Announcing the Final Examination of Theodoros Panagiotakopoulos for the degree of Doctor of Philosophy in Physics.

Date: November 5, 2025
Time: 9:00 am
Room: PSB 160-161
Dissertation Title: AB Initio Studies of Electrochemical Processes: Insights into CO_2 Reduction and Hydrogen Evolution Reactions

Abstract:
This dissertation advances the design of electrochemical systems for clean energy by elucidating the role of electrolyte cations in modulating the Carbon Dioxide Reduction Reaction (CO_2RR) and the Hydrogen Evolution Reaction (HER). Achieving an atomistic understanding of the electrified solid-liquid interface is essential for improving these reactions, yet remains a formidable challenge. By applying advanced *ab initio* computational methods, this work overcomes this challenge to deliver a molecular-level picture of interfacial reaction mechanisms, revealing how non-metal cations can fundamentally alter catalytic pathways to enhance performance.

The first part of this work investigates the effect of cations on the electrochemical reduction of carbon dioxide (CO_2) on bismuth (Bi) electrodes using grand-canonical density functional theory (GC-DFT) with an implicit solvation model. The simulations reveal that ammonium-based non-metal cations, such as ammonium (NH_4^+) and methylammonium ($CH_3NH_3^+$), are not passive spectators but active participants that stabilize CO_2 adsorption on the electrode through favorable electrostatic interactions at the electrode-solvent interface. This stabilization lowers the kinetic barriers for key intermediates along the CO_2-to-CO pathway, while CO_2 reduction to formate on Bi is found to be largely insensitive to cation identity. These theoretical predictions are supported by experimental measurements confirming enhanced catalytic activity in the presence of ammonium-based electrolytes.

The second part examines the effect of metal and non-metal cations on the hydrogen evolution reaction (HER) on a gold electrode (Au(111)) in neutral media. Using grand-canonical *ab initio* molecular dynamics, the simulations reveal that ammonium-based cations enable novel, low-energy proton-transfer mechanisms inaccessible to conventional metallic cations. These include proton shuttling through the interfacial water network and direct proton donation from the cation itself. By actively participating in the rate-limiting Volmer step, these species open new reaction pathways that lower the activation barriers for hydrogen formation.

Together, these computationally driven insights, supported by experimental evidence, demonstrate that electrolyte design is as critical as catalyst design. By elucidating the active mechanistic role of non-metal cations in two key clean-energy reactions, this work provides a clear and practical design principle for accelerating electrocatalysis, paving the way for next-generation technologies for carbon utilization and sustainable hydrogen production.

Outline of Studies:
Major: Physics

Education Career:
M. S. University of Central Florida, Orlando Florida, 2024
M. S. National and Kapodistrian University of Athens, Greece, 2019

B. S. National and Kapodistrian University of Athens, Greece, 2017

Committee in Charge:
Dr. Talat S. Rahman (chair)
Dr. Abdelkader Kara
Dr. Mihai Vaida
Dr. Vasileios Anagnostopoulos (External Committee Member)

Approved for distribution by Talat Rahman, Committee Chair, on October 20 2025

The public is welcome to attend.