Ab Initio Modeling of Iron in Molecular, Surface and Bulk Environments

Project Manager
Dr. Young-Joon Song

Researchers
Adrian Valadkhani and Paul Wunderlich

Principal Investigator
Prof. Dr. Roser Valentí

Project Term
2021 - 2022

Clusters
Lichtenberg II Cluster Darmstadt

Software
VASP

Institute
Institute of Theoretical Physics

University
Goethe Universität Frankfurt am Main

Introduction

In a hydrogen fuel cell, that consists of an anode and a cathode, oxidation and reduction reactions occur simultaneously. However, reduction reactions are generally much slower than oxidation reactions, therefore, catalysts are indispensable to balance them. Nowadays, Pt-based catalysts are the most widely used in the world. However, Pt is too expensive and its reserves are not very large on Earth. FeN4Cx-type materials are known as promising alternatives to replace Pt-based catalysts due to their good active properties which are comparable to the low limit of the activity in Pt-based catalysts. However, their catalytic properties still remain unclear because of various unexpected phases. We applied periodic boundary conditions to the well-known nitrogen coordination environments: pyridine and pyrrole. In particular, we considered chlorinated Fe-porphyrin molecules corresponding to pyrrolic nitrogen coordination on a graphene sheet. In this case, our goal is to understand Fe’s electronic and magnetic properties and their changes when deposited on graphene.

Methods

In this project, we performed density functional theory (DFT) based on first principles calculations to investigate the electronic and magnetic properties of chlorinated Fe-porphyrin molecules on graphene systems including periodic boundary conditions. For this, we used Vienna Ab initio Simulation Package (VASP), which is widely being used, to simulate the systems. This program has highly advanced parallel functions to deal with a large scale of systems, which can be performed on the Lichtenberg HPCs.

Results

By means of geometry optimization functions in VASP, we first relaxed crystal structures by considering four possible initial sites. In other words, a chlorinated Fe-porphyrin molecule is placed on different graphene sites and the systems are fully relaxed. According to our DFT results with the relaxed structure, a high spin configuration (S=5/2) of Fe can be realized by three major effects, (1) crystal field splitting, (2) strong p-d hybridization, and (3) Hubbard U. We found that the van der Waals interaction between the molecule and graphene, which is the dominant interaction, marginally affects the electronic and magnetic states of Fe. On the other hand, if Cl is removed from the molecule, the interaction increases slightly as Fe moves closer to the graphene layer, and the system becomes nearly S=2.

Discussion

The role of the spins of Fe in catalytic properties is not yet clear. In the following project, we will focus on geometric effects and the spin states of Fe to figure out to what extent they affect catalytic properties by applying the nudged elastic band method.

Publications

Song Y.-J.: Effect of Graphene Sheets on Chlorinated Iron Porphyrin. 31st Topical Meeting of the International Society of Electrochemistry, Aachen, Germany, May 15-19 (2022)

Last Update: 2023-06-07 16:23