

Title: Electronic, mechanical and transport properties of molecular junctions

Author: Narendra Prabhakar Arasu

Department: Department of Condensed Matter Physics

Supervisor: Dr. Héctor Vázquez, Institute of Physics of the Czech Academy of Sciences, Department of surfaces and molecular structures, Molecular Transport Group

Abstract: Research and development in the single-molecule circuit are interesting from a fundamental perspective and have a great potential impact on electronics, catalysis, and organic energy cells. In this thesis, I present my contributions to molecular junctions through theory and simulations. Chapter 1 starts with a basic overview of fundamental concepts in the electronic structure of molecules and molecular electronics. Starting from simple models, I introduce the main ideas governing electron transmission through molecular structures, such as confinement and quantization of energy levels, tunneling through a potential barrier, or transmission through a single electronic level. I then present the fundamentals of electronic structure and Green's function methods. The concepts and simulation methods outlined here are the theoretical background for the works presented in this thesis. I also briefly discuss a few widely used experimental techniques studying molecular circuits.

Chapters 2 and 3 describe the behavior of novel individual molecules adsorbed on a metallic substrate. Using theory and simulations, we study the electronic properties of molecular systems in collaboration with experimentalists. I worked on two systems. The first is a donor-bridge-acceptor molecule studied on a Pt surface. We investigate the preservation of donor-acceptor properties of the molecule upon adsorption on a highly reactive substrate. The second work is a surface study of a class of molecules called carbene. We study the geometrical and adsorption properties of a novel carbene molecule on the Au surface. Chapter 4 acts as a bridge between molecular surface science and molecular electronics. We propose a new bipodal molecular platform that is mechanically robust, as it forms two covalent bonds to the Au substrate. We then contact the molecule from the top with a tip and study the electron transport properties. Our study provides a guideline for designing molecular platforms on Au.

Finally, chapter 5 focuses on conductance and antiaromaticity. Aromaticity is a key concept in chemistry, describing the stability of conjugated molecules, which play a central role in molecular electronic studies. Antiaromatic compounds were long predicted to have remarkable conducting properties but not previously tested. Our study, carried in close collaboration with synthetic and experimental partners, was the first to study the conductance of genuinely antiaromatic molecules. Calculations revealed the origin of this increased conductance. In a subsequent article, we generalized our previous work to reveal the relationship between (anti)aromaticity, molecular connectivity, and quantum interference.

Keywords: Molecular electronics, Molecular transport, Density functional theory-DFT, Donor-acceptor molecule, Carbenes, Aromaticity, Antiaromaticity