Electronic Structure of Functional Materials: From Laboratory Photoemission to Synchrotron-Based Spectroscopies

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Course Description

Understanding the electronic structure of materials is essential for the development of modern energy technologies, including organic photovoltaics, photocatalysts, batteries, and molecular electronic devices. This short course introduces a set of complementary spectroscopic techniques used to probe occupied and unoccupied electronic states, with particular emphasis on the interpretation of experimental data through electronic-structure calculations.

The course begins with laboratory-based photoemission techniques, including X-ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS), and Inverse Photoelectron Spectroscopy (IPES), highlighting the information that can be obtained regarding chemical composition, oxidation states, work function, ionization energy, electron affinity, and density of states.

The second part of the course focuses on synchrotron-radiation-based techniques, including Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and Resonant Photoemission Spectroscopy (ResPES). Particular attention will be given to the interpretation of element-selective electronic structure, molecular orientation, orbital character, and charge-transfer processes. Examples from organic semiconductors, self-assembled monolayers, photocatalytic materials, and energy-conversion systems will be discussed throughout the course.

A recurring theme will be the integration of spectroscopy with Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT), demonstrating how theoretical calculations can be used to assign spectral features and establish structure–property relationships in functional materials.

Tentative Program

Each session is planned as a 45-minute lecture followed by a 15-minute break.

Day 1 – Electronic Structure at the Home Laboratory

Session 1: Introduction to Electronic Structure of Materials

- Occupied and unoccupied states

- Molecular orbitals and density of states
- Electronic structure and functionality

Session 2: X-ray Photoelectron Spectroscopy (XPS)

- Photoelectric effect
- Core-level spectroscopy
- Chemical shifts and oxidation states
- Applications in energy materials

Session 3: Ultraviolet and Inverse Photoelectron Spectroscopies (UPS/IPES)

- Valence electronic structure
- Work function, ionization energy, and electron affinity
- Mapping occupied and unoccupied states
- Examples from organic semiconductors

Session 4: From Laboratory Sources to Synchrotron Radiation

- Limitations of laboratory photoemission
- Tunable photon energies
- Polarization and high-resolution spectroscopy
- Why synchrotron light?

Session 5: Introduction to NEXAFS Spectroscopy

- Core excitations and selection rules
- Partial density of unoccupied states
- Carbon K-edge spectroscopy

Day 2 – Synchrotron-Based Electronic Structure and Charge Transfer

Session 6: Interpretation of NEXAFS Spectra

- Orbital assignments
- DFT and TDDFT calculations
- Natural Transition Orbitals (NTOs)
- Case studies

Session 7: NEXAFS Spectroscopy of Functional Materials

- Molecular orientation and linear dichroism
- Carbon, nitrogen, and sulfur absorption edges
- Electronic structure of organic semiconductors

Session 8: Resonant Photoemission Spectroscopy (ResPES)

- Resonant excitation processes
- Participator and spectator channels
- Element-selective valence electronic structure

Session 9: Applications of Resonant Spectroscopies

- Charge-transfer processes
- Hybridization at interfaces
- Electronic coupling in functional materials

Session 10: Core-Hole Clock Spectroscopy and Ultrafast Charge Transfer

- Fundamental concepts
- Charge-transfer timescales
- Selected examples from energy materials
- Perspectives and future developments