pseudopotentials makes the calculation possible without significantly affecting the accuracy by ignoring relatively unimportant inert electron interactions.

Berkeley XAS considers a rigid molecule in calculating spectra, however this is not a realistic picture. Excited states have short lifetimes and molecules at finite temperature will distort and break bonds, resulting in peak broadening and shifting. These differences can be alleviated computationally through molecular dynamics or experimentally using fast measurements. Further, calculated peak widths are expected to be more narrow than experiment due to underestimation of bandwidth within DFT.

3 Using Berkeley XAS

3.1 Quick Start

You can get started immediately by selecting a structure from the loader or by uploading your own xyz coordinates from a textfile without headers. It is important that an input structure consist of the following atom types only: H, C, N, O. To prevent invalid experimental data from appearing, you should also change the molecule name.

Once the desired structure is input at the Molecule Structure page, continue navigating to the computation page and hit simulate. The tool will begin prepping input files and submitting jobs to the cluster. You will receive periodic updates regarding the status of each job as it sits in queue or completes. Once the simulation is finished (typically about an hour for small molecules), the tool will draw a pymol image of the input structure. You can use the drop down tab to view spectra for atom averages as well as for individual atoms. The log tab will also display some output information as well as the time elapsed during the simulation.
3.2 Molecule Structures

1. The Loader contains examples with predefined input values. You can also adjust these parameters before simulation.

2. The upload drop down can be used to paste text from the clipboard or to upload a text file into the coordinates input.

3. The molecule name is used to distinguish between data sets and experimental data. It will not affect the simulation.

4. The coordinates input takes xyz coordinates of the structure in angstroms. Each row contains a single atom and has the format "Atom X Y Z". Whitespace is used to separate columns while carriage returns complete rows. The following atom types are currently supported: H, C, N, O.

5. The check system button will allow you to view a model of the input structure in pyMol before running a time-consuming calculation.

6. Excited Atom Species indicates which atoms will be given core-hole excitations in the simulation. Entire atom species can be selected by providing the element (C, N). Individual atoms can also be selected by giving the name and number of the atom (C1, O2, O3). The number is given from top to bottom, beginning from 1.
3.3 Calculation Settings

1. K-space resolution controls the number of uniform grid subdivisions in momentum-space. Increasing this value will yield greater spectrum resolution as well as required wall time. This is necessary to converge the high energy portion of the spectrum. See exercise 2.

2. The electron band factor is a multiplier that affects the number of electron bands examined. A factor of 4 will enable the tool to consider $N$ occupied states and $3N$ unoccupied states in the calculation. Increasing the electron band factor will probe higher energies beyond the k-edge. See exercise 3.

3. Using Bloch's theorem, the simulation will solve the Schrodinger Equation as a superposition of periodic plane waves. To make a fourier transformation computationally feasible, ecut sets the maximum kinetic energy of those plane waves. Although low energy states have more significant contributions to the spectrum, higher energy states provide greater detail at the cost of increased wall time.

4. Using DFT and Bloch's theorem, the XAS simulation sets periodic boundary conditions by repeating the cell structure in a 3 dimensional lattice. To prevent unwanted interactions between neighboring cells, the cell size must be set to be significantly larger than that of the input structure so that the wave function tails approach zero. A general rule of thumb is to set the cell size to at least double the size of the structure.

5. The number of processors dictates how many cores are given to each excited atom. Increasing this value will reduce the runtime of the simulation, but will also greatly increase the time spent waiting for available cores.
3.4 Post Processing

1. Enabling Post Process Only will replot the previous simulation with new settings from this page. This feature will not run properly unless a complete simulation has completed.

2. Gaussian broadening indicates the width of the peaks. This is set to compensate for finite state lifetimes and nonzero temperatures. However, reducing this value may help reveal otherwise hidden peaks.

3. The number of points is the number of data points plotted in each spectrum.


5. The energy shifts are applied to each atom type, independent of the structure. These values were fit from the McMaster University Core Excitation Data Base.

6. Min and Max energies indicate the energy axis of the spectrum for a given atom type. These can be altered to focus a spectrum on a specific point of interest.
3.5 Simulate

After hitting the simulate button, Berkeley XAS will begin preparing input files for job submission. The display will log status updates of these jobs and some output information. Berkeley XAS will run several calculations on each atom type (ground state (GS) and excited core hole (XCH) reference) and calculate a spectrum for each excited atom. The individual atoms will run in parallel. Once these jobs are completed and transferred back to the user, Berkeley XAS will then analyse the data and prepare output files to be plotted back to the user.

Once completed, the tool will display the molecule. The dropdown can be used to view spectra for atom averages as well as individual atoms. A red line will illustrate the maximum transition considered in the calculation. The region of energies above this line will not be accurate. Atom average spectra will also plot...
experimental data (from the Hitchcock Group at McMaster University) when available.

If multiple simulations have been executed in a single session, the bottom "Parameters" tab will allow the user to compare changes in the spectrum. A side effect of this feature is that changing the input structure types results in persistent spectrum windows that may not be relevant to the selected output.

![Simulation Results](image)

Ethanol with K-Space Resolution = 12, E-Band Fac = 6, Ecut = 25
Elapsed 2:08:00 using 8 processors.

The log will display some output information as well as the total time elapsed in the simulation.

4 Limitations

- Unfortunately Berkeley XAS does not provide a great deal of information regarding failures. However, one common cause is insufficient memory.
nanoHUB provides each user about 1 terabyte of memory, which Berkeley XAS quickly exceeds if k-space resolution > 15 and/or for large structures. Try the simulation again with reduced resolution and after clearing your storage space.

- The progress bar is not accurate: The bar will progress to 10% and will remain there until the submitted jobs complete at which it will progress to 95%. This feature may be fixed in the future.

5 Exercises

1. Bond Length

- Select the carbon dioxide molecule from the loader and run a simulation using the default settings.
- Once the simulation is completed, return to the Molecule Structure page and adjust the length of the bonds by changing the last Oxygen to "O 0 0 1.45". Run the simulation again.
• In the above images, I calculated the spectra for CO2 without a lengthened bond, a single bond lengthened, and both bonds lengthened. You may have intuited that increasing distance would decrease the strength of the bond due to Coulomb attraction, which is inversely related to distance squared. The plots demonstrate that increasing distance 20% reduced bond energy by about 3 eV. Increasing the bond length of the other Oxygen also reduced the bond energy of the first. More interestingly, increasing the bond length of O2 revealed the presence of a second peak that was not present in the original spectrum due to degenerate energy states. Removing the system’s symmetry lifted the degeneracy, revealing a second peak.

• Examine other bond lengths and determine an estimated relationship between bond length and binding energy. At what distance will the atoms be effectively noninteracting?

2. K-Space Resolution
• Run a simulation with K-space resolution set to 1. Recall that K-space is the reciprocal lattice given by a fourier transform to momentum space.
• Run the simulation again, but set K-space resolution to 4, 8, and 12. How does increasing the resolution affect the output spectrum?

3. Electron Band Factor
• Run a simulation with Electron Band Factor = 2. This means that the electron states considered in the calculation consist of the N occupied states and the N unoccupied states above it. Therefore, the greatest transition energy is limited by the energy in the $2N^{th}$ state.
• Run the same simulation again, but with Electron Band Factor = 4. This time, 3N excited states are allowed in the calculation, increasing the allowed transition energy in the simulation. How will increasing this value impact the spectrum? Will all regions of the spectrum be affected?