Understanding the structure and reaction of single molecules on metal surfaces from first principles

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To my father

献给我的父亲

To my father
Abstract

The study of surface adsorption and reaction is not only interesting from a scientific point of view, but also important in many application fields such as energy, environment, catalysis, corrosion, electronic device, and sensor. Theoretical calculations are essential in these studies.

In this thesis, first principles studies for the structure and reaction of some important single molecules on the surface are presented. Dehydrogenation of single trans-2-butene molecule on a Pd(110) surface is the first example. The adsorption configurations of both reactant and produce are assigned and the whole dehydrogenation pathway is revealed. Our calculations show that the reactant, i.e. trans-2-butene molecule, undergoes a rotation before dehydrogenation occurs, which is an important detail that cannot be observed directly in scanning tunneling microscopy (STM) experiments. The dissociation and rotation processes of single oxygen molecule on a Pt(111) surface have been a subject of extensive studies in the past. A new intermediate state with a peculiar configuration is identified. The puzzled adsorption site is well explained. The calculated energy barriers agree well with experimental results for both dissociation and rotation processes.

Another aspect addressed in this thesis is the mechanism of molecular electronic switches induced by molecular structural changes. By carefully examining the tautomerization process of a naphthalocyanine molecule, an intermediate state is located on the potential surface of the tautomerization. Our calculations indicate that the experimentally observed switching involves four-states, rather than the two-state as proposed by the experimentalists. In a joint experimental and theoretical study the dehydrogenation, tautomerization, and mechanical switching processes of a single melamine molecule on a Cu(100) surface have been comprehensively examined. A new dual-functional molecular device with integrated rectifying and switching functions is made for the first time. In collaborating with another experimental group, we have simulated the switching process of a single 1,1,2,3,4,5-hexaphenylsilole molecule on a Cu(111) surface. The role of the orientation of theses molecule is carefully examined and a new switching mechanism is proposed.

Switching processes are strongly associated with the inelastic electron tunneling. We have proposed a statistical model that allows explaining the non-integer exponent in the power-law relationship between the switching rate and tunneling current. In this model, the importance of the randomness in inelastic electron excitations and the lifetime of the immediate state are emphasized. It has shown
that the inelastic electron tunneling is a collection of various n-electron processes with different statistical weight.
The work presented in the thesis has been performed at the Department of Theoretical Chemistry & Biology, School of Biotechnology, Royal Institute of Technology, Stockholm, Sweden.

**List of papers included in the thesis**

Paper 1. First-principles Calculations of Adsorption and Dehydrogenation of trans-2-butene Molecule on Pd(110) Surface,

Qiang Fu, Jinlong Yang, and Yi Luo,


Paper 2. A First Principles Study on the Dissociation and Rotation Processes of a Single O$_2$ Molecule on the Pt(111) Surface,

Qiang Fu, Jinlong Yang, and Yi Luo,


Paper 3. Mechanism for Tautomerization Induced Conductance Switching of Naphthalocyanine Molecule,

Qiang Fu, Jinlong Yang, and Yi Luo,


Paper 4. Design and Control of Electron Transport Properties of Single Molecules,

Shuan Pan, Qiang Fu, Tian Huang, Aidi Zhao, Bing Wang, Yi Luo, Jinlong Yang, and Jianguo Hou, (Pan and Fu contribute equally)


Paper 5. Single Molecule’s Conductance Depending on its Orientation,

Yuesheng Ning, Jun Jiang, Ziliang Shi, Qiang Fu, Jianzhao Liu, Yi Luo, Ben Zhong Tang and Nian Lin,


**List of papers not included in the thesis**

Paper 6. Theoretical Study of Molecular Nitrogen Adsorption on $W_n$ Clusters,

Xiurong Zhang, Xunlei Ding, Qiang Fu, and Jinlong Yang,

Paper 7. Exploring at Nanoscale from First Principles,

Qiang Fu, Lan-Feng Yuan, Yi Luo, and Jinlong Yang,


Paper 8. Understanding the Concept of Randomness in Inelastic Electron Tunneling Excitations,

Qiang Fu, Yi Luo, Jinlong Yang, and Jianguo Hou


Paper 9. Electron Affinities and Electronic Structures of o-, m-, and p-Hydroxyphenoxyl Radicals: A Combined Low-Temperature Photoelectron Spectroscopic and *Ab Initio* Calculation Study,

Xue-Bin Wang, Qiang Fu, and Jinlong Yang,


Qiang Fu, Jinlong Yang, and Xue-Bin Wang,


**Comments on my contributions to the papers included**

- I was responsible for the calculations and the writing of the first draft for Paper 1, 2, and 3.

- I was responsible for the calculations and assisted in the writing for Paper 4.

- I was responsible for a part of calculations, and participated in the analysis and discussions for Paper 5.
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Chapter 1

Introduction

1.1 What is a "surface"?

A surface denotes the outermost layer of atoms that terminates one material. However, such a layer cannot only be regarded as a boundary. In fact, many interesting phenomena and novel properties are firmly related to the surface.

Because the perpendicular extension of a material ceases at the surface, the surface atom is in a completely different environment compared with atoms in bulk. At the surface, the atoms are under-coordinated, and therefore are not fully bonded. Thus, atoms at the surface usually interact more strongly with exotic atoms or molecules. In addition, surface atoms can also adjust the bonding among themselves to gain greater coordinate numbers, which leads to the
reconstruction of surface structures. Fig. 1.1 shows the geometries of an unreconstructed Si(100)-1×1 and a reconstructed Si(100)-2×1 surface. One can see that after reconstruction, two adjacent Si atoms in the topmost layer are bonded with each other to form a "dimer". Through the formation of this "dimer", the number of dangling bonds, which come from unsatisfied bonding, is greatly reduced.

The structure of the surface is not ideally smooth. In reality, many different types of defects, such as steps, kinks, vacancies and adatoms, could exist on the surface, as Fig. 1.2 shows. Compared with other types of atoms on the surface, atoms related to defects usually have lower coordinate numbers. As a result, atoms at defects have stronger interaction with adsorbates, and usually play the role as an "active site" in surface reactions. In addition, surface defects could cause changes of electronic structure of the surface. For example, the bridging oxygen vacancy of a rutile TiO$_2$(110) surface introduces a localized state 1eV below the conductance band$^1$, which may be crucial in the process of catalytic water splitting.

![Figure 1.2](image_url) Schematic diagram to show the structure of various defects on surface. Here atom is indicated by little cubes. Reproduced with permission from ref.$^2$. Copyright © 2003 Springer Science+Business Media.

### 1.2 Surface study is complex but important

It should be noted that the study of surface property and dynamic process is not an easy task. The complexity of the surface structure is one of the important reasons. Even for the adsorption of simple atoms on the surface with low Miller index, complicated reconstruct could take place. For example, when oxygen atoms adsorb on the Cu(100) surface, the oxygen atoms not only induce missing row reconstruct of the surface, but also locate at the edge of the "copper strips", forming the Cu-O-
Cu chains\cite{3} (Fig. 1.3). Another famous example which relates to the complexity of the surface structure is the Si(111)-7×7 surface. Si(111)-7×7 is an important type of silicon surface, however, its detailed structure has been debated for a long time. Now the "dimer-adatom-stacking fault" (DAS) model, which includes two different half unit cells (the faulted and unfaulted one), twelve adatoms, six rest atoms and many other underlying silicon atoms, are well accepted\cite{4–7}. It is worth noting that 398 atoms are needed in first-principles calculations in order to gain a reasonable description for the properties of this surface.

![Figure 1.3](image)

Figure 1.3 Top view of the adsorption structure of oxygen atoms on a Cu(100) surface. The Cu(100) surface undergoes reconstruction by the adsorption of oxygen atoms. Reproduced with permission from Chem. Rev. ref.\cite{8}. Copyright © 1996 American Chemical Society.

Compared with static adsorption structure, the dynamic process at surface is more complex. For example, in the oxidation process of a CO molecule on a Pt(110) surface, typical spiral waves appear in the photoemission electron microscopy (PEEM) image, as shown in Fig. 1.4\cite{9}. It should be noted that the lateral extension of the spiral wave pattern could be up to tens of μm. Detailed studies of the phenomena show that the appearance of the spiral wave comes from a complex nonlinear dynamic process, which involves in adsorption, reaction, and reversible transformation of surface structures induced by the coverage change of adsorbates\cite{9–12}. The adsorption of the CO molecule could change the Pt(110) surface from a 1×2 "missing row" reconstructed structure to the 1×1 unreconstructed one over a certain coverage. This unreconstructed Pt(110) surface favors the dissociative adsorption of oxygen molecule, which produces more active oxygen atoms to react with CO and thus reduces the corresponding coverage of CO
molecules. As the coverage decreases, the Pt(110) surface returns to its original reconstructed structure, which lowers the production of oxygen atoms, and results in the increase of CO coverage as well as the transformation of Pt(110) surface again\cite{12}. From this example one can see that even for a simple reaction between two diatomic molecules on a simple surface with low Miller index, a very complex process could take place.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{PEEM image of typical spiral waves in the catalytic oxidation reaction of CO on a Pt(110) surface. Dark and bright zone corresponds to the O-cover and CO-cover area respectively. The diameter of the image is 500 $\mu$m. Reproduced with permission from Prof. Ertl’s Nobel Lecture in Dec. 2007\cite{9}. Copyright © 2007 The Nobel Foundation.}
\end{figure}

Many important processes, which are closely related to human being, take place on the surface, which makes the study of the surface process more significant. One of the most outstanding examples is the industrial synthesis of ammonia from hydrogen and nitrogen. Ammonia is an important raw material to produce fertilizer, which is critical in agriculture. However, although the process is exothermic from a thermodynamics point of view, this reaction is not so easy to take place, because of the high energy barrier that relates to large bond energy within the nitrogen molecule. Special catalysis for ammonia synthesis is therefore urgently needed. Thanks to the studies of surface reaction for many years, knowledge related to the detailed process of surface reaction between hydrogen and nitrogen as well as some important factors which could significantly influence the conversion towards ammonia had been quickly accumulated. With the discovery and continuous improvement of the catalysts, the industrial synthesis of ammonia has been a mature field for many years since the discovery of the Haber-Bosch process. Fig.
1.2 Surface study is complex but important

1.5 shows the growth of both world population and ammonia production, which highlights the importance of this great achievement.

Figure 1.5 The variation of world population (in $10^9$) and amount of ammonia production (in $10^6$ metric tons of nitrogen). Reproduced with permission from ref.\textsuperscript{[13]}. Copyright © 1999 WILEY-VCH Verlag GmbH.

Another outstanding example is about the reduction of polluting exhaust from automobiles. The emission from the combustion engine of the automobile contains nitric oxide, carbon monoxide, and some unburnt hydrocarbons, which are severe harmful to our environment. It is found that three precious elements, \textit{i.e.} Pt, Pd and Rh, could be used to reduce the amount of such pollutants. These metals could promote to transfer the pollutants to less harmful gases through catalytic reactions, such as reaction between CO and NO to generate CO\textsubscript{2} as well as N\textsubscript{2}; oxidation of CO to generate CO\textsubscript{2}; and oxidation of unburnt hydrocarbons to generate CO\textsubscript{2} as well as H\textsubscript{2}O. It should be noted that all of these reactions occurred on the surface. Through the studies of the surface reaction process, one could understand the corresponding underlining mechanisms, and further improve the performance, such as increasing the efficiency of conversion, making the conversion easily occur at a lower temperature, and decreasing the amount of precious metals used.

Modern surface science began in 1950s, when the study of surface property and process at the atomic level became a reality. With the development of surface analysis technologies, the structure, composition, and electronic state of the surface system can be well explored. For example, Auger Electron Spectroscopy
(AES) can be employed to determine the composition of surface layers; and the X-ray Photoelectron Spectroscopy (XPS) can be used to study the electronic structure of surface system. The invention of Scanning Tunneling Microscopy (STM) represents a significant breakthrough in surface science studies. With the help of STM, for the first time one can see the surface morphology at an atomic level. It is worth noting that STM is not only a tool for imaging, but can also be used for manipulation, excitation, characterization, and so on.

The actual surface system in real life is in fact even more complex and extremely difficult to study. It is the hope that a good understanding of different aspects of the well-defined surfaces could allow us to put all puzzles together. As Langmuir once pointed out: "If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies". This philosophy has been widely employed, although the "pressure gap" and the "material gap", which come from the difference between model system and the actual one, should one day be finally bridged.

1.3 Importance of first-principles calculations in surface studies

First-principles calculation is important in the study of the surface. Not only it can provide reliable structure information that could be compared directly with experiments, but also it can reveal the underlying mechanisms behind experimental observations. With the development of theoretical methods and the continuous expansion of computing capabilities, first-principles calculations are playing an increasing important role in surface studies.

One of the examples is about first-principles calculations on ammonia synthesis from nitrogen and hydrogen molecules on the ruthenium surface. Fig. 1.6 shows the energy profile in the ammonia synthesis process on both Ru(001) and Ru step surfaces. The calculations could give a detailed description of surface process and also provide some other important information. It is revealed that the dissociation of the nitrogen molecule is the rate-limiting step, and the surface step could significantly reduce the energy barrier of the dissociation, making the reaction occur at a lower temperature. With a microkinetic model employed, the reaction rate on an actual ruthenium nanoparticles was calculated from first-principles calculations and the simulated results agree quite well the experimental values. With the known reaction mechanism, first-principles calculations can
be used to design and predict better catalysis for ammonia synthesis, for example, the one with better performance or lower cost, as in the work of Jacobsen et al.\cite{17}.

![Figure 1.6](image)

Figure 1.6  The potential energy surface of ammonia synthesis process on both Ru(001) and Ru step surfaces from first-principles calculations. Reproduced with permission from Science ref.\cite{15}. Copyright © 2005 American Association for the Advancement of Science.

Another example to show the importance of first-principles calculations is the theoretical study of early stages in graphene growth on flat and stepped surface\cite{18}. Graphene has aroused great interest because of its intriguing properties in electronic structure, optics, mechanics and so on. Producing high-quality single-layer graphene in large scale is important in practical applications of graphene. Chemical vapor deposition (CVD), through which the hydrocarbon molecule dehydrogenate and then the produced carbon atoms polymerize on transition metal surface, is one of the most popular methods to produce graphene. However, the quality of graphene is affected by the existence of domain boundaries\cite{19}. In the work of Chen et al., the initial stage of carbon nucleation on flat and stepped surfaces is investigated by first-principles calculations\cite{18}. The detailed information gained from theoretical calculations will be useful for the experimentalists to produce better graphene single layer with CVD method.
1.4 Outline of our works based on first-principles calculations

In this thesis, I will present our first-principles studies on adsorption and reaction of some interesting single molecules on metal surfaces. It is our belief that our studies could shed light on the understanding of some important surface processes. My thesis work is closely related with STM experiments, and can be divided into two parts.

The first part is about the changes of a single molecule on the metal surface under STM excitations. In the studies of adsorption and dehydrogenation of a single trans-2-butene molecule on a Pd(110) surface, our assignment of the reactant and product as well as the calculated height of the energy barrier agree well with the experiments\cite{20}. The calculated dehydrogenation pathway shows that the process occurs in a stepwise way. More interestingly, the rotation of the trans-2-butene molecule is revealed by our calculations, which is not possible to be detected in the STM experiments. In the investigation of dissociation and rotation of a single oxygen molecule on a Pt(111) surface, we focus on several questions raised by experiments: the preferred occupation of the metastable hcp hollow site by oxygen atoms after the dissociation; the low energy barrier of the rotation. The first question is well solved by the finding of an intermediate state with a particular configuration combined with the "cannon ball" mechanism, while the second question is answered by identifying an effective rotation pathway.

The second part of my thesis work is about the mechanism of molecular electronic switch, which is also closely related to the surface process and can be theoretically investigated by exploring the possible pathways. The first switch we studied was related to the naphthalocyanine molecule. We found that this molecule is in fact a four-state switch rather than a two-state switch due to the existence of an intermediate state. The second one is related to the adsorbed melamine molecule. With STM stimulations, the melamine molecule can undergo a tautomerization process by transferring one of its hydrogen atoms in top amino group to an adjacent nitrogen. The modified molecule behaves as both a rectifier and a switch. Our calculations provide a detailed description of the whole process, and provide the mechanism for the dual-functionality of the molecule. The third switch is the 1,1,2,3,4,5-hexaphenylsilole molecule on a Cu(111) surface. Theoretical calculations reveal that the two conductance states come from two orientations of the molecule adsorbed on the surface.
During the studies of the molecular switches, we have developed a statistical model to explain the non-integer exponents in the power law relationship between the switching rate and the tunneling current. It is known that the exponent corresponds to the number of inelastic electrons that are needed in the process to overcome the energy barrier, and thus an integer value is always expected. However, some experiments\cite{21,22}, including ours for the melamine\cite{23}, observed non-integer exponents in many cases. We have introduced the concept of the randomness for the electron tunneling and put forward a statistical model with the inclusion of the intermediate state’s lifetime to simulate the inelastic electron tunneling processes. We have found that the non-integer exponent is in fact a value of statistical average, coming from the contribution of various different n-electron processes. The statistical model has been used to reproduce the experimental results for both melamine switching and the rotation of single oxygen molecule.

First-principles calculations rely on effective solution of Schrödinger equation. The complex many-body problem is simplified through several approximations. In Chapter 2, I will briefly introduce the first principles methods as well as those approximations applied in the calculations. In Chapter 3, experiment investigations on STM characterization, manipulation and molecule switch, which are closely related to my thesis work, are reviewed. The simulation models, such as the slab model to describe a surface system, the Tersoff-Hamann approximation to simulate STM image, the climbing image nudged elastic band (c-NEB) method to explorer the reaction pathway, and the statistical model to describe inelastic excitations, will be introduced in Chapter 4. The summary of my work is collected in Chapter 5. Finally, in Chapter 6 I give an outlook about my future studies.
Chapter 2

Methods in First Principles Calculations

2.1 Hamiltonian of the system

The property of a system in an atomic length scale can be well understood by quantum mechanics. Through solving the Schrödinger equation, one can obtain the wave function, which is very important in the description of microscopic particles. By applying quantum mechanics into the area of chemistry, one can thus study and predict the properties of the multi-particle system composed by nuclei and electrons.

The Hamiltonian can be expressed as a summation of several terms (Eq. 2.1):

\[ H(\vec{r}, \vec{R}) = -\sum_i \frac{\hbar^2}{2m_e} \nabla^2 r_i + \frac{1}{2} \sum_{i,i'} \frac{e^2}{|r_i - r_{i'}|} - \sum_j \frac{\hbar^2}{2M_j} \nabla^2 R_j + \frac{1}{2} \sum_{j,j'} \frac{Z_j Z_{j'} e^2}{|R_j - R_{j'}|} - \sum_{i,j} \frac{Z_j e^2}{|r_i - R_j|} \]  

(2.1)

Here \( \vec{r} \) and \( \vec{R} \) denote the coordinate, while \( m \) and \( M \) represent the mass of electron and nucleus respectively. The five terms include the kinetic energy of electrons, the repulsion between electrons, the kinetic energy of nuclei, the repulsion of nuclei, and the attraction between electrons and nuclei in turn. It should be noted that the orbit and spin motion of electrons are treated separately, therefore, relativistic effects such as spin-orbit coupling are not taken into account. This is the first approximation we use: the non-relativistic approximation.
The second approximation, **Born-Oppenheimer approximation**, can be employed to simplify the complex many-body problem including both electrons and nuclei. Because the mass of the nucleus is much larger than that of the electron, the velocity of the nuclei is thus much less than that of electrons. On one hand, when we consider the motion of the nuclei, the movement of electrons is so fast that they can always adapt to the moving nuclei, and interacts with nuclei averagely. The energy change associated with the variance of nuclear coordinates thus constitutes a potential energy surface (PES), as shown in Fig. 2.1, from which the dynamics as well as the vibrational properties of the nuclei can be studied. On the other hand, when we consider the movement of electrons, the nuclei can be treated as frozen. The Hamiltonian can therefore be simplified into three terms in Eq. 2.2, *i.e.* including the kinetic energy of electrons, the repulsion between electrons and the attraction between the electron and nuclei (the coordinates of nuclei are fixed here), and only involves the freedom of electrons.

$$H_{el} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_{\vec{r}_i}^2 + \frac{1}{2} \sum_{i,i'} \frac{e^2}{|\vec{r}_i - \vec{r}_{i'}|} - \sum_{i,j} \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|} \quad (2.2)$$

### 2.2 Wave function approach

Bohn-Oppenheimer approximation has reduced the complexity to a large extent in solving the Schrödinger equation. However, the corresponding electronic Schrödinger equation is still too complex due to the interaction between electrons. In 1928, Hartree proposed a solution to this problem\[^{24}\], which is usually called **Hartree approximation**, **orbital approximation**, or **independent particle approximation**.
approximation. In this approximation, the interaction that comes from other electrons is treated averagely and is approximated as a mean potential field. The electron is considered to move independently under such a potential field, and its motion can be described using a spin-orbital wave function. The total electronic wave function of the system is therefore expressed as a product of all occupied spin-orbital wave functions.\(^{[24]}\) As a result, a complex many-body problem is approximated to be a single-body problem.

The Hartree approximation significantly reduces the complicity in solving the electronic Schrödinger equation. However, the anti-symmetric property under the exchange between two electrons, which is required by Pauli exclusion principle, is not hold within the total electronic wave function. In 1930, Fock considered this effect and rewrote the total electronic wave function in the form of a Slater determinant of all the occupied spin-orbital wave functions.

Through a series of derivation based on the variational principle, the Hartree-Fock equation can be written in Eq. 2.3.

\[
F\varphi_i = \varepsilon\varphi_i \quad \text{(2.3)}
\]

Here \( F \) denotes the Fock operator, which has three terms as shown in Eq. 2.4: the Hamiltonian of a single electron \( h \), including both the kinetic energy and the attraction interaction with nuclei; the Coulomb interaction between electrons \( J \), and the exchange interaction of electrons \( K \).

\[
F = h + \sum_i (J_i - K_i) \quad \text{(2.4)}
\]

The Hartree-Fock equation can be approximately regarded as an effective Schrödinger equation of a single independent electron. All the spin-orbitals can be calculated by solving this equation. It is a kind of non-linear equation, in which the construction of one electron’s Fock operator comes from the spin-orbital of other electrons, \textit{i.e.} from the results of the Hartree-Fock equation itself. Therefore, it is nearly impossible to solve this equation analytically, and iterative method may be the only way to get the solution. When a “self-consistence” is achieved between the Fock operator and its solutions, the self-consistent effective potential as well as the spin-orbitals can be obtained.

In Hartree-Fock method, the interaction between electrons is considered in an average form. In reality, the motion of one electron could inevitably correlate with
the motion of another. Electrons with parallel spin cannot appear at the same point in space. This effect has been well considered in Hartree-Fock method in the exchange interaction item. However, electrons with anti-parallel spin also cannot be found at the same place because of the Coulomb repulsion between each other. This effect, which is usually called Coulomb correlation, has not been taken into account in Hartree-Fock method. As a result, the energy of the system that is calculated from Hartree-Fock equation is usually higher than the true value, which should be obtained by fully including correlation effects. The energy difference between the two values is called correlation energy. Compared to the total energy of the system, the correlation energy is much less; however, its value is usually very close to the energy changes associated with the chemical reaction. As a result, in our study of the surface reaction, especially when it is related to the height of energy barrier, the correlation effect should not be negligible.

In order to gain an improvement from the Hartree-Fock level, a series of more accurate methods were put forward, such as configuration interaction method (CI), many-body perturbation theory method (MP
), coupled cluster method (CC) and so on[25], which are collectively referred as post-Hartree-Fock methods. In these methods, the correlation interaction between electrons is considered in a more accurate way, and results can usually be improved systematically. However, the computational cost of these methods is too huge, which limits their application to system that only contains a small number of atoms. Even to the present, it is still safe to say that these post-Hartree-Fock methods cannot be directly employed to study of surface reaction that involves too many atoms.

2.3 Approach based on electron density

In the approach based on wave functions, each electron is described by three variables, thus a system with N electrons has 3×N degrees of freedom. In fact, it is not necessary to use so many variables in description of properties. In the method based on electron density, the properties of the ground state of system can be well described only by electron density that varies with the spatial coordinates x, y, and z, no matter how large the system is. Therefore, it seems that one may significantly reduce the computation efforts through the approach of electron density.
2.3 Approach based on electron density

2.3.1 Thomas-Fermi theory

In 1927, Thomas\cite{26} and Fermi\cite{27} made a first attempt to describe the property of system with electron density, which is known as Thomas-Fermi model. In this model, the kinetic energy of the system can be expressed as a functional of electron density. In combination with the classical expression of the nucleus-electron attraction and electron-electron repulsion, the properties of the system can be described with electron density. In 1928, Dirac added another term, which includes the exchange energy between electrons\cite{28}. The Thomas-Fermi-Dirac model is the first important step in electron density based approach. However, due to the rough description of the kinetic energy, the error in the expression of the exchange energy and the complete neglect of electron correlation, the results from this model is far from accurate and even incorrect qualitatively in many applications.

2.3.2 Density functional theory

The electron density based approach did not have a rigorous many-body theory until Hohenberg and Kohn put forward two theorems in 1964 for the properties of the system with a non-degenerate ground state\cite{29}. These two theorems are considered as the foundation of the famous Density Functional Theory (DFT). The first theorem points out that electron density can uniquely determine the external potential $V_{\text{ext}}$ of the system except a constant. As a result, the total energy as well as the ground state properties can be expressed as a functional of electron density (Eq. 2.5). This first theorem establishes the rationality to describe the properties of the system only with its electron density. The second theorem points out that the electron density of the system can be calculated with the variational method, i.e. when the true electron density of the system $\rho_0$ is used ($\rho$ denotes an arbitrary electron density), the energy functional $E[\rho_0]$ gives its minimum.

$$E[\rho] = T[\rho] + \int \rho(\vec{r}) V_{\text{ext}}(\vec{r}) d\vec{r} + E_{\text{ex}}[\rho]$$

Because the expression of the functional $E[\rho]$ has not been known, how to apply these two theorems to a particular calculation is the next question. Kohn and Sham proposed a famous method to solve this problem, which is called Kohn-Sham equation\cite{30}. In this approach, Kohn and Sham introduce a fictitious system, which has the same electron density as the true one, but the electrons do not
interact with each other in the fictitious system. It should be noted that the non-interacting property plays a key role in this approach. The non-interacting property is very similar to the "independent particle approximation" as used in Hartree-Fock approach. As a result, the wavefunction of the fictitious system can be expressed as a Slater determinant of a serial of spin-orbitals, which is called Kohn-Sham orbitals. Thus the three terms in Eq. 2.5 can be easily expressed in the form of Kohn-Sham orbitals, and the energy functional of the true system can be written as:

\[
E_{tot} = T + \int \rho(\vec{r}) V_{\text{ext}}(\vec{r}) d\vec{r} + E_{ee} = T_s + \int \rho(\vec{r}) V_{\text{exts}}(\vec{r}) d\vec{r} + E_{ees} \\
+ (T - T_s) + (E_{ee} - E_{ees}) = T_s + \int \rho(\vec{r}) V_{\text{exts}}(\vec{r}) d\vec{r} + E_{ees} + E_{xc} 
\]  

(2.6)

The subscript \( s \) denotes the energy term of fictitious system. Here the last term \( E_{xc} \) in Eq. 2.6 is called the exchange-correlation functional. It represents the difference of the kinetic energy and electron-electron repulsion between the true and the fictitious system. The expression of \( E_{xc} \) is also not known. It can be seen that the unknown expression of the whole functional in the Hohenberg-Kohn theorem is now transferred to the only one term \( E_{xc} \) in the Kohn-Sham approach. Through the variation of the energy functional with respect to the Kohn-Sham orbitals, the famous Kohn-Sham equation could be obtained (Eq. 2.7).

\[
[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{ext}}(\vec{r}) + E_{ee}(\vec{r}) + E_{xc}(\vec{r})] \phi_i(\vec{r}) = \epsilon_i \phi_i 
\]  

(2.7)

It should be noted that the expression of Kohn-Sham equation here is physically strict. However, some approximations should be introduced for the exchange-correlation functional due to its unknown format. Through the comparison of the expression between the Hartree-Fock and Kohn-Sham equation, one can see that they have a similar form. The only difference is that in the case of Hartree-Fock method, the exact exchange interaction is considered, while in the case of Kohn-Sham method, this term is replaced by a exchange-correlation functional. Because of this difference, on one hand, the correlation effect between electrons, which is omitted in Hartree-Fock equation, is now taken into account to some extent. On the other hand, in most functionals, the exchange effect between electrons is no longer exact, which will cause some problems especially in the description of electronic structure. Another thing that should be concerned is the spin-orbitals
solved from the two kind of equations. The Fock orbital has its physical meanings and meet the Koopmann’s theorem. Its orbital energy could be used to interpret experimental results from photoelectron spectroscopy. The Kohn-Sham orbital, just a mathematical symbol in the derivation of Kohn-Sham approach, holds no physical meaning. However, in practical applications, the Kohn-Sham orbital and its corresponding energy can also be employed to provide qualitative explanations, just like the Fock orbital.

Different types of approximation to the exchange-correlation functionals have been proposed and developed. According to the level of complexity in different approximations, the concept of ”Jacob’s Ladder” was put forward. Currently the most popular approximations for practical calculations include the Local Density Approximation (LDA), the Generalized Gradient Approximation (GGA) and the hybrid functional containing a certain percentage of exact exchange interaction.

### 2.3.3 Exchange-correlation functionals

In the local density approximation, the exchange-correlation functional is expressed only in the form of electron density at each point of space. In the generalized gradient approximation, the gradient of electron density at the same point is also added to construct the functional, i.e. the variation of electron density is also taken into account. If the distribution of electron density is uniform in space, a good description of its properties is expected with the LDA functional. However, if the variance of electron density is large in space, LDA may not be adequate, while GGA can improve the description as this effect has been considered to some extent. In the system of molecule adsorption on the surface, the variance of electron density in space usually cannot be neglected because of the different electron distribution between the surface and the adsorbed molecule, as well as the charge transfer between the two parts. As a result, GGA is the choice of more appropriate than LDA in our studies.

However, GGA functional is not always better than LDA in the description of surface systems. One of the typical examples is the adsorption of polycyclic aromatic hydrocarbon on the metal surface. In this kind of system, van der Waals interaction between the adsorbate and the substrate is pivotal. LDA usually gives better description on the adsorption structure than GGA. Fig. 2.2 shows the interaction energy between a PTCDA molecule and a Ag(111) substrate as a function of distance between them. One can see that the LDA curve is much closer to the accurate one than the GGA result. The LDA curve indicates that the PTCDA
molecule bonds on the substrate, but the GGA result shows no bonding at all, inconsistent with the experiments\cite{33}. We find the same phenomenon in our own calculations. Fig. 2.3 shows the optimized structure of single chloronitrobenzene molecule (ClNB) adsorption on a Cu(111) surface. Both LDA and GGA functionals are used. One can see that with the LDA functional, ClNB molecule bond on Cu(111) well, while with GGA, the repulsion between the benzene ring and the Cu(111) substrate is obvious because such kind of interaction cannot be well described by GGA.

It should be noted that the dispersion force related with the van der Waals interaction is essentially nonlocal. Both LDA and GGA cannot sufficiently account
such effect, although LDA has been applied well to some studies\textsuperscript{[34]}. Recently, the van der Waals interaction can be well described by the van der Waals density functional\textsuperscript{[35–37]} which has been applied to several systems\textsuperscript{[38,39]}. For example, very recently, it was found that the consideration of dispersion force is of great importance in the predication of adsorption structure of water ice on metal surfaces\textsuperscript{[39]}.

The hybrid functional is another type of functional, in which some percentage of exact exchange is included. B3LYP\textsuperscript{[41,42]}, PBE0\textsuperscript{[43,44]}, and HSE\textsuperscript{[45,46]} functionals are typical examples. One of significant advantages of hybrid functionals is that they could give an improved description of electronic structure for system with band gap, compared with GGA. A well-known problem associated with GGA is the self-interaction error (SIE). This error originates from the interaction of one electron with itself in the summation of electron-electron interaction, although such self-interaction does not exist in reality. As a result, GGA calculation gives the band gap that is usually two-thirds, and sometimes only a half of the experimental value\textsuperscript{[47,48]}. In addition, there is strong tendency that the electron state is described as a delocalized state, although in fact it is localized\textsuperscript{[47,48]}. This is a se-
vere problem when one studies semiconductor surface, such as the popular reduced rutile $\text{TiO}_2(110)$ surface. The self-interaction error does not exist in the Hartree-Fock method, because the electron self-interaction comes from the Coulomb and exchange items cancel with each other. As a result, adding a percentage of exact exchange interaction is expected to improve the description and in fact it indeed does. Fig. 2.4 shows the calculated density of state of the reduced $\text{TiO}_2(110)$ surface with oxygen vacancy. Both GGA and hybrid functional are employed. One can see that the GGA functional underestimates the band gap, while B3LYP predict an improved value$^{[40]}$. In addition, a localized state is located about 1eV below the bottom of valence band with B3LYP functional, while it is missed in GGA calculations$^{[40]}$.

However, the hybrid functionals are not suited for studying metal surface system, although it can give better description on semiconductor surface with band gap$^{[47,48]}$. It is because the exact exchange interaction at large electron-electron distance is approximately canceled by electron correlation in metal system$^{[47]}$. This problem results in a nonphysical vanish of density of state at the Fermi level in metal system from Hartree-Fock calculations$^{[49,50]}$. Thus, hybrid functional calculations usually give worse results for metal surface system, compared with the GGA calculations, as in the case of NO adsorption on Cu-SAPO-34 and Co-SAPO-34 systems$^{[51]}$. Another problem related to hybrid functionals is that it cost much more computational time than GGA functionals$^{[48]}$. Since our work focused on molecular adsorption on the metal surface, hybrid functional is thus not appropriate.

Based on the above discussion, it is clear that GGA functionals are the best choice for the systems studied in this thesis. I have mainly employed two GGA functionals, PBE$^{[52]}$ and PW91$^{[53]}$, for my studies.
Chapter 3

Inelastic Excitation with STM

When tunneling electrons pass through a sample, most of them could maintain their energy unchanged, known as elastic electrons. This part of electrons contributes to the imaging of STM. Another part of them, which is called inelastic electron, could lose their energy through the excitation of vibrational or electronic freedom of the adsorbates. Although the proportion of inelastic electrons is usually much lower than that of elastic electrons, inelastic excitation, which involves the coupling and energy transfer between the tunneling electrons and the adsorbates, is very important not only in fundamental research but also for some applications. According to the strength of the interaction between inelastic electrons and the adsorbates, inelastic excitation can be divided into two regimes: the weak one and the strong one\(^{[54]}\).

3.1 Inelastic electron tunneling spectroscopy (IETS)

A weak inelastic excitation is the basis of the inelastic electron tunneling spectroscopy (IETS). During the process of the electron tunneling, if the incident energy of the inelastic electron matches the energy interval between vibrational levels, inelastic electrons will excite the vibrational level of the adsorbate, and cause an additional contribution to the tunneling current. The contribution from inelastic excitation is usually very small compared to the one from elastic electrons, however, its second derivative with respect to the external bias, is a reproducible feature and can be clearly observed in experiments. In 1998, Stipe et al. realized the IET spectrum of single \(C_2H_2\) and \(C_2D_2\) molecules on a Cu(100) surface\(^{[55]}\) (Fig. 3.1). It is the first IES spectrum realized at a single molecule level. Later, IETS experiments were extended to many other systems by several groups\(^{[56-58]}\).
The IES spectrum is very sensitive to the adsorbate’s composition, configuration, and its bonding to the substrate. As a result, IETS can be regarded as a powerful tool to provide unambiguous information about the adsorbed molecule. For example, the identification of the dehydrogenation product of a benzene molecule on the Cu(110) could be achieved only after an IETS study was performed\textsuperscript{[59]}. It was found that the product is the phenyl (C\textsubscript{6}H\textsubscript{5}) molecule rather than the initially assigned benzyne (C\textsubscript{6}H\textsubscript{4})\textsuperscript{[59]}. It was noted that STM image studies cannot give such identification due to the similar feature of both molecules in the topographic STM images\textsuperscript{[59]}.

### 3.2 STM manipulations

The energy provided by weak inelastic electron excitations is usually small. Therefore, the adsorbed molecule cannot receive enough energy to overcome the barrier which separates it from one configuration to another. As the excitation becomes stronger, inelastic electrons can provide more energy. Correspondingly, the inelastic electron excitation turns into another type.

The scanning tunneling microscope (STM) cannot just be regarded as an imaging tool. In fact, it is such a versatile tool that can be used for many different purposes. For example, STM can be used to manipulate individual atom and molecule on the surface through pulling or pushing mode\textsuperscript{[60]}. However, the most outstanding functions of STM is that it can be employed to provide inelastic elec-
trons and thus stimulate the translation, rotation, tautomerization and chemical reactions through inelastic excitations\cite{61,62}.

We take the adsorbed oxygen molecule on a Pt(111) surface as the first example. Under inelastic excitations, single oxygen molecule can be induced to rotate reversibly among three equivalent orientations\cite{21}. It should be noted that through STM stimulus under higher sample bias, the O-O bond of single adsorbed oxygen molecule can also be ruptured\cite{63}. In fact, not only oxygen but also some other adsorbed molecules could be induced to rotate under STM excitations. Stipe et al. observed the reversible rotation of an individual acetylene molecule on a Cu(100) surface through the coupling between vibrational excitation and rotational motion\cite{64} (Fig. 3.2). The bending of the Cu-Co bond in linear CuCo, molecule on a Cu(111) surface was reported by Stroscio et al.\cite{22}, and recently, Morgenstern et al. reported their work of bending an individual C-Cl chemical bond within single adsorbed chloronitrobenzene molecule\cite{65}.

In addition to induce rotation of a single molecule, inelastic excitation from STM can also provide enough energy to break one individual chemical bond. The single oxygen molecule on the Pt(111) surface\cite{63} is one of such examples. Moreover, Kawai et al. achieved the rupture of a C-H bond within a single \textit{trans}-2-butene molecule on a Pd(110) surface, and changes the molecule to 1,3-2-butadiene\cite{20}. The rupture of the disulfide bond was realized by Maksymovych et al. through the inelastic excitation of a single \textit{CH}_3SS\textit{CH}_3 molecule on a Au(111)
surface\cite{66} (Fig. 3.3). It is interesting to see from this study that the conformation of the parent $CH_3SSCH_3$ molecule can be maintained with a probability as high as 75\% after the disulfide bond is broken\cite{66}. It is worth nothing that with the help of STM the rupture of a chemical bond can also take place on semiconductor surfaces. For example, the C-I bond within a single chlorobenzene molecule on the Si(111)-7x7 surface was ruptured by STM stimulus through a two-electron process\cite{67}, and under inelastic excitations an individual cyclopentene molecule is dissociated into a $C_5H_7$ fragment and a hydrogen atom\cite{68}.

![Figure 3.3](image_url) The dissociation of individual dimethyl disulfide molecule on the Au(111) surface. The conformation can be preserved with a high probability. Reproduced with permission from J. Am. Chem. Soc., ref.\cite{66}, Copyright © 2006 American Chemical Society.

Selective excitation of the molecule adsorbed on the surface is a desirable goal to achieve. With it we could actively control the evolution of the molecule, maximizing the desired results and minimizing the unwanted by-products. In this context, vibrational excitation is one of the most efficient ways. In fact, it has been a mature field to selectively control the molecule in gas phase. However, due to the interaction between the adsorbed molecule and the substrate, the lifetime of vibration excited state within the adsorbate is very short, so it is difficult to achieve the selectivity as in the gas phase. In 2003, Pascual et al. achieved the selective excitation of a single ammonia molecule on the Cu(100) surface\cite{69}. Through the selective excitation of the vibrational freedom within the ammonia, the molecule can be induced to translate on or desorb from the surface\cite{69}. Electronic excitation is also a way to induce selective change of the adsorbates. For example, individual biphenyl molecule, which adsorbs on the Si(100) surface with a weakly chemisorbed configuration, could be induced to diffuse on surface under a negative bias or to change to a strong chemisorbed state under a positive bias\cite{70}. Theoretical calculations show that the difference of the electronic structure between the transient positive and negative charged states is responsible for the different behavior of biphenyl molecule under the two opposite polarities\cite{70}.
Collective excitation of adsorbed molecules becomes an active area of research in recent decades. One of the well-known examples is the collective reaction of a dimethyl disulfide molecule chain under STM stimulus\(^71\). Dimethyl disulfide molecules can form dimer, tetramer, and even longer chains through a self-assemble process\(^71\). When the STM tip is located at one side of the chain, and the inelastic stimulus is exerted, a series of bond breaking and reforming processes will take place, which makes the reaction propagate along the whole chain\(^71\). It is interesting to see that as many as ten molecules could be involved in the propagation of the chain reaction\(^71\).

### 3.3 Molecular electronic switch

Under STM excitations, the adsorbed molecule could change its configuration from one to another. If the two configurations are both stable, and the process of conformational change is reversible, then the adsorbed molecule can be employed as a device, i.e. single molecular switch. The area of molecule device, which is usually called molecule electronic, has been a very active research field with exciting new development. As the continuous miniaturization of the traditional silicon-based electronic devices is close to the limit, alternatives for these traditional devices are highly desired. Molecules, which have a wide variety of properties, could be the suitable choice. It is hoped that in the near future, devices based on single molecules could be manufactured and further commercialized. Molecular switch is one of important electronic components.

The first switch made at an atomic level is the Xenon atomic switch by Eigler et al. in 1991\(^72\). The two conductance states can be switched back and forth, corresponding to a single Xenon atom moving reversibly between the Ni(110) surface and the STM tip\(^72\). Later, considerable efforts were focused on azobenzene molecule and its derivatives. Azobenzene is the molecule in which two phenyl rings are connected by a nitrogen-nitrogen double bond. This molecule has two different isomers: trans- and cis-. In the trans- isomer, the two phenyl rings locate within the same plain, while in the cis- one, there is a dihedral angle between them. One of the most remarkable properties of azobenzene molecule is that the two isomers can be interchanged between each other under external stimulus. In addition to optical\(^73\) and electric field\(^74\) excitations, inelastic excitation with STM can also be employed to induce such isomerization, as has been realized in 2006\(^75\) (Fig. 3.4). The isomerization of one azobenzene’s derivative, Disperse Orange 3, was also achieved\(^76\). Grill et al. investigated the conformational
change of another derivative, meta-TBA molecule, on the Au(111), Cu(111), and Au(100) surface[77]. It was found that the isomerization could take place only on the Au(111) surface, while the excitation was completely suppressed on the other two surfaces, reflecting the substrate dependence of the switching behaviors[77].

![Figure 3.4](image)

Figure 3.4 Conformational change between trans- and cis- isomer of the azobenzene molecule under STM excitations. Reproduced with permission from Phys. Rev. Lett., ref.[75], Copyright © 2006 American Physical Society.

Although the azobenzene molecule and its derivatives have shown good switching performance, the significant structure change during the switching process is not a desirable property for practical applications. Later, another type of molecular switch, which does not involve dramatic structure change, is proposed and realized in experiments. The naphthalocyanine[78] and tin-phthalocyanine[79] molecules are two of the outstanding examples. Under inelastic excitations from STM, the inner two hydrogen atoms could inter-change its positions reversibly within the heterocyclic macrocycle[78]. The two structures before and after the hydrogen transfer correspond to two conductance states, which could make the molecule an ideal two-state switch[78]. It should be noted that from our theoretical calculations on the pathway of involved tautomerization process, an intermediate state is located, which implies that the naphthalocyanine molecule is in fact a four-state switch[80]. In the example of tin-phthalocyanine molecule, the tin ion could be induced to reversibly switch between both sides of the molecular plane, which also corresponds to two conductance states[79] (Fig 3.5). In the case of both molecules, the conductance change only involves the movement of individual atoms, while the whole skeleton structure changes little during the switching process. This is a superior property compared with azobenzene molecule and its derivatives. It is worth noting that the molecular switch based on the adsorbed melamine in our work[23] also belongs to this type of switch.

Recently, Mohn et al. proposed and realized a new type of molecule switch[81]. The two conductance states which could be changed reversibly are originated from a bonded and a nonbonded state between a gold atom and a complex organic
molecule PTCDA\textsuperscript{81}. It should be noted that the bond breaking and making is not induced by direct inelastic excitations, but through the adjustment of Coulomb repulsion between gold atom and PTCDA by electron attachment and detachment at different sample bias\textsuperscript{81}. This mechanism avoids the "over-dosing" problem\textsuperscript{68} in inelastic excitations and could result in the switching event with certainty\textsuperscript{81}. It is interesting to note that the switching process does not accompany dramatic structure change neither. This type of switch represents a new direction in the development of molecular switch and could be the basis for future practical applications.
Chapter 4

Theoretical Studies of Surface Adsorption and Reaction

4.1 Surface model

A surface system can be well described by employing a slab model. In the slab model, several layers of atoms are used to model the properties of the surface system. The adsorbate could be placed on one side (Fig. 4.1 left), or on both sides of the slab (Fig. 4.1 right), which is usually called one-sided or double-sided slab models, respectively. In the one-sided slab model, several top layers of atoms as well as the adsorbate are allowed to relax, while the bottom layers should be kept frozen during the optimization and are used to simulate the corresponding bulk properties. In the double-sided slab model, several layers at both top and bottom as well as the adsorbates on two sides are relaxed, while the left layers in the middle are frozen. One advantage of the one-sided slab model is that it does not require as many atoms as two-sided one, which could reduce the computational cost to some extent. In addition, different from double-side slab model, there is no symmetry constraints that force the adsorbates to behave the same on both sides. As a result, the single-sided slab model is more appropriate than double-sided one in the study of the surface reaction and dynamics. However, the one-sided slab model could lead to a dipole moment due to the charge transfer between the substrate and the adsorbate on one side. The dipole moment not only causes a slower energy convergence in self-consistent calculations, but also introduces an unphysical energy term due to the interaction between one supercell and its virtual copies. These issues can be well solved by adding dipole (and even quadrupole) corrections in calculations\textsuperscript{82,83}. In our works, the one-sided slab...
model is employed to study the adsorption and reaction of adsorbates on surface.

Figure 4.1 The single-sided (left) and double-sided slab model (right) in simulation of surface system. Red, green, and blue denotes adsorbate, surface and bulk layers respectively.

In practice the construction of a slab model can be divided into several steps. First, the unitcell of the corresponding bulk is optimized, and the lattice constant is thus obtained. In fact, the lattice constant can also be found from experimental crystal structures. However, it is recommended to optimize the values in calculations for the sake of consistency. The lattice constant which comes from GGA calculations is usually a little longer than the experimental value, while LDA calculations generally give a smaller value. In the next step, the surface structure with a regular $1\times1$ supercell and a suitable thickness is cleaved along a particular crystal orientation. After that, the $1\times1$ supercell should be symmetrically enlarged parallel to the surface. This is to guarantee that the slab model can reflect the reality of the surface. For example, if one studies adsorption at a single molecule level, and the adsorbed molecule happens to be large, the supercell should be large enough to ensure that the molecule and its virtual copies are far away from each other, as a result the spurious interaction between adsorbate and its mirror images is eliminated; if one wants to perform calculations on self-assembly of molecules on surface, the supercell should be selected to match the periodicity in experiments. Moreover, the supercell should also be separated from its virtual copies along the normal direction of surface to eliminate the spurious interaction between them. This is realized by adding a vacuum layer, and it is usually safe to set the thickness of vacuum to be 10 to 12 Å. When all the above steps are finished, the adsorbates can be put on one side of the surface. After selecting the atoms that should be frozen, the optimization could start.
4.1 Surface model

It is worth noting that caution should be exercised when one sets the thickness of the slab model, i.e. the number of layers. Thicker slab contains more atoms involved in the model, which inevitably increases the computational cost. However, if the slab is too thin, the model is inadequate to describe the real surface system. Fig. 4.2 shows the average atomic displacement within a layer as a function of the slab thickness in the rutile $\text{TiO}_2(110)$ surface. A single-sided slab model with two bottom layers frozen was used to describe the system. One can see that a four-layer slab is enough to give a good description of the surface structure\cite{84}. Convergence of the calculated values should be achieved as the thickness increases, otherwise a good description of surface properties cannot be expected. This issue can be well demonstrated in the example of a single trans-2-butene molecule adsorption on a Pd(110) surface\cite{85}. There are two types of bonding mode between the trans-2-butene molecule and the Pd(110) surface, i.e. the $\pi$ and the di-$\sigma$ bonding mode\cite{85}. In experiments, only the configuration with a $\pi$ bonding mode can be observed at low temperature\cite{86}. However, using a four-layer slab model, the di-$\sigma$ configuration (Sigma-1) is found to be 0.10eV more stable than the one with a $\pi$ bonding mode (Pi-1)\cite{85}, which is an unaccepted discrepancy between calculations and experiments\cite{86}. After increasing the thickness of the slab from four layers to six layers, it was found that the two configurations have almost the same energy\cite{85}. The discrepancy cannot be well resolved until we used an eight-layer slab model. With this mode, the configuration of $\pi$ bonding mode is 0.05eV more stable than the one of di-$\sigma$ bonding mode\cite{85}, which agrees well with the experiments\cite{86}.

![Figure 4.2](image-url) Average atomic displacement within a layer of the rutile $\text{TiO}_2(111)$ surface as the thickness of slab model increases. Reproduced with permission from J. Chem. Phys, ref.\cite{84}. Copyright © 2006 American Institute of Physics.


4.2 STM image simulations

As have been mentioned, scanning tunneling microscope (STM) plays a huge role in the visualization of the surface structure at an atomic level. However, the STM image cannot be simply interpreted from an intuitive understanding of what it is or what is meant, because the contrast of STM image does not directly correspond to the location of atoms, but to the spatial distribution of electronic density of states.

Figure 4.3  (Left) Schematic diagram of structure of the rutile TiO$_2$(110) surface. (Right) STM image of the corresponding surface from the experiments. Reproduced with permission from Dr. X. F. Cui’s PhD thesis ref. [87].

The STM image of the rutile TiO$_2$(110) surface is one of the best examples to illustrate this point of view. The structure of the rutile TiO$_2$(110) surface is shown in Fig. 4.3 left. It can be seen that the two-coordinated bridging oxygen atoms locate higher than the five-coordinated titanium atoms. However, in the STM image (Fig. 4.3 right), the bright strips correspond to five-coordinated titanium atoms instead of the higher bridging oxygen. Another interesting thing to say is about the oxygen vacancy, which is generated by removing a bridging oxygen atom from chain. Although there is no oxygen atom here, its STM image is much brighter than the one of other two-coordinated bridging oxygen. The brightness of both five-coordinated titanium strips and oxygen vacancies can be attributed to an electronic effect. Thus a proper understanding on STM image cannot be obtained unless extra theoretical modeling is employed.

In 1961, Bardeen proposed an approach in the study of electron tunneling between two metals separated by oxide thin layers[88]. This work can be regarded as a milestone of STM image simulations. In Bardeen’s approach, the tip and sample are treated as two isolated systems, and electron tunneling between the two is so weak that it can be dealt with using the perturbation theory[88]. The perturba-
tion approach is consistent with actual situation because in STM experiments the
distance between the tip and substrate is usually large enough to ensure that the
influence of the tip on the adsorbate is negligible. The electron tunneling between
one state of the tip and the other state of the substrate can be well described
using Fermi-golden rule. The expression of the tunneling current involves three
terms: the electron state of tip, the electron state of substrate, and the tunneling
matrix between two sides. Detailed derivation of Bardeen formula can be found
in the review paper of Gottlieb et al.\cite{89}.

From Bardeen’s approach, we can see that after knowing the electron states
of the tip and the substrate as well as the coupling matrix between each other,
the tunneling current and the simulated STM image can be obtained in principle.
However, it seems a little complicated to apply Bardeen’s approach to an actual
system. For example, because it is rather difficult to know the detailed structure
of a STM tip, it is not easy to get the corresponding electron state neither. In
addition, obtaining the tunneling matrix is also not a trivial task. Thus, it would
be much better if the approach could be further simplified. In 1983, Tersoff and
Hamann suggested a simpler approach to simulate the STM image\cite{90,91}. In this
approach, a locally spherical orbital is employed to represent the electron state
of the tip\cite{90,91}. After a series of derivation, the tunneling current is finally found
to be proportional to the density of state of the substrate at the site of STM tip
within an energy interval around the Fermi level\cite{90,91} (Eq. 4.1), i.e., the tunneling
current is only related to the electronic structure of the surface itself.

\[ I \propto \int_{E_p-eV}^{E_p} \rho_s(r_0, E) dE \]  \hspace{1cm} (4.1)

It should be noted that some approximations are employed in the derivation
of Eq. 4.1, i.e. Eq. 4.1 works well only under the condition of low temperature
and low bias voltage. The low temperature makes the Fermi-Dirac equilibrium of
electron be approximated as a Heaviside function, and the low bias voltage makes
it reasonable to use the perturbation theory and to approximate the tunneling
matrix to be constant within the energy interval. The STM image which we in-
tend to simulate comes from experiments at low temperature in order to reduce
the diffusion of the adsorbed molecule, and at low bias voltage thanks to the per-
fected conductivity of metal surface. Therefore, the application of Tersoff-Hamann
approach\cite{90,91} is reasonable in our works, and the excellent agreement between
experiments and simulations supports this point of view.

In experiments, when positive sample bias is applied, the Fermi level of STM
tip locates higher than the sample, as a result, electron tunneling takes place
from the tip to the empty state of the sample, and therefore the unoccupied state of sample is detected. Similarly, when one applies a negative sample bias, the occupied state of the sample is observed. The direction of electron tunneling at different kinds of sample biases is well shown in Fig. 4.4. As a result, the experimental STM image can be well interpreted through the analysis of electronic structure of sample around the Fermi level. The evolution of the intensity of local density of state from the sample with respect to the energy around Fermi level reflects the change of STM image at different sample biases. Thus electronic structure analysis plays an essential role in the interpretation of STM images.

However, the electronic structure analysis, which reflects the distribution of density of state in the energy space, cannot directly produce the simulated STM image. In order to perform such simulations, one should know the distribution of density of state in the position space. Following Eq. 4.1, we integrate the spatially resolved density of state within an energy window which is determined by the sample bias, thus the integrated density of state is obtained. One can simply select a thin layer, which parallels to and locates several Å above the substrate, and then takes out the date of integrated density of state within the thin layer. Changes of the integrated density of state value reflect the information in the constant-height STM image. One can also set a suitable value for the electron density, and investigate the contour of the electron isodensity surface. The up and down of isodensity surface corresponds to the height change of STM tip during scanning in the constant-current mode. Thus such kind of STM image is simulated.
4.3 Reaction pathway

Through inelastic excitations, the configuration of adsorbate can be changed. In general, experiments can show what has happened, *i.e.*, it could give the chemical formula and even the configuration of the adsorbate. However, due to the limitation of temporal resolution associated with STM apparatus, it is difficult to reveal the detailed process of the change, related to the whole pathway from the initial to the final state in STM experiments. Such information of reaction pathway is important and sometimes indispensable in understanding surface processes and related properties. For example, although experiments have shown that naphthalocyanine molecule behaves as a two-state switch\[^{78}\] it is the tautomerization pathway from calculations that reveals the existence of an intermediate state and the corresponding property of four-state switch\[^{80}\], which could affect its performance in practical applications. Therefore, it is desired to provide information about reaction pathway from theoretical calculations.

The description of reaction pathway means to find the transition states associated with the whole process. Usually it is not so difficult to obtain the structures of both initial and final states, especially when the experiments could provide a lot of important information on this issue. However, it is not so easy to explore the structure of transition state, not only because quite little information could be given from experiments, but also because searching transition state often relies on experience and a deep understanding of the reaction mechanisms.

Several methods have been developed to locate transition state, from the simplest and most intuitive way, such as scanning the potential energy surface along a particular bond length or bond angle, to some more complex and mature methods. The efficiency and computational cost are two of the most important factors in the exploration of transition state. Now the climbing image nudged elastic band (c-NEB) method\[^{92}\], which is developed by Henkelman *et al.*, is one of the most popular ways to search the transition state. In our works, this method has been widely used to study the reaction mechanism on the surface. Here some basic principles of this method will be briefly introduced. Information about some other methods can be found in ref.\[^{93}\].

The schematic diagram of the nudged elastic band method is shown in Fig. 4.5. After obtaining the structures of the initial ($r_0$) and final ($r_n$) states, some intermediate states are constructed, intuitively or through the interpolation of the coordinate between the reactant and the product, thus an initial guessed pathway is obtained. The intermediate states will evolve on the potential energy surface
Figure 4.5  Schematic diagram to show the principle of the nudged elastic band method. The initial constructed pathway, two optimization steps during the calculations, and the fully optimized pathway are shown. Reproduced with permission from Proc. Natl. Acad. Sci., ref.\(^{[94]}\), Copyright © 2005 The National Academy of Sciences.

during nudged elastic band calculations, until they locate on a right pathway with minimal energy barrier.

The principles of c-NEB method are well reflected by its name - climbing image nudged elastic band method. In the following part, I will introduce the mechanism of c-NEB method in three aspects, \(i.e.\) the meanings of the elastic band, the nudged, and the climbing image.

In c-NEB calculations, the generated intermediate images are not independent during the optimizations. In fact, these images are connected by the elastic force, as Fig. 4.6 shows. The N (N=4 in Fig. 4.6) intermediate images behave as a series of beads, connect each other through N-1 springs, and are strung to the reactant and the product with another two springs. As a result the intermediate images form an elastic band. The advantage of adding the elastic force is to evenly distribute the images between the reactant and the product. One can image that if the distance between two adjacent images deviates from the average value, the elastic potential energy tends to make this distance return to the average in order to minimize the total energy of the system. Without the spring force the intermediate images could scatter on both sides of the transition state and give no resolution to describe the reaction process. Thus the spring force between adjacent images should be large enough to hold the elastic band. However, the elastic force is not the larger the better, since after all this force is artificially
introduced. The elastic force, holding no physical meaning in reality, will affect the true contour of the potential energy surface, and makes the images deviate from the true transition state. Therefore, choosing an appropriate value for the spring force is important in c-NEB calculations. Fortunately, the default value provided by Henkelman et al. is good enough in most cases, and the solution of the problem associated with artificial spring force is further achieved by a method related to the word “nudged”.

There are two problems which are related to the artificial elastic force: the sliding-down problem and the corner-cutting problem\textsuperscript{[93,94]}. The former is originated from the parallel component of the true force (the derivative of the true potential energy surface with respect to the position)\textsuperscript{[93]}. Because the intermediate images are not local minimum, they tend to move towards the reactant or the product during the optimizations, and thus give a low resolution within the area of transition state, as the right line in Fig. 4.7 shows. The latter comes from the perpendicular component of the elastic force\textsuperscript{[93]}. This part of force tends to make the intermediate images deviate from the true pathway, as a result, the image with the highest energy does not locate on the true transition state. The left line in Fig. 4.7 shows this problem. In order to avoid these two problems, in c-NEB calculations, the force felt by intermediate images only contains the perpendicular component of the true force and the parallel part of the spring force\textsuperscript{[93]}. The former part could relax the band towards the true reaction pathway, while the latter force could hold the elastic band of images, and prevent them from sliding down.
towards the two local minima. The division of the perpendicular and parallel components of the force depends on the choice of tangent direction along the elastic band. The simplest way is to use the normalized line segment between adjacent images. In addition, some more complex methods have also been developed in order to improve the performance of c-NEB calculations\cite{93}.

Figure 4.7 Schematic diagram to show the sliding-down and corner-cutting problem in the elastic band method without nudged. Reproduced with permission from Proc. Natl. Acad. Sci., ref.\cite{94}, Copyright © 2005 The National Academy of Sciences.

It should be noted that some other chain-of-states methods, which are related to the c-NEB method here, employ similar scheme to locate the reaction pathway. For example, the Elber-Karplus formula\cite{95} and the Self-Penalty Walk algorithm\cite{96,97} add artificial interaction among intermediate images, similar as it does in c-NEB method to construct an elastic band; the Locally Updated Planes (LUP) method\cite{98} optimizes each imaged independently along the direction normal to the local tangent, in a similar way as the "nudged" does in c-NEB method, although no elastic band is constructed. Thus one can see that the c-NEB method combines the advantage of above two types of methods.

In the exploration of the reaction pathway, the transition state is of the most importance. In ordinary NEB calculations, it is not guaranteed to locate one of the intermediate images exactly on the transition state, and there is no efficient method to improve the situation except simply increasing the number of images. However, more images would mean more computational cost. This issue is well resolved in the climbing image NEB method\cite{92}. First, the image which holds
the highest energy after a few optimization steps is found. Then its elastic force from adjacent images is fully removed on this image, and the parallel component of the true force, is reversed and added to the image. As a result, the image is made to move uphill along the potential energy surface, and finally locates on the highest point of the potential energy surface, \textit{i.e.} the position of transition state. Fig. 4.8 gives a comparison of results between ordinary and climbing image NEB calculations. One can see that the transition state is well located in the c-NEB but not in the ordinary NEB calculations.

![Energy vs Reaction Coordinate Graph](image)

Figure 4.8  Comparison of results between the ordinary NEB and the climbing image NEB calculations for the dissociation of \(CH_4\) molecule on an Ir(111) surface. Reproduced with permission from J. Chem. Phys., ref.\cite{92}, Copyright \(\copyright\) 2000 American Institute of Physics.

The advantage of the c-NEB method can also be seen in our own calculations. Fig. 4.9 shows the structure of the transition state from both ordinary NEB (Fig. 4.9A) and climbing image NEB (Fig. 4.9B) methods. One can see that the transition state from the ordinary NEB calculations is unreasonable, as the bond length between carbon and hydrogen atoms within the breaking bond is too long (2.50\(\AA\)). It seems that this image has slide down towards the product of the dehydrogenation. However, the bond length of the C-H bond in transition state from the c-NEB method is only 1.59\(\AA\), well within the range of a transition state. The difference between these two results can also be seen from the obtained energy barrier. Energy barrier from the c-NEB method is as high as 1.16eV, a reasonable value for such reaction; while the value from the ordinary NEB method is less than 0.5eV, in accordance with its long bond length of transition state.
Another advantage that should be noted is that only the first derivative of energy with respect to position is needed in NEB calculations. It is in sharp contrast with the all-mode following methods, such as the one developed by Miller et al.\cite{99}. In the all-mode following methods, not only the first but also the second derivative, \textit{i.e.} the Hessian, is needed. It is feasible to calculate the transition state for reaction that involves small molecules with only a few atoms. However, the application of such methods to surface reaction is quite difficult because the computational cost is rather huge that too many atoms are involved in the model. The c-NEB method is thus an appropriate choice to study the process of reaction on surface.

In c-NEB calculations, one thing should concern is the number of the images. If there is only one transition state along the reaction pathway, one to four images are usually enough to obtain the exact location. However, if more than one transition states exist, more images should be used in order to explore all energy barriers. This point of view can be well shown in Fig. 4.10, in which four and eight images were used to explore the rotation pathway of an oxygen molecule on a Pt(111) surface\cite{100}. One can see that only one transition state is located by the four-image c-NEB calculations, while eight images is finally enough for the studies of the rotation pathway. Another important thing one should keep in mind is that the result of reaction pathway from NEB calculations depends on the initial guessed pathway we constructed to a large extent, \textit{i.e.} different initial guess usually results in different final reaction pathway. In our c-NEB calculations of dissociation of \textit{trans}-2-butene\cite{85} and tautomerization of naphthalocyanine\cite{80}, different reaction pathway, the stepwise or the concerted one, could be obtained by constructing different initial guesses for the intermediate images.
4.4 Statistical model

In experiments, the configuration change of adsorbed molecule is reflected by a sudden change of the tunneling current. When the adsorbate changes reversibly between two different configurations, as in the case of molecular switch, the tunneling current changes back and forth between two conductance states. Fig. 4.11 shows the variation of tunneling current over time from two experiments\cite{64,78}.

One can see that the current change is rather irregular, \textit{i.e.} one cannot know how long one current state would last and when the next change would happen.

Through a statistical analysis, one can find that there is an exponential dependence of the conversion rate on the tunneling current. Such dependence, which
is usually called power-law relationship, has been demonstrated in many experiments\cite{20,23,63,67,69,78}. At the same time, much theoretical effort has also been devoted to the interpretation of such a relationship\cite{101-106}. Now it has been widely accepted that the exponent in the exponential relationship corresponds to the number of inelastic electrons needed to induce one structure change, \textit{i.e.} the exponent value $n$ means that $n$-electron process occurs in the convention. However, non-integer exponents were also found\cite{21,23} in a few experiments. According to the traditional interpretation\cite{101-106}, non-integer exponent means the occurrence of a fractional electron tunneling, which is impossible in reality.

From a microscopic point of view, in experiments the electron tunneling is a regular process, which is controlled by the current. However, only a proportion of tunneling electrons can lose and transfer their energies to the adsorbate, behaving as inelastic electrons. One cannot know in advance when the next inelastic process occurs, therefore, the appearance of inelastic electron is an irregular process, and the interval between two successive inelastic processes is not constant but follows a statistical distribution. Therefore, the appearance of inelastic electron is in fact a random process.

![Figure 4.12](image_url)

\textbf{Figure 4.12}  Schematic diagram to show the evolution of adsorbed molecule on the potential energy surface under inelastic excitations. $P$, $\tau$, and $T$ are the three parameters we used in our statistical model. Reproduced with permission from Phys. Chem. Chem. Phys., ref.\cite{107}, copyright \textcopyright 2010 Royal Society of Chemistry.

Under excitations by inelastic electrons, the adsorbed molecule evolves on the potential energy surface. Fig. 4.12 shows such a process. On one hand, the
4.4 Statistical model

Adsorbate could gain energy from inelastic electrons and move towards a higher place on the potential energy surface; on the other hand, the adsorbed molecule could lose its energy because of the interaction with the substrate. The adsorbate could cause phonon and electron-hole pair excitation of the substrate through the energy transfer\(^{103}\). Thus the evolution process of the adsorbed molecule is in fact a competitive process. It should be noted that all the traditional interpretations adopt the same competitive picture\(^{101-106}\), although the non-integer exponent was not explained.

It seems that the inelastic electron excitation cannot be fully described unless the randomness of inelastic electron tunneling is taken into account. Combining the competitive picture with the randomness, a new statistical model is put forward\(^{23,107}\).

In the statistical model, inelastic excitation is treated as an instantaneous event, i.e., the energy transfer between inelastic electron and adsorbed molecule takes place immediately. This process is described in Eq. 4.2:

\[
E_{tot}(t) = E_{tot}(t - \delta \tau) + E_0
\]  

(4.2)

Here \(E_{tot}\) represents the total energy within the adsorbed molecule, \(E_0\) is the incident energy of inelastic electron, and \(\delta \tau\) is an infinitesimal positive, which denotes the moment of inelastic excitation. A parameter \(P\) controls whether an inelastic electron tunneling takes place. \(P\) represents the probability of inelastic excitation, and usually holds a very small value. Monte Carlo simulation is then carried out to determine when inelastic excitation happens.

The energy relaxation within the adsorbed molecule is regarded as a continuous process, in sharp contrast with the inelastic excitation. In the statistical model, this process is assumed to evolve with time in a general way, which is described with a parameter \(\tau\), i.e., the energy within the adsorbate decays exponentially over time. The relaxation process is well described with Eq. 4.3:

\[
E_{tot}(t + \Delta t) = E_{tot}(t) \times \exp(-\Delta t/\tau)
\]  

(4.3)

Here \(\tau\) can be regarded as the lifetime of transition state where the adsorbate locates on the potential energy surface.

Another parameter used in the model is \(T\). It represents the probability that the energy barrier is passed over by adsorbate. The value of \(T\) is mainly determined by the energy within the adsorbed molecule \(E_{tot}\), and determination of \(T\) can be divided into three cases. When \(E_{tot}\) is much larger than the barrier height
The adsorbed molecule could overcome the barrier with certainty, and \( T \) has the value of 1. When \( E_{tot} \) is smaller than \( E_b \), the value of \( T \) could be calculated with a quantum tunneling model, and usually hold a very small value that can be negligible. A slightly more complex case is the one when \( E_{tot} \) is only a little larger than \( E_b \). In this case, the value of \( T \) is smaller than 1 because reflection could occur when the adsorbed molecule is trying to pass over the barrier.

After the randomness of inelastic electron tunneling is considered, the non-integer exponent in the power-law relationship could be well explained. When the adsorbed molecule obtains energy from one inelastic electron, it will wait for some time until the next inelastic electron arrives. During the time, the adsorbate could lose part of its energy due to the energy relaxation. Because the appearance of inelastic electrons is not a regular process, the time interval between two successive tunneling inelastic electrons always changes. As a result, the energy loss during the time interval correspondingly changes. Longer time interval means more energy loss, thus more inelastic electrons are therefore needed to induce the conversion, and vice versa. Therefore, various \( n \)-electron processes will contribute to the inelastic excitation, and the exponent measured by experiments is in fact an average of different contributions. The simulation results based on the statistical model agree with the analysis.

Figure 4.13 shows how the statistical model works. After setting the initial values of the three parameters, Monte Carlo simulation is then performed. During this process, the total number of inelastic electrons \( m \) and the number of various \( n \)-electron event \( t(n) \) are recorded. After performing the simulation for enough long time, the exponent \( N \) can be calculated following Eq. 4.4:

\[
N = m/(\sum_n t(n)) = (\sum_n n \cdot tn)/(\sum_n t(n)) = \sum_n n \cdot c(n)
\]

Here \( c(n) \) represents the proportion of the \( n \)-electron event in all inelastic electron tunneling processes. The exponents under different biases, which correspond to different incident energies of inelastic electrons, are compared with experimental values. The parameters will be adjusted until all the simulated exponents agree well with experiments. From the simulated results one can see that indeed various \( n \)-electron processes contribute to the inelastic excitations, as we have revealed in ref.\([23]\). It should be noted that the final results do not depend on the absolute value of \( P \) and \( \tau \) but their product, i.e. the inelastic excitation depends on a comparison of rate between energy excitation and relaxation. Thus, only two parameters are in fact employed in the statistical model.
4.4 Statistical model

Figure 4.13 Flowchart to show how statistical model runs in the simulations. \( P, \tau, \) and \( T \) are the parameters we used. \( \delta \tau \) is the time interval between successive electron tunneling events. \( E_{\text{tot}} \) is the total energy within the adsorbate. \( E_0 \) is the incident energy of inelastic electrons. \( \{t(n)\} \) is a series of counts for various \( n \)-electron processes. \( i \) and \( m \) are the number of tunneling electrons and inelastic electrons respectively. Reproduced with permission from Phys. Chem. Chem. Phys. ref.\[107\], copyright © 2010 Royal Society of Chemistry.

Randomness is an intrinsic nature of inelastic electron tunneling excitations, and is not related to any experimental method or apparatus. If the excitation from inelastic electrons is the driving force of the molecule device such as the molecular switch, its random property may cause problems in practical applications. In the operation of the molecular switch, one would always expect that the desired change takes place at the right time under inelastic excitations. However, because the inelastic electron tunneling is an irregular process, one cannot know in advance how much time is needed to induce the change. Inelastic electrons is easily overdosed to induce unwanted conversion, for example, the molecular switch could be induced to return to the initial or other undesired states under excitation from excess inelastic electrons, which causes the molecular switch unstable in
operation. Thus some measures should be taken to deal with the problem.

One of the effective methods is the feedback-controlled chemistry (FCC) method\textsuperscript{[68]}. To control the amount of inelastic electrons, a second feedback loop is employed to detect the change of tunneling current. Once the current change related to the desired conversion is detected, the stimulus is terminated immediately. Thus the molecule could maintain the present state until the next stimulation is exerted. Another method is to modify the potential energy surface. Fig. 4.14 shows that the asymmetry of the potential energy surface could be reversed by adding bias with opposite direction. Then it is more easily to access one state than the other. When the desired state is set to be the most stable one in energy, this state could be maintained even overdosing of inelastic electrons occurs for a period of time.
Chapter 5

Summary of papers

5.1 Studies on single-molecule surface process

Scanning tunneling microscope (STM) has been a versatile tool to manipulate the molecules adsorbed on the surface. Under the excitation of inelastic electrons, the adsorbed molecule could rotate\(^{21,64}\), dissociate\(^{63}\), isomerizes to another configuration\(^{75}\) or react with other atoms or molecules nearby\(^{108,109}\), showing a variety of interesting behavior. In most cases, the initial and final states of the adsorbed molecule can be confidently identified from high resolution STM images, especially after comparison with theoretical simulations. However, it is usually non-trivial to explore the detailed dynamic processes of the adsorbed molecule, i.e. the pathway from its initial to the final states. Due to the poor temporal resolution of STM, in experiments it is a challenge to follow every elementary steps of the surface process. Therefore, first principles calculations can come in to provide the necessary interpretations.

In this section, I will give a brief summary of our studies on the surface processes of adsorbed single molecules under STM excitations. This work is divided into two parts: one is about the adsorption and dehydrogenation of \textit{trans}-2-butene molecule on a Pd(110) surface, and the other one is about the dissociation and rotation of oxygen molecule on a Pt(111) surface.

5.1.1 Trans-2-butene molecule on the Pd(110) surface

In 2002, Kawai \textit{et al.} realized a controlled chemical reaction with STM on the Pd(110) surface\(^{20}\). The reactant is a single \textit{trans}-2-butene molecule, and the product was assigned to be a 1,3-butadiene molecule through a comparison of both
 STM image and IET spectra between the product and the corresponding target molecule\cite{20}. A dehydrogenation reaction was considered to occur, but the whole process is unclear. In Paper I, we studied the adsorption and dehydrogenation of a *trans*-2-butene molecule on the Pd(110) surface to explore the whole process under STM excitations.

We first studied the adsorption configurations of *trans*-2-butene (reactant) and 1,3-butadiene (product) molecules on the Pd(110) surface. Through the analysis of adsorption energies as well as simulated STM images, we could conclude that the \(\pi\)-1 configuration (Fig. 5.1 left), in which *trans*-2-butene molecule is perpendicular to the Pd row and bonds to one surface Pd atom, is the configuration of the reactant; while the N-type configuration (Fig. 5.1 right), in which the whole 1,3-butadiene molecule aligns along the Pd row, is the dehydrogenation product.

![Figure 5.1](image)

**Figure 5.1** A *trans*-2-butene molecule with the \(\pi\)-1 configuration is transferred to a 1,3-butadiene molecule with the N-type configuration under STM stimulus. Reproduced with permission from J. Chem. Phys., ref.\cite{85}, copyright © 2009 American Institute of Physics.

Then we performed calculations to understand the dehydrogenation process with the c-NEB method\cite{92}. Since in the whole process there are two C-H bonds that are broken, the stepwise and the concerted pathways were both taken into account. Our results show that the energy barrier is only 0.55eV in stepwise dehydrogenation but up to 1.31eV for the concerted pathway, which means that the step-by-step dehydrogenation is energetically favorable, and the concerted one cannot occur in the experiments.

From our calculations it was found that the *trans*-2-butene molecule should rotate by a certain angle before the occurrence of the dehydrogenation, which seems more interesting. Of course, other questions arise: why rotation should take place and why it could happen. We found that the emerge of a Pd-C-H three-membered ring is essential in the dehydrogenation process. From the charge difference analysis of the transition state, it was found that charge depletion...
appears within the center region of the C-H bond and charge accumulation appears at the center of Pd and C/H atoms, which mean that the C-H bond is weaken while the interaction between Pd and C/H atoms is strengthen to a certain extent. However, according to the analysis of adsorption geometries, the most favorable one, \( \text{i.e.} \) the \( \pi \)-1 configuration, cannot form such a three-membered ring, whereas in the \( \pi \)-2 configuration, the three-membered ring could form, because the C-H bond is very close to surface Pd atom. As a result, the adsorbed \( \text{trans} \)-2-butene molecule should rotate from the \( \pi \)-1 to \( \pi \)-2 configuration in order to make the following dehydrogenation feasibly.

In addition, our results show that such a rotation is also easy to take place. According to the pattern of chemical bonding between alkenes and (110)-oriented surface, there are two possible bonding modes: one is the \( \pi \) bonding mode in which the carbon-carbon double bond interacts with only one surface Pd atom, while the other is the di-\( \sigma \) bonding mode, where two chemical bonds form between carbon and surface Pd atoms. In order to give a detailed analysis for such interaction, we decomposed the adsorption energy into two parts. One part is the deformation energy, which shows the geometric deformation as a result of the interaction between \( \text{trans} \)-2-butene molecule and Pd(110) surface. The other part is the interaction energy, which shows the strength of the interaction between the surface and adsorbates. Calculations have shown that the interaction between the adsorbed molecule and the substrate is very close to each other and the deformation is more or less the same although the orientations of the molecule with respect to the Pd row are quite different from each other. Therefore, because the energy variation is always quite small no matter what the orientation of the adsorbed molecule is, one could expect that the rotation is a nearly barrierless process and is easy to take place under STM excitation.

As the dehydrogenation occurs in a stepwise way, an intermediate state, in which only one C-H bond breaks, exists between the two steps. This intermediate has not been observed in experiments. We calculated the adsorbed structure and simulated the corresponding STM image, hoping that these results could provide some useful information for future experimental investigations.

In summary, we performed calculations on the adsorption and dehydrogenation of \( \text{trans} \)-2-butene molecule on a Pd(110) surface. Our results are in good agreement with experiments\(^{[20]}\), and more importantly, the results could reveal detailed information of the process which has not been observed in experiments. The calculations would also shed light on some dynamics of reaction processes.
5.1.2 Oxygen molecule on the Pt(111) surface

In the pioneering work of Ho et al., the adsorbed oxygen molecule could be induced to dissociate into two oxygen atoms\(^{[63]}\) or to rotate among three equivalent orientations\(^{[21]}\) on a Pt(111) surface under STM excitations. It was found that after the dissociation, the two oxygen atoms could locate on the hcp and fcc hollow site respectively, or both atoms occupy the hcp hollow sites\(^{[63]}\). However, the adsorption energy of the hcp hollow site is found to be about 0.4eV lower than the one of the fcc hollow site\(^{[110]}\). Thus a question arises why the hcp hollow site has the priority to be occupied by oxygen atom under STM stimulations. In the oxygen rotation process, a quite low energy barrier (0.15eV < \(E_{\text{rot}}\) < 0.175eV) was obtained in experiments\(^{[21]}\). Eichler et al. studied this rotation process with a small supercell and found the barrier is 150meV\(^{[111]}\), but the effects of coverage and substrate relaxation were not taken into account. Another question is related to the observation of non-integer exponents in the power law relationship between rotation rate and tunneling current. According to the traditional interpretation\(^{[101-106]}\), the exponent in the relationship corresponds to the number of inelastic electrons needed to induce a rotation. Such kind of non-integer values makes this interpretation difficult in view of the fact that there is no fractional electron tunneling. In paper II we performed theoretical studies on the dissociation and rotation processes of oxygen molecule on a Pt(111) surface with density functional theory calculations as well as a statistical model, in order to answer the above three questions.

We performed systematic calculations to explore the dissociation pathway of oxygen molecule with the c-NEB method\(^{[92]}\). An intermediate state, in which one oxygen atom locates on the hcp hollow site, was found (Fig. 5.2 B). Such intermediate state is inevitable during the dissociation pathway of \(O_2\), and its existence rationalizes the preferential occupation of the metastable hcp hollow site. After the intermediate state, the oxygen atom which has already occupied such hcp hollow site was trapped, while the other one continues to move towards another hcp hollow site through an almost barrierless process. It is the case in which both oxygen atoms occupy the hcp hollow sites after the dissociation. In addition, the movable oxygen atom could travel further towards an fcc hollow site. This behavior could be explained from a "cannon ball" mechanism\(^{[112]}\) (Fig. 5.2 D). The oxygen molecule can absorb energy from inelastic electrons under STM stimulations, and it can also release certain energy during the dissociation process. The energy gained from both excitations and exothermic dissociation could be
Figure 5.2 Structures of the initial (A), intermediate (B), and the final (C) state in the dissociation process of \( \text{O}_2 \) molecule on a Pt(111) surface. (D) Schematic diagram of the cannon ball mechanism. Reproduced with permission from J. Phys. Chem. C, ref.\[100\], copyright © 2011 American Chemical Society.

distributed asymmetrically. Depending on the amount of energy obtained, the movable oxygen atom could move closer or further away from its original position, which therefore results in the occupation of hcp or fcc or even further adsorption sites (Fig. 5.2 D). In a word, the existence of the intermediate state results in the location of one hcp hollow site, and the "cannon ball” mechanism\[112\] makes another atoms occupy hcp or fcc hollow site, depending on the energy distribution.

We also studied the \( \text{O}_2 \) rotation process, and found that it takes places in an effective way. During the process, the two oxygen atoms exchange the adsorption site with each other, i.e. the atom initially at the bridge site locates on a top site after the rotation, while the top one moves to a bridge site. As a result, the two atoms move only a little while the molecule holds intact in the rotation, which results in a low rotation barrier. Through the comparison between our results (with a large supercell) and the Eichler’s\[111\], we found that the coverage does not significantly affect the rotation barrier, in sharp contrast with the situation of \( \text{O}_2 \) dissociation\[113\].

The non-integer exponents were well explained with a statistical model\[107\]. A brief description of the statistical model has been given before. From the simulation results we found that not a particular n-electron process but various n-electron processes contribute to the inelastic electron excitations. As a result, the non-integer exponent comes from a statistical average of various n-electron events.
5.2 Adsorbed single molecule as a switch

The manipulation with STM can be employed to change the configuration of the adsorbed molecule from one to another. In some cases, two different stable structures are adopted and can be reversibly interchanged between each other under STM stimulations. Difference in geometry usually results in distinction of conductance, because the local density of state at the position of STM tip changes. Thus the adsorbed molecule behaves as a switch and can be used as building blocks for the fabrication of further electronic components.

Theoretical studies based on first principles calculations can not only be used to understand the mechanism of molecular switching process, but also be employed to design new molecule device with novel functions. In this section, I will give a brief summary of our theoretical studies on the adsorbate as a molecular switch. This work is divided into three parts. The first one is about the switching of naphthalocyanine molecule induced by a tautomerization process. The second one is about the artificial modification of a single melamine molecule on a Cu(100) surface, as well as the corresponding changes of its transport properties. The last part is about the conductance dependence of the 1,1,2,3,4,5-hexaphenylsilole (HPS) molecule on its adsorption orientations.

5.2.1 Naphthalocyanine molecule

Recently, Liljeroth et al. found that the two inner hydrogen atoms within the cavity of naphthalocyanine molecule can change their relative positions under the stimulus of STM\cite{78}. As a result, naphthalocyanine was realized as a single molecular switch in experiments. It was believed that there are two tautomers that are responsible for the conductance changes. Thus the molecule behaves as an ideal two-state switch\cite{78}. Although the switching phenomenon was firmly established in experiments, the proposed underlying mechanism has not been confirmed. In paper III, we studied the mechanism of the tautomerization in naphthalocyanine molecule as well as its effects on the switching properties.

We performed first-principles calculations on the tautomerization pathway of naphthalocyanine molecule. In experiments, a NaCl(100) bilayer was put between naphthalocyanine and Cu(111) substrate in order to eliminate the electronic coupling between each other\cite{78}. Thus we employed an isolated molecule to model the system. This was justified by experiments that the molecular orbitals directly imaged with STM are not perturbed by the substrate\cite{78}. With c-NEB
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calculations\(^{[92]}\), we locate the pathway of the concerted tautomerization, *i.e.* the two hydrogen atoms transfer synchronously inside the naphthalocyanine molecule. However, it is not the most favorable way from an energetic point of view (the energy barrier is 0.72eV). In fact, a stepwise tautomerization pathway has a lower energy barrier (0.51eV only). In this pathway, the hydrogen atoms change their positions one after another. As a result, an intermediate state, which is 0.33eV higher in energy compared to the initial and final state (Fig. 5.3 left), is located. This state corresponds to the process in which only one hydrogen atom transfers.

![Figure 5.3](image)

Figure 5.3  (Left) The tautomerization pathway of the naphthalocyanine molecule; (Right) Schematic diagram of switching among four conductance states. (i) and (f) represent the initial and final states. (ts1) and (ts2) are the transition states. (t) is the intermediate state. (a) and (b) represent the two energetically equivalent but spatially different reaction paths. Reproduced with permission from Appl. Phys. Lett., ref.\(^{[80]}\), Copyright © 2009 American Institute of Physics.

The existence of the intermediate state will affect the switching performance of naphthalocyanine molecule. As have been mentioned, change of configuration usually corresponds to alteration of conductance, so this intermediate state will contribute to new conductance state. In fact, not only one but two new conductance states are generated. One of the new states has a conductance very close to the low state of the switch, while the other one has a much larger conductance. The naphthalocyanine molecule actually behaves as a four-state instead of a two-state switch (Fig. 5.3 right).

In the experiments, only two conductance states were observed\(^{[78]}\). This fact can also be rationalized from our simulations. It is found that the energy barrier of tautomerization is as high as 0.51eV for the initial and final states, but is
only 0.18eV for the intermediate state. This means that it is much easier to transfer the second hydrogen atom than the first one. As a result, the lifetime of the intermediate state may be too short to be observed by STM, in view of the fact that experiments cannot be carried out in an ultrafast fashion. In fact, by performing Monte Carlo simulations, we obtained the current profile of the naphthalocyanine switch. A two-state molecular switch was eventually shown after taking the temporal resolution into account. In a word, the naphthalocyanine is in fact a four-state molecular switch, but behaves as a two-state switch apparently.

5.2.2 Melamine molecule on the Cu(100) surface

In paper IV, in a joint experimental and theoretical study, we have investigated the structure evolution of a single melamine molecule adsorbed on the Cu(100) surface under STM excitations, and the corresponding effects on the transport properties.

![Experimental topographic STM image (a), adsorbed structure (b-d), and the simulated STM image (e) of single melamine molecule on a Cu(100) surface.](image)

Figure 5.4 Experimental topographic STM image (a), adsorbed structure (b-d), and the simulated STM image (e) of single melamine molecule on a Cu(100) surface. Reproduced with permission from Proc. Natl. Acad. Sci., ref.\textsuperscript{[23]}, Copyright © 2009 The National Academy of Sciences.

Melamine is a kind of organic molecule with a triangular structure (Fig. 5.4 (b)). They can form clusters at low temperature because of the hydrogen bond interaction between them. After the molecules were thermally evaporated on the Cu(100) surface, a symmetric "dumbbell" shape protrusion with mirror symmetry was observed in the topographic STM images\textsuperscript{[23]} (Fig. 5.4 (a)). Our theoretical calculations show that the melamine molecule dehydrogenates first and then stands up on the Cu(100) surface with a vertical configuration (Fig. 5.4 (b)).
(c,d)). The bottom three nitrogen atoms (two of them lost one hydrogen atom each) locate at the bridge site and form chemical bond with the Cu substrate. The simulated STM image agrees very well with the experiments (Fig. 5.4 (e)). The observed "dumbbell" appearance in STM image is originated from the π orbital of the molecule.

After applying a positive high-voltage pulse (+2.3V to +2.8V) to the adsorbed melamine, we found that the STM image appears as an asymmetric "cashew nut" pattern\textsuperscript{[23]} (Fig. 5.5(a)). Besides, the transport behavior of the molecule is changed from a normal conductor to a rectifier\textsuperscript{[23]} (Fig. 5.5(c)). After systematic tests and analysis, it was found that the change corresponds to one hydrogen atom transferring from the top amino to a neighboring nitrogen of the triazine ring (Fig. 5.6). Our calculations confirmed that this configuration indeed has a rectifying property, and this behavior comes from an asymmetric distribution of the local density of state on the two sides of Fermi level. Energy barrier of the tautomerization process is estimated to be 1.90eV (Fig. 5.6), which agrees well with the threshold of pulse bias in the experiments\textsuperscript{[23]}.

Figure 5.5  (a) The asymmetric "cashew nut" STM image of the modified melamine molecule after a pulse (1' and 3'); (b) The reverse of the opening in the "cashew net" image (1") after another pulse, the insert shows the symmetric pattern which comes from fast switching under a higher voltage; (c) the I-V curves of the melamine molecule before and after tautomerization. Reproduced with permission from Proc. Natl. Acad. Sci., ref.\textsuperscript{[23]}, Copyright © 2009 The National Academy of Sciences.

The opening of the "cashew net" image can be reversed under STM excitations\textsuperscript{[23]} (Fig. 5.5 (b)). It is interesting to see that this process is reversible in experiments\textsuperscript{[23]}. When the STM tip is placed above the molecule, the measured current could change between two conductance states back and forth\textsuperscript{[23]}. As a result, the modified melamine could behave as a molecular switch. It should be noted that the functionality of both rectifier and switch can be integrated into a single molecule. Our theoretical calculations show that the reversion of the
"cashew net" opening corresponds to the position change of the top hydrogen atom through a rotation of N-H bond (Fig. 5.6). After one hydrogen atom transfers to the neighbor nitrogen, there are two locations left for the other hydrogen atom. The two positions are not equivalent in energy because the hydrogen atom below exists on only one side. Our calculation shows that the energy of the trans-configuration is 0.28eV lower than the one with a cis- configuration (Fig. 5.6), and this result is also verified from the experiments. For example, two-electron process dominates below the voltage of 0.7eV for one side, while below 0.9eV for the other side, indicating that there is an energy difference of about 0.2eV between the two configurations\textsuperscript{23}. We also studied the pathway of the switching process (Fig. 5.6), and the values of energy barrier agree well with experiments\textsuperscript{23}.

![Figure 5.6](image.png)

Figure 5.6  Reaction pathway of the adsorbed melamine molecule under STM excitations. Simulated STM images are also shown for comparison with the experiments. Reproduced with permission from Proc. Natl. Acad. Sci., ref.\textsuperscript{23}, Copyright © 2009 The National Academy of Sciences.

An exponential relationship exists between the switching rate and the tunneling current, which is called the power-law relationship. In the switching process of the modified melamine molecule, such a relationship was also observed. According to the traditional theoretical interpretation\textsuperscript{101–106}, the exponent here corresponds to the number of inelastic electrons needed to induce a conversion. Thus integer values are always expected. In our experiments, some non-integer exponents were observed\textsuperscript{23}. In order to explain the phenomena, we put forward a statistical model by taking the randomness of inelastic excitations into account.
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In this statistical model, the molecule evolves on the potential energy surface through a competition between energy gaining and losing. On one hand, the modified melamine molecule could gain energy from inelastic electrons. The inelastic excitation is regarded as a random process, and the time interval between successive excitations is therefore not constant but changeable. On the other hand, the molecule could lose energy through a relaxation process. The energy relaxation is treated as a continuous process and the total energy of the molecule decays exponentially. Rotation of the N-H bond can take place when the molecule accumulates enough energy.

The statistical model can indeed reproduce the experimental results in the switching process of modified melamine. The simulated exponents under different biases agree quite well with the experiments. It can be seen that the non-integer exponent does not correspond to one particular n-electron process, but is a statistically averaged value that comes from contributions of various n-electron events (Fig. 5.7). For example, at the external bias of -0.6 V, for one state the inelastic electron tunneling excitation is mainly a mixture of 80% two-electron and 18% three-electron processes, while for another state, it is composed of a combination of 48% two-electron and 40% three-electron processes. Because of the energy relaxation within the interval, the energy value which truly contributes to the barrier overcoming process changes time and again and also has a statistical distribution, which is the reason why various n-electron processes take place.

![Figure 5.7](image.png)

Figure 5.7 Contribution from different n-electron events to the switching process under inelastic excitations under different biases. L and H represent the low and high conductance states. Reproduced with permission from Proc. Natl. Acad. Sci., ref.\(^{23}\), Copyright © 2009 The National Academy of Sciences.

In experiments it can be seen that the exponents are different from each other at the bias voltage with opposite direction but the same absolute value\(^{23}\). From an energetic point of view, one should expect an identical exponent value
because the adsorbed molecule obtains the same amount of energy from inelastic electrons. Our analysis revealed that the direction of the bias voltage is associated with the direction of the electric field, and results in a change of energy barrier. The calculations have shown that the dipole moment of the modified melamine in the transition state is larger than the ones at the initial and final state. As a result, energy barrier will increase when the electric field is parallel with the dipole moment (at negative voltage) and decrease when the two directions are anti-parallel with each other (at positive voltage).

In summary, we performed theoretical calculations to study the adsorption, tautomeration and rotation of melamine molecule on the Cu(100) surface. The effect of this evolution on the transport property was also investigated. Our results agree quite well with experiments. We also put forward a statistical model and successfully explain the non-integer exponent in the power-law relationship between switching rate and tunneling current.

5.2.3 1,1,2,3,4,5-hexaphenylsilole molecule on the Cu(111) surface

On the Cu(111) surface, STM experiments found that the 1,1,2,3,4,5-hexaphenylsilole (HPS) molecule could show two conductance states, and the two states could be switched between each other with the help of STM tip.

Through the analysis of the possible interaction between HPS molecule and Cu(111) surface, we thought that there is only weak interaction between the two parts, which means that the HPS molecule physisorbes on the surface. In addition, the HPS molecule itself cannot undergo an isomerization under STM stimulus because a very high energy barrier, which will be higher than the external bias, is needed for such transition. Besides, there is no such degree of freedom to change its configuration reversibly. Based on the above analysis, we thought that the two conductance states should correspond to two configurations of HPS molecule in weakly bound states. The switching of the two states corresponds to the transition of the two configurations, which takes place through a rotation process rather than an isomerization.

Theoretical calculations confirm our previous analysis. It was found that the two conductance states indeed correspond to two different adsorption configurations: one with the silole ring parallel to the surface, and another having a vertical silole ring (Fig. 5.8). Further calculations on the transport properties of the surface system show that the conductance state is contributed from the molecular
orbitals that spatially bridge between STM tip and substrate. This study shows that the conductance of the adsorbed complex molecule could depend on its orientation.
Chapter 6

Further Outlook

6.1 Dynamic picture of surface processes

A surface process usually corresponds to the evolution of the adsorbed molecule with time, thus direct molecular dynamics (MD) simulation seems to be an appropriate choice. It should be noted that MD simulation is indeed very important and useful in the investigation of surface processes, and has been successfully applied in some studies\[^{115}\]. However, direct MD simulations could suffer from the "rare event problem"\[^{93}\]. In surface processes, especially the one with a high energy barrier, the configuration change that one interests in is usually several orders of magnitude slower than the vibrations of atoms, thus simulation of the corresponding surface process may contain up to as many as $10^{10}$ vibrations\[^{93}\]. As a result, direct MD simulations require rather huge computational cost, which is usually unaffordable in actual calculations even now.

The climbing image nudged elastic band (c-NEB) method\[^{92}\] has been employed to study surface processes. This method is based on the transition state theory (TST), and focuses on the location of the transition state. After knowing the energy barrier, the transition rate could be accurately estimated. The c-NEB method is very useful and effective in surface process studies, however, results from c-NEB simulations could only provide a static or kinetic point of view, and some dynamic effects in the process might be missed. In fact, in one of our unpublished works, this problem has been encountered. In addition, the final result and the obtained reaction pathway from c-NEB calculations depend on the construction of the intermediate images.

The transition state theory could also be used to model surface processes in a long time scale when the traditional trajectory from direct MD simulations is
replaced by a Wigner, Keck, Eyring (WKE) trajectory\cite{116}. The WKE trajectory is constructed in several steps. First, a dividing surface is constructed to separate the initial state from other configurations. This kind of surface corresponds to the region with a low probability to access. It should be noted that knowing the location of the transition state in advance is very useful in the construction of a good dividing surface. A short-time trajectory is then constructed forward to the final state and backward to the initial state. After estimating the lifetime of the initial state, the WKE trajectory is made and can be regarded as an effective trajectory without the vibrational degrees of freedom. It is striking to see that with the employment of the variational principle the WKE trajectory could give the right mechanism of Al adatom diffusion on the Al(100) surface even through the initial guess is wrong\cite{117}.

In the future, I plan to use the approach of WKE trajectory to investigate the surface processes, hoping that this method will provide more detailed information.

### 6.2 Oxygen reduction reaction (ORR)

Great concern for the environment problem such as pollutant and greenhouse gases makes hydrogen a kind of desirable energy source. Proton exchange membrane fuel cells can be used to convert the chemical energy stored in hydrogen to electricity. However, the practical application of proton exchange membrane fuel cells is hindered by the slow rate of the oxygen reduction reaction (ORR) on the cathode electrode, and thus an effective catalysis that can promote this reaction is urgently needed.

Platinum has excellent performance to dissociate oxygen molecule. Now it is widely used as catalysis of the oxygen reduction reaction on the electrode. However, there are several shortcomings that are related to the employment of platinum. For example, the commercialization of the platinum electrode is limited by its high price, and the platinum electrode can be severely "poisoned" by a small amount of carbon dioxide. In addition, the durability of platinum electrode as well as the temperature range in which platinum electrode could work well in practical operation of fuel cells is another two important factors.

Experiments play an important role in finding better catalysis for the oxygen reduction reaction, with better performance, higher stability and lower cost. For example, the $Pt_3Ni(111)$ surface is confirmed to have better activity for the oxygen reduction reaction than pure $Pt(111)$ surface because of its unusual electronic
structure and surface atom arrangement\textsuperscript{[118]}. The "Pt skin" of the core-shell cluster is also shown to have higher activity. In addition, this system can greatly reduce the amount of the expensive platinum element\textsuperscript{[119]}.

From a theoretical point of view, the above systems can be studied through investigating the electronic structure of the surface, as well as the dissociation process of the oxygen molecule on different surfaces. We have had some experiences in these two aspects, therefore, some theoretical calculations could be carried out in the future to search for better material that are appropriate as the cathode electrode catalysis.
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