

論文の内容の要旨

論文題目 Theoretical Study of Electron Transport and
Dynamics of Molecules on Metal Surfaces based on
First-Principles Calculations

(第一原理計算に基づいた金属上の分子の電気伝導と
ダイナミクスの理論的研究)

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This thesis presents a theoretical study about electron transport and dynamics of molecules on metal surfaces based on first-principles calculations. Molecular/metal interface is one of the most important subjects in surface and nano science because it is the spot where chemical reactions happen and is the place which determines functions of organic devices. Controlling catalytic reactions and functions of devices is a goal for many scientists although this is hindered by unpredictable behaviors of molecules on metal surfaces. This unpredictability comes from the fact that a molecular orbital (MO), of which energy is well defined in the gas phase, is shifted and broadened due to the interactions with metal surfaces. The degree of the modification of the MO varies a lot with metal species. Although the MO on metal surfaces can be described using a conventional first-principles calculation such as density functional theory (DFT), it is difficult to connect the information of the MO directly to macroscopic properties of devices such as current (I)-voltage (V) curves or reaction rates. One reason for the difficulty is that usually molecular layers are required to measure I - V curves. The orientations of the surrounding molecules, which are also affected by metal surfaces, significantly modify the energy level alignment of the MO. The observation of electronic structures at “buried” interfaces is experimentally difficult. Another reason is the presence of an external driving force to transport carriers or induce the atomic dynamics. No electric devices start to work without an applied bias. Such an external driving force also modifies the MO and then the consequent electric current forces the system to leave from the ground state.

However, once we can understand observable properties from microscopic information by overcoming above difficulties, it will be possible to design and control a molecular device and chemical reaction by adjusting the position and width of MOs from tremendous combination of molecules and metals. This is the chemical engineering in the literal meaning. To achieve this goal, constructing a correct model without *ad hoc* parameters is mostly required. The first-principles calculation is a useful method to describe the electronic state of a molecule near the metal surface without empirical parameters. If the first-principles calculation is able to identify MOs contributing mainly to transport, find a vibrational motion promoting the reaction and determine those properties in nonequilibrium conditions in addition to the ground state properties, more experimental results can be explained from a microscopic point of view. We list three scientific objects to be studied in this thesis: the surface Peierls transition, the energy level alignment at metal/organic interfaces and the molecular switch. Through these works, quantum schemes to shed light on the origins of those phenomena are developed by extending the conventional DFT to calculate physical quantities which are not obtained before.

In this work, properties of atoms and molecules on metal surfaces in contexts of above phenomena are investigated using DFT. The electron transport properties under nonequilibrium conditions are studied mainly by the nonequilibrium Green's function (NEGF) formalism implemented into the HiRUNE module. Within the scheme of the NEGF, the inelastic electron tunneling spectroscopy (IETS) signal is also calculated as well as the electron-phonon coupling matrix. The nudged elastic band method is generalized to be able to calculate the reaction path under current and is implemented into the SMEAGOL package. The resonance model to treat the vibrational heating is extended for systems having a high barrier and wide working bias.

This thesis consists of 8 chapters and chapter 1 gives the general introduction. Chapter 2 presents the basic concepts of DFT and its practical implementation in the SIEATA program, which is used throughout in this work. We show that the electronic states can be solved in the form of the eigenvalue problem using Kohn-Sham orbitals, under the scheme of DFT. In SIESTA the Kohn-Sham orbitals are expanded by localized basis functions, which are suitable to calculate transport properties because interactions between molecules and electrodes can be straightforwardly written in the matrix form. Therefore it is important to understand how to describe electronic states in the periodic cell using localized

basis sets. We start from basic concepts such as the pseudopotential and construction of basis functions, and then describe how to practically calculate the total energy and atomic forces.

In chapter 3 we investigate the charge density wave (CDW) on Cu(001) covered by In, Pb and Bi using DFT. Although this study is not related to the transport properties, it contains some important concepts such as surface states, surface phonons and electron-phonon coupling between them. We explain the origins of surface states of In, Pb and Bi/Cu(001)-0.5 ML having $c(2 \times 2)$ structure that cause a phase transition via the generation of a CDW. Band-structure analysis suggests a common mechanism of CDW transition for In and Pb/Cu(001)-0.5 ML. The absorption of In and Pb on Cu(001) leads to a reduction in the energy of the band composing the edge of bulk band gap. As a result, the band enters the bulk band gap and has the character of the surface state. Since these surface states compose a well-nested Fermi surface, CDW transition would be induced. In addition, we study the relationship between the lattice distortions and the band dispersions of the surface states of In/Cu(001)-0.5 ML and W(001) in terms of the Jahn-Teller effect (JTE). While we find promoting modes that resolve the degeneracy of surface states of W(001), any surface-localized mode of In/Cu(001) does not split the band of surface state. Therefore, the static electron-phonon interaction of In/Cu(001) is weak. We propose that the dynamic JTE contributes to the CDW transition of In/Cu(001) and the dynamic nature is related to the spatial coherence length of the CDW. Our strategy of analysis based on the real-space movement of atoms and MOs will be useful in terms of chemical engineering of the Peierls transition.

Chapter 4 describes NEGF method, which is useful to study transport properties of molecules between electrodes. The HiRUNE module is designed to bring out the advantage of MO theory. The difference between HiRUNE and existing programs for transport calculations is explained. Not only the transport without scattering by nuclear vibrations (ballistic transport), but also corrections caused by the electron-phonon interaction are introduced.

In chapter 5 we study charge transport of PTCDA molecular layer on Ag and Al electrodes using NEGF-DFT method. To analyze roles of organic/metal interfacial states for transport, we examine two kinds of electrodes: Ag(111) and Al(111). By quantitative evaluation of the coupling strength between PTCDA molecular orbitals and electrodes, we find the creation of the Shockley-type state at the interface of PTCDA and Ag(111). In contrast, the Al(111) surface forms a strong chemical bond with PTCDA. A clear Shockley-type state is not created, and an ohmic $I-V$ is found

for contacts consisting of thin PTCDA layers and Al(111) electrodes. We also predict that further stacking of PTCDA layers will make I - V characteristics more Schottky-like for both Ag and Al electrodes, regardless the different microscopic mechanism.

Chapter 6 outlines two important concepts related to current-induced dynamics, current induced forces and vibrational heating. The high bias applied to the molecule between electrodes induces changes in structures and excites molecular vibrations. These effects can be observed as a breaking of metal wires or switching of conformations probed by changes in the electronic conductance. We present how we can interpret such a phenomenon from a microscopic view. Finally we describe a practical way to address these phenomena using first-principles calculations.

In chapter 7 we study dynamics of STM-induced switch of melamine/Cu(001) using all of methods described in previous chapters. We evaluate the conformation dependent transport properties, the reaction path and the bias dependent energy barrier from first principles by using the non-equilibrium Green's function formalism combined with density functional theory. Furthermore we calculate the IETS signal to identify the modes promoting the conformational changes of the molecule. The IETS signal also reveals why the high-energy molecular conformations do not relax back to the lowest energy state even for large applied bias voltage. We then formulate a vibrational heating model to describe the STM-induced switching in this system, where the switching rates and their dependence on the voltage and current are obtained by using parameters extracted from our first principles results. We find that the different switching behavior for positive and negative bias originates from the different electronic properties of the empty and filled states of melamine on Cu, combined with changes of barrier height with the applied bias.

Chapter 8 gives the general conclusion.