

Multi-code Benchmark on Ti K-edge X-ray Absorption Spectra of Ti-O Compounds

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Abstract

X-ray absorption spectroscopy (XAS) is an element-specific characterization technique that is sensitive to a material's structure and electronic properties. First-principles XAS simulations have been widely used as to interpret spectra and draw physical insights. Recently, there has also been a growing interest in building computational XAS databases to enable machine learning applications. While several codes are widely used to calculate XAS, non-trivial differences exist both in their underlying formalism and implementation. A systematic comparison between these codes is crucial for assessing reliability and reproducibility of computational XAS data. In this work, we benchmark Ti K-edge XAS simulations of Ti-O binary compounds using three state-of-the-art codes: XSPECTRA, OCEAN, and EXCITING. We study their convergence behavior with respect to input parameters and present a workflow to automate and standardize inputs to ensure reliable spectra. This allows us to quantitatively compare the results from the three codes and understand the effects due to differences in their treatment of the electron-core-hole interaction.

Background

- Many choices of methods (e.g., multiple scattering, band structure and model Hamiltonian) and codes
- Stumbling blocks in first principles spectral simulations
 - Reliability of the results
 - Choice of code
 - * Protocol for numerical convergence
 - Computational cost
 - * Workflow and metadata for reproducibly

Multi-code Benchmark

- Systematic code vs. code comparison
- Automated workflow
 - Identical structures
 - Ensure data reliability and reproducibility
 - Fully converged spectra from each code
 - Ready for high throughput spectral simulation and database construction
 - Quantitative multi-code spectral comparison

Workflow diagram

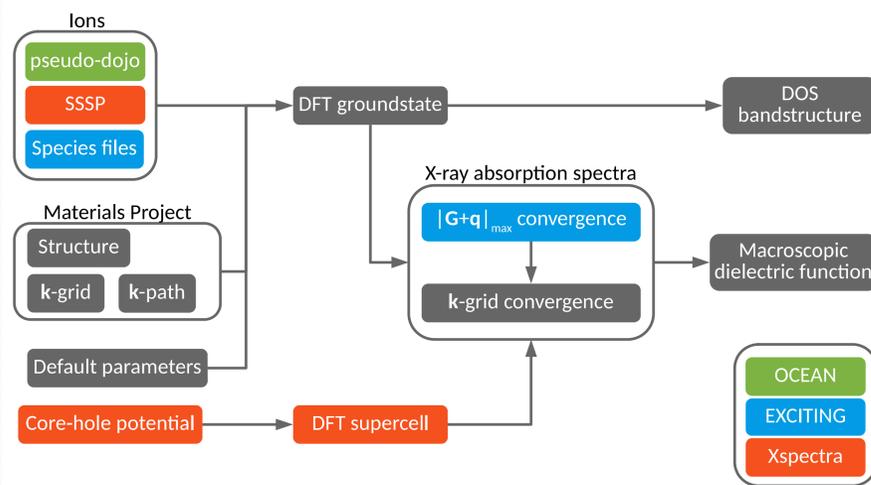


TABLE I. Summary of the main features of the three codes used in XAS simulation

	EXCITING	OCEAN	XSPECTRA
Boundary Condition	Periodic	Periodic	Periodic
Method	Bethe-Salpeter Equation	Bethe-Salpeter Equation	Core-hole DFT
Treatment of Core	All-electron	Pseudopotential	Pseudopotential
Basis	Linearized augmented PW + local-orbitals	Planewave	Planewave
Simulation Cell	Unit cell	Unit cell	Supercell

Choice of dataset

- 10 TiO_x compounds: 5 insulators and 5 metals
- Cover the available range of symmetry, oxidation states, coordination numbers in the Materials Project

TABLE II. Ten materials being benchmarked in this work

mpid	Band gap (eV)	Oxi. State	Coord. Num.	Num. of Nonequi. Site	Formula	Space Group
mp-390	2.06	4+	6	1	TiO ₂	I4 ₁ /amd
mp-2657	1.77	4+	6	1	TiO ₂	P4 ₂ mm
mp-1840	2.29	4+	6	1	TiO ₂	Pbca
mp-1203	0.00	2+	4, 5	3	TiO	C2m
mp-430	2.23	4+	7	1	TiO ₂	P2 ₁ /c
mp-458	0.00	3+	6	1	Ti ₂ O ₃	R3c
mp-10734	0.00	2.5+	6	1	Ti ₄ O ₃	I4/m
mp-1215	0.00	1+	3	1	Ti ₂ O	P3m1
mp-2664	0.00	2+	6	1	TiO	Fm3m
mvc-11115	2.46	4+	4, 6	2	TiO ₂	R3m

Ground State Comparison

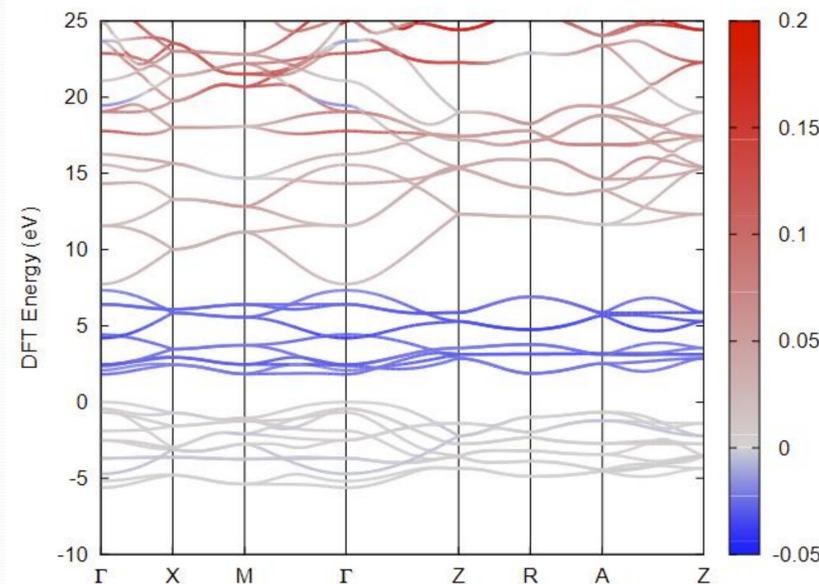


Fig 1. The band structure of mp-2657 as calculated using the exciting code. The colors signify the difference between the same results using the Quantum ESPRESSO code with the PseudoDojo (ocean) pseudopotentials. Both calculations were aligned with the valence

k point convergence

- M × N mesh in reciprocal space → 1 k-point an effective crystal size of M × N times of the unit cell
- Radius of inscribed sphere as the control variable for K-point convergence
- Spectral similarity is measured by log(1-S), where S is the Spearman's rank correlation

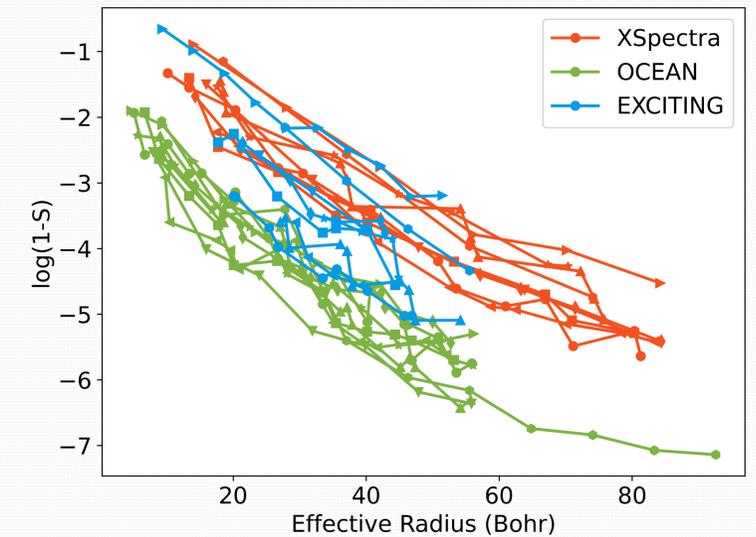


Fig 2. Convergence behavior of the three codes with respect to k-mesh. Different shape of the data points indicates different materials being considered in this work.

Spectra Comparison

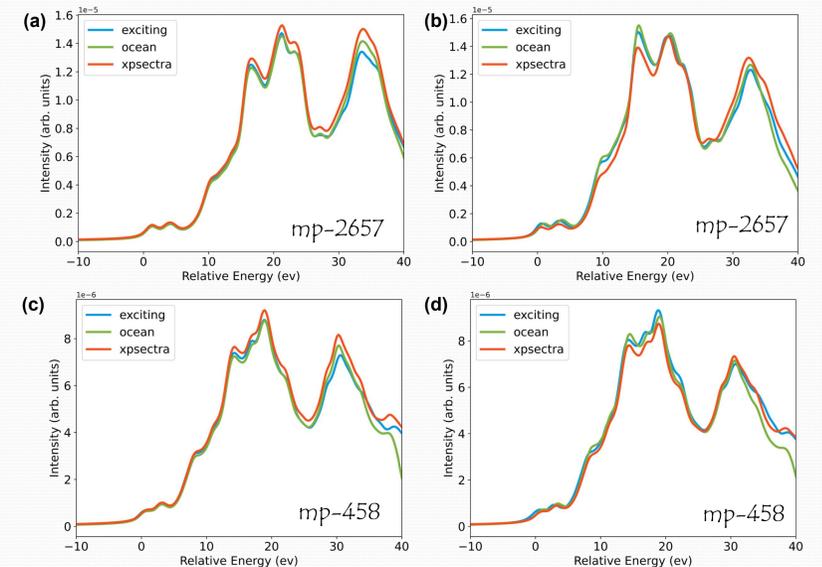


Fig 3. Comparison of independent particle level spectra (a) and (c) as well as full spectra (b) and (d). (a) and (b) are for mp-2657, while (c) and (d) are for mp-458.

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Summary and outlook

- General workflow for X-ray absorption calculations
- Good agreement despite different theory & implementation
- Data and workflow will be released with publication