Study the Morphology of Organic Molecules on Substrate by Analytical Microscopy

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Abstract

In recent years, scientists pay their concentration for investigating the surface structure of different molecules by Scanning Probe Microscopy (SPM). Although a variety of SPM techniques are developed, the Scanning tunneling microscopy (STM) and Atomic Force Microscopy (AFM) are powerful tools for the examination of surfaces to a variety of materials. The atomic level image of the surface can be obtained either by physical experimental setup or using theoretical calculations. In our undergraduate level project work, we use the theoretical concept as the physical STM and AFM instrumental setup takes a long time for imaging the surface structure. Also, it is very expensive and maintenance is complex in our environment. Hückel molecular orbital theory and probe particle model can give almost identical result as the experimental result within a second on a computer.

Organic molecules occur throughout the nature and the synthetic versions of these molecules have enormous applications. Benzene (C_6H_6) and Porphine ($C_{20}H_{14}N_4$) are two useful organic molecules with great interest in the field of science. Both can generate a large number of derivatives which have potential uses in nano technology.

The main focus of this report is to describe how the surfaces of benzene and porphine are arranged. The entire text contains the background and fundamentals of physical STM and AFM setup, the theoretical aspects of imaging process and the STM and AFM images of molecules by experiment and simulation.

Acknowledgements

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On a personal note, I would like to thank my worshipful parents for their sacrifice and support over the years. Their love and encouragement always give me mental support to continue my study smoothly.

Certification of Approval

Title of the Project: Study the Morphology of Organic Molecules on Substrate by Analytical Microscopy.

I approved this project work for submission to the Department of Physics, in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours in Physics at Jashore University of Science and Technology, Jashore-7408, Bangladesh.

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Chapter 1

Introduction

It is very amazing that the number of fundamental elements throughout the nature is very limited, only 118 according to IUPAC [1]. However, the whole universe is consisted of an infinite number of molecules, made up by the composition of these limited number of elements. So, it is very important to analysis the structure of a molecule and use this for the development of science. To achieve the information about the interaction among the atoms and molecules, it is necessary to investigate the electronic properties of the molecule. We can use a scanning probe microscope to image the arrangement of electrons in the atomic or molecular level.

Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) are two major imaging techniques of Scanning Probe Microscopy (SPM) based on the principle of tunneling effect and inter atomic forces respectively. A variety of properties of a molecule can be explored by using STM or AFM experimental tools. But, the experimental setup requires very sensitive environment and also the maintenance cost is very high. A theoretical understanding of physics behind the experimental technique can solve this problem. In our project work, Benzene and Porphine are taken as sample molecules to investigate their surface morphology theoretically.

1.1 Scanning Probe Microscopy (SPM)

Microscopy is the observation and examination of any minute object and the area of the object, which can not be seen with our naked eyes. Microscopy can be divided into three categories, i.e. optical microscopy, electron microscopy and the scanning probe microscopy. Optical or light microscopy involves passing visible lights transmitted through or reflected from any sample through a single lens or multiple lens to allow a magnified view of the sample. In electron microscopy system, a beam of accelerated electrons is used as a source of illumination. It has a higher resolving power than light microscope and can reveal the structure of smaller objects.

Scanning Probe Microscopy (SPM) is the branch of microscopy which forms images of the surface at the atomic level. It uses a physical probe or tip to scan the specimen. A two dimensional image is then formed in false color with different brightness and contrast depending on the electron density and intermolecular bonding. The tip may be in contact or no contact with the specimen to form the image to run a constant interaction mode or constant height mode. The probe tip and sample interaction can also modify the atomic arrangement, called lithography. Scanning Tunneling Microscopy (STM), Scanning Force Microscopy (SFM), Atomic Force Microscopy (AFM), Frictional Force Microscopy (FFM), Magnetic Force Microscopy (MFM) etc are remarkable SPM techniques which have a large contribution in surface science. In spite of rapid progress in SPM as an experimental tool, its theoretical basis has not yet been well established. The Scanning Tunneling Microscopy (STM) and non-contact Atomic Force Microscopy (NC-AFM) do present theoretical understanding of SPM mechanism satisfactory and can image the molecules with good resolution [2].

1.1.1 Scanning Tunneling Microscopy (STM)

In 1961, Giaever developed tunneling spectroscopy for the research purpose in the field of superconductivity [3]. Subsequently, it was extended to surface studies for the investigation of atomic arrangement as Scanning Tunneling Microscopy (STM) by Gerd Binning and Heinrich Rohrer at IBM Zürich in 1981. Its development earned them Noble Prize in Physics in 1986 [4]. The basic principle behind the operation of this instrument is the quantum mechanical tunneling of electrons between a conducting sample and a sharp tip. The electron wave functions in the tip overlap electron wave functions in the sample surface, a finite tunneling conductance is then generated. The current that is produced from this tunneling is used to create a topographical map of the local density of states (LDOS) of the sample surface [5].

For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm (10 pm) depth resolution [6]. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra-high vacuum but also in air, water, and various other liquid or gas ambients, and at temperatures ranging from near zero Kelvin to over 1000 K [5]. It can be operated either in constant current mode or in constant height mode. The first time STM was used to resolve the structure of a surface with the Si(111)-(7×7) reconstruction [7]. With the successful result, scientists start to use STM for investigating numerous surfaces of molecules to understand their properties.

1.1.2 Atomic Force Microscopy (AFM)

The Atomic Force Microscopy (AFM) allows measurement and manipulation of atomic surfaces and was invented by Gerd Binnig, Calvin Quate, and Christoph Gerber in 1986 [8]. Unlike the STM, the AFM does not require a dry, clean and conducting surface, and so can be used to measure insulators or biological samples. The basic modes of operation for the AFM can be divided into two main categories, contact and non-contact. In contact mode, the tip is static, and is pushed in sufficiently close to the surface such that a repulsive force is produced through the Pauli exclusion principle. The tip is then dragged along the surface, and the force mapped. In non-contact mode, the tip is oscillated much further away from the sample, such that the force experienced is van der Waals (vdW) in nature, and hence attractive. Again the force is used to produce the image, although as the vdW force is much weaker than the Pauli repulsion, it is often detected through changes in frequency of the tip.

In manipulation, the forces between the tip and sample can be used to change the properties of the sample in controlled way. Scanning probe lithography and local simulation of cells can be considered as the instance of this atomic manipulation. Simultaneous with the acquisition of topographical images, other properties of the sample can be measured locally and displayed as an image with high resolution. Examples of such properties are mechanical properties like stiffness or adhesion strength and electrical properties such as conductivity or surface potential. Most recently, Prokop Hapala *et al.* [9] utilized fictionalization of the AFM probe to produce simulating images of PTCDA molecules on Ag(111) surface with Xe tip. This same technique can also be used to determine the chemical structure of many molecules with interesting properties.

1.2 Surface Morphology

Surface morphology is a subset of Analytical Imaging, which is an advanced form of high spatial resolution imaging that uses sophisticated microscope to produce images of products, samples and objects that can not be seen with the naked eyes. Such images originate from the exposed surface of the sample or product. There are two main aspects of surface morphology: structure, the crystallography of defect free surfaces, and the micro-structure, the distribution of point and line defects that interrupt that perfect crystallography. At present, STM is a powerful tool for analyzing metallic and semi-conducting surfaces. The most important feature of STM is the real-space visualization of surfaces on atomic level. What is converted into an image in STM is either the spatial variation of tunneling current or the spatial variation of the tip height. The tunneling current decreases exponentially with the increase in the tip-sample distance. In AFM, the spatial variation of the tip-sample repulsive force is converted into an image as the repulsive force is universal. AFM is applicable to conducting as well as insulating materials. AFM enables one to detect the surface morphology by atom-atom interaction.

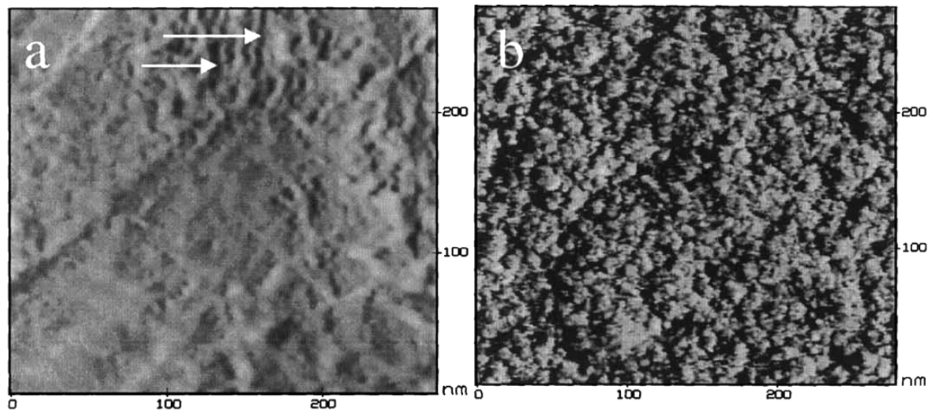


Figure 1.1: STM images of the morphologies of Ni/W alloys in the scanning scale of 270 nm × 270 nm, (a) $Ni_{93}W_7$, (b) $Ni_{80}W_{20}$ [10]

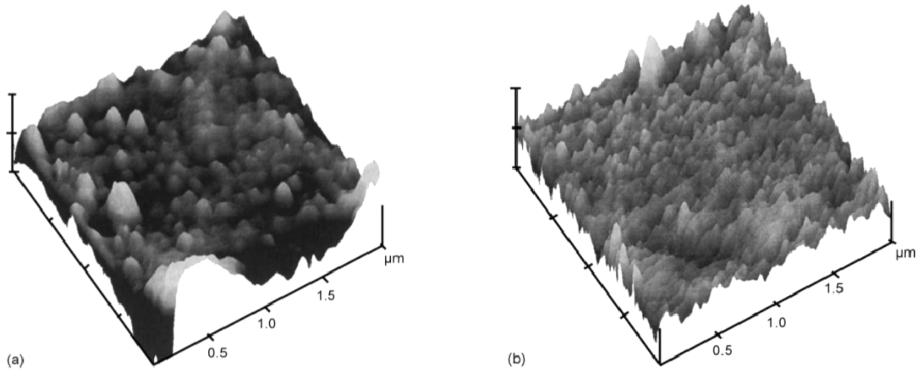


Figure 1.2: AFM 3D-view images of topography of the alloys in the scanning scale of 2μm × 2μm, (a) $Ni_{50}W_{50}$, (b) $Ni_{33}W_{67}$ [10]

When the geometry of a sample is known, we can calculate its electronic density. It is important to determine the electronic density for a number of times to get a good match between the theory and experimental result.

1.3 Benzene and Porphine

Benzene is the simplest organic compound with chemical formula C_6H_6. It is a planer hexagonal ring shaped molecule of six carbon atoms, each of which is bounded to a hydrogen by strong σ -bond. Although there is alternating CC single and double bond in the molecule, two adjacent carbon atoms are of equidistant (1.39 Å) [11]. The three delocalized π orbitals revolve around the six carbon atoms and form the resonance structure [12].This structure contributes to the properties of aromaticity.

Benzene is one of the elementary petrochemicals and a natural constituent of crude oil. It is used in the production of polystyrene and nylon fibers. In refrigerator, air-conditioner, space heater and radio communication device, benzene is broadly used. It is also the parent compound of other aromatic compound. Many important chemical compounds are derived from benzene by replacing one or more of its hydrogen atoms with another functional group.

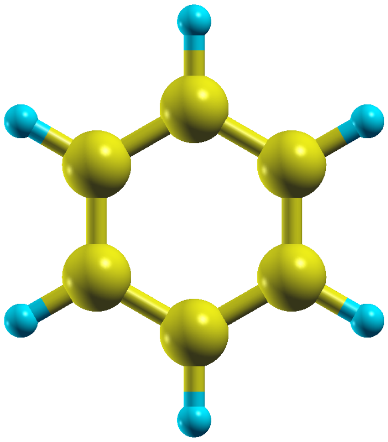


Figure 1.3: Structure of Benzene (C_6H_6) in Ball and stick model.

Porphine is a ring of four pyrrole rings linked by methine groups which chemical formula is $C_{20}H_{14}N_4$. It is an aromatic and heterocyclic planar compound, solid at room temperature [13]. Porphine does not occur in nature, it is the parent structure of a large family of natural compounds called porphyrins, many of which are essential to life.

Porphines have many potential applications including light conversion, autoxidation catalysis, sensors, nonlinear optical materials and light-emitting diodes. In nano-grafting and nano-processing with single electron tunneling, porphine and its derivatives are widely used.

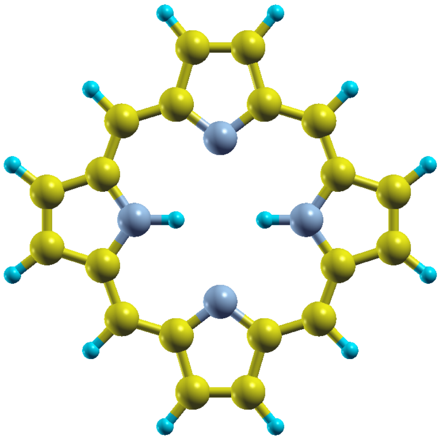


Figure 1.4: Structure of Porphine ($C_{20}H_{14}N_4$) in Ball and stick model.

Both benzene and porphine are parent molecules which are capable of forming a large number of daughter compounds. Since these are planar compounds, it is comparatively easy to investigate the molecular structure. Also, benzene and porphine have huge applications in every field of science. In condensed matter physics, these two compounds along with other molecules can form useful complex compound.

Chapter 2

Experimental Techniques

With the Scanning Probe Microscopy (SPM), a sample is scanned by a probe in order to gather information about the properties of the surface. The fundamental components of SPM includes a scanner, probe (tip), probe motion detector, feedback control system and a computer system. The probe-tip needs to be positioned in high accuracy in relation to the surface and that's why a scanner is made of piezoelectric material. Piezoelectric materials can change their shape by self-adjusting mechanism. When the sample surface is scanned by probe in a two-dimensional pattern, a surface image is produced with atomic scale resolution. Depending on the tip-sample interaction, the image may represent not only the topography but also the electric or magnetic properties of the sample. When the probe scans the surface of the sample, the tip-surface interactions can be sensed with a probe motion detector system which is straightly connected with the probe. This system is usually optical or electrical, and can detect the vertical position of the probe with high accuracy. It produces a signal representing the magnitude of probe-sample interaction. This signal is referred to as detector signal. In the case of atomic force microscope the detector is a laser and a photo diode and in the case of scanning tunneling microscopy it is simply an ampere-meter. In order to detector signal to be meaningful, a feedback control system is used which is connected to a computer system. The feedback loop process is continuously repeated in order for the probe to properly track the surface. In the computer system, a software interface is used to define parameters like x, y, z values for lateral and vertical movement, the number of samples per scan line and the scanning speed. Finally we found the topography of the sample surface on the screen. To achieve the highest resolution, the microscope must be vibrationally isolated from its surroundings [14].

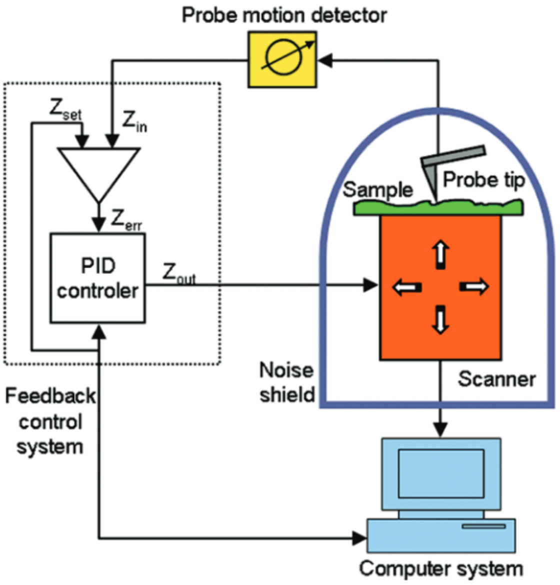


Figure 2.1: Schematic of Scanning Probe Microscopy (SPM) experimental setup and its operation. [14]

2.1 Basics of STM

In the Scanning Tunneling Microscope, the sample is scanned by a very fine metallic tip, which is controlled by a piezo-electric scanner. The sample may be positively or negatively biased so that a small amount of current, i.e. the tunneling current flows between the tip and sample when they are kept at a very close distance of angstrom (Å) scale. This feeble tunneling current is then amplified by the probe motion detector and measured by the ampere-meter. If the tip electrode is very sharp, i.e. ends at one atom, it is possible to detect the current variations between the top of a surface atom (relatively higher electron density of states) and the valley between two surface atoms (lower electron density of states) [14]. The value, z_{in} which is the measured tunneling current, is compared to the preset tunneling current value, z_{set}. The difference, $z_{in} - z_{set}$, is sent to the PID controller and the processed signal, z_{out} moves the scanner up and down responding to the topography by keeping the tunneling current and hence the tip sample distance constant. Operation can also be run by keeping the height constant to form the topography of the sample. The shape of the surface is reproduced by the path of the scanner, which can be inferred directly from the voltage, z_{out} applied to the scanner in terms of lateral (x, y) coordinates.

2.1.1 Working Principle

The quantum mechanical tunneling of electrons between tip and sample surface, is the fundamental principle of STM operation [4]. Although the classical picture restrict the movement of a particle through a barrier, the quantum mechanics describe it by wave function in accordance with the wave-particle duality. When two atoms come sufficiently close to each other, the wave function of the two atoms overlapped and thus an electron can tunnel through the vacuum or other insulating material i.e. the potential barrier. The number of electrons that will actually tunnel is very dependent upon the thickness of the barrier. The wave function of an electron approaching such a potential barrier decays exponentially according to the formula:

$$\psi(z) = \psi(0)\ e^{\pm\kappa z}$$

where $\psi(z)$ is the wavefunction at position z within the barrier, κ is the rate at which the wavefunction decays, which is dependent on the height of the potential barrier. The ± sign in the exponent is chosen such that the wavefunction decays for either positive or negative z.

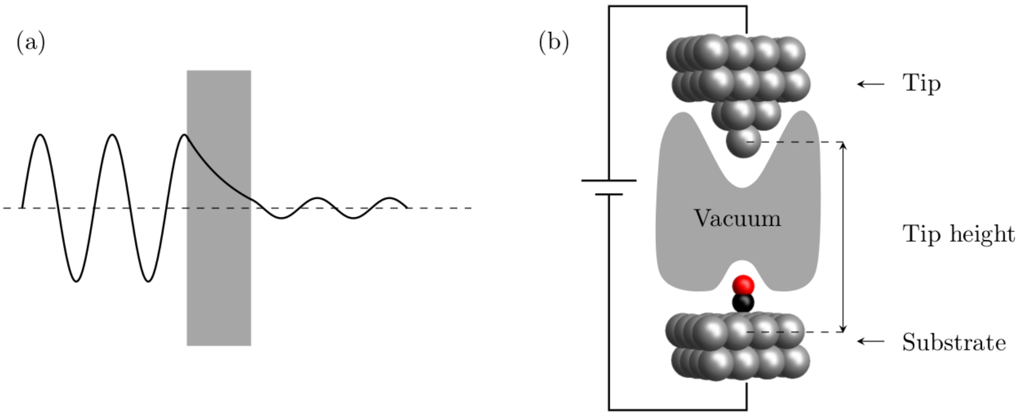


Figure 2.2: (a) Schematic of an exponentially damped wavefunction when passing a potential barrier. (b)Schematic of tunneling effect under applied potential [15].

In case of STM, the potential barrier can be considered as the vacuous region between the tip and sample. This barrier or gap may be of air, vacuum or liquid. By monitoring the current through the gap, we have very good control of the tip-sample distance. When no bias is applied, the height of this barrier is given by the work function associated with the electron. To construct an image, a current needs to be detected by the tip, so it is therefore necessary for a net flow of electrons to occur between the tip and sample. In order for tunneling to occur, the tip needs to be brought sufficiently close to the sample so that the wavefunction has not decayed such that the flow would be too weak to detect. However, even if the tip and sample are close enough for sufficient tunneling to occur, with them both considered at the same energy, the electrons would tunnel equally in both directions, resulting in no net current being observed. It is for this reason a bias is applied to the sample, in order to favour the flow of electrons in one direction or the other, and is why insulating samples can not be imaged through STM. If a negative sample bias is applied, the Fermi level of the sample electrons will be increased, favouring a flow from the sample to the tip. If a positive sample bias is applied, the Fermi level will be decreased, and the net current will be in the opposite direction. The resulting current is a function of tip position, applied voltage and the local density of states of the sample.

2.1.2 Construction

The basic components of STM experimental setup includes metal tip, piezoelectric scanner, current amplifier, bipotentiostat (bias), feedback loop, vibration isolation system and computer [16]. Figure 2.3 shows a schematic of the basic components of STM.

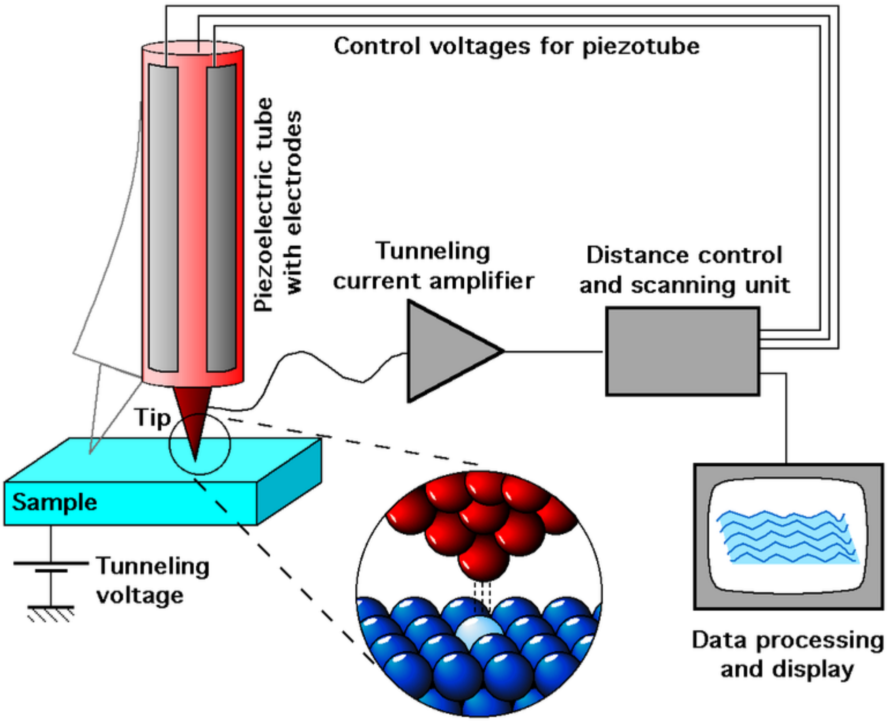


Figure 2.3: Basic components of Scanning Tunneling Microscopy (STM) [17].

The scanning tip generally made of tungsten or platinum [4], tunnel electrons from the sample or vice-versa and it creates tunneling current. The piezoelectric crystals expand and contract very slightly depending on the voltage applied to them and this principle is used to control the horizontal position x, y and the height z of the scanning tip. As the produced tunneling current is too weak, an amplifier is needed to reproduce the signal from tunnel current. Other electronics of the setup record the current and the computer monitor shows a three-dimensional map of the sample surface.

2.1.3 Modes of Operation

There are two basic modes of operation for STM, one is constant current mode and the another is constant height mode [4].

Constant Current Mode: In this mode, the tip is moved across the surface at constant current. To keep the tunnel current constant, the vertical tip position will be continuously changed. The height control mechanism of the piezoelectric tube, adjust the tip to move vertically up and down (along the $z-$ direction of the sample) to maintain constant current through the feedback voltage. Thus, the tip topography the surface of the sample and gives a constant charge density surface image. The entire process is slower but it contains a detail information.

Constant Height Mode: In this mode, the height of the tip is kept constant above the surface of the sample, although the tunneling current being changed during the scanning process. The tip is moved across the sample in XY$-$plane, which causes change in charge density of states. Theses changes are mapped in images. The changing current as a function of surface charge density conveys the information of the substrate. Though it carries lower detail, the tip runs at faster speed than the constant current mode. There is a problem with this mode is that the tip may be destroyed by crashing with the sample in some critical situations.

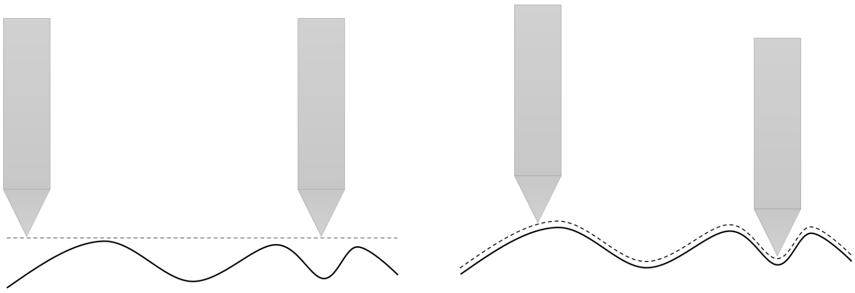


Figure 2.4: Schematic of Constant height mode (left) and Constant current mode (right) for STM.

2.2 Basics of AFM

Since a tunneling current between tip and sample is needed for the STM technique, it can not image the insulating samples. To overcome this limitation with SPM technique, the Atomic Force Microscopy (AFM) idea was introduced which is applicable for both metal and insulating sample. AFM measures the force between the surface and scanning tip to describe the surface topography.

2.2.1 Working Principle

The basic principle of the AFM is the inter atomic attractive and repulsive force between the tip and sample surface at sufficient close separation (pico-meter scale). The long-range attractive van der Waals force and the short-range repulsive forces, such as chemical bonding forces and the Pauli repulsion, contribute to the tip-sample interaction. It is possible to image in both the attractive and repulsive regions in AFM.

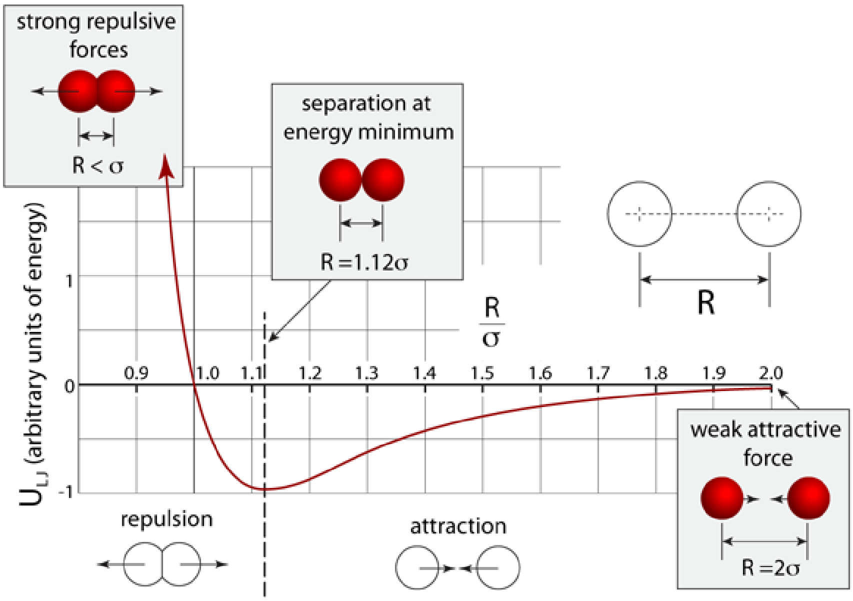


Figure 2.5: Schematic diagram of inter molecular attractive and repulsive forces.

The nature of the force can be understood by Lennard-Jones (LJ) potential, where the attractive-repulsive interaction of two atoms in plotted as a function of distance. It is seen from figure 2.5 that the energy decreases in the attractive region as the distance between two atoms increases. When the atoms are pushed together i.e. the separation decreases, there is an increase in force in repulsive region. At the finite separation, denoted by σ, the energy is zero.

2.2.2 Modes of Operation

According to the nature of the tip position, AFM can be operated either in static mode or in dynamic mode. The static mode includes contact mode and the dynamic mode includes tapping and non-contact mode.

Contact Mode: Contact mode or repulsive mode is the simplest mode of operation for AFM. This mode of operation involves soft physical contact with the sample and the scanner gently traces the tip across the sample surface by the force of repulsion. This mode is associated with some disadvantages which prevents the use of contact mode. It yields very low resolution with large soft samples. As biological substances are very soft and delicate, the vertical and shear forces exerted by the tip can damage the sample. Therefore, contact mode is not ideal for every systems. This lacuna can be overcome by applying tapping and non-contact mode that reduces the shear forces and minimizes the damage to biological samples.

Non-Contact Mode: The Non-Contact AFM (or NC-AFM) operates with increased tip-sample separation without being in contact with the samples under normal imaging conditions. The cantilever oscillates above the sample surface with small amplitude at a frequency larger than its resonance frequency. This results in increased sensitivity in comparison with tapping mode AFM. Outstanding spatial resolution can be achieved by performing NC-AFM in ultra high vacuum.

Tapping Mode: Tapping mode or the intermittent contact AFM is the most preferred operating mode for high-resolution topographic imaging. In this mode, a small piezoelectric crystal makes the cantilever oscillate up and down at or slightly below its resonance frequency. The tip oscillates vertically, alternately contacts the surface and lifts off. Both the amplitude and (or) frequency of the cantilever may vary in the entire scanning process. The oscillating tip lightly touches or taps on the sample surface during scanning. When the tip comes close to the sample surface, forces like van der Waals force, dipole-dipole interactions, electrostatic forces, etc. act on the cantilever and lead to oscillation of the cantilever. Thus, the image is obtained by imaging the force of the oscillating contacts of the cantilever tip with the sample surface.

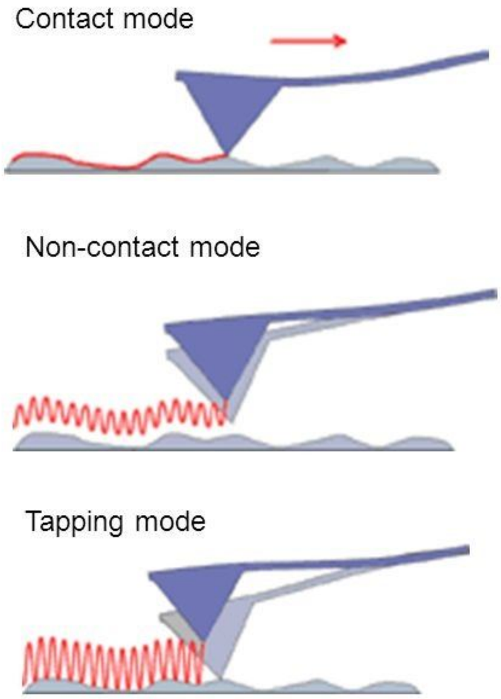


Figure 2.6: Schematic of modes of operation in AFM.

2.2.3 Construction

A general AFM consists of a probe tip attached to a cantilever, piezoelectric scanner, laser diode, position sensitive photodetector, feedback loop and a computer. The atom-atom interaction causes bending to the cantilever and the photodetector measures the deflection of the cantilever.

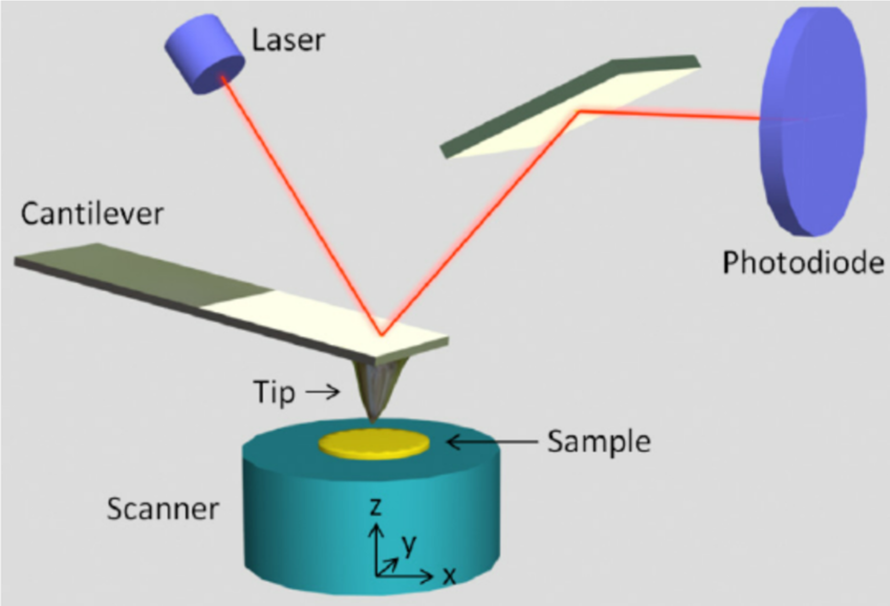


Figure 2.7: Schematic of the basic components of AFM [18].

At present time, the non-contact mode atomic force microscopy (NC-AFM) is very popular. It includes a q-pulse tunning fork sensor instead of cantilever.

The q-Pulse Sensor

A q-Plus sensor is used in many ultra-high vacuum NC-AFMs. The sensor was originally made from a quartz tuning fork from a wristwatch. In contrast to a quartz tuning fork sensor that consists of two coupled tines that oscillate opposed to each other, a q-Plus sensor has only one tine that oscillates. The tuning fork is glued to a mount such that one tine of the tuning fork is immobilized, a tungsten wire, etched to have a sharp apex, is then glued to the free prong. The sensor was invented in 1996 by physicist Franz J. Giessibl [19]. The AFM deflection signal is generated by the piezoelectric effect, and can be read from the two electrodes on the tuning fork. The q-Pulse sensor works on two modes, i.e. the frequency modulation and amplitude modulation.

Frequency Modulation: Frequency modulation atomic force microscopy, introduced by Albrecht, Grütter, Horne and Rugar in 1991, [20] is a mode of NC-AFM where the change in resonant frequency of the sensor is tracked

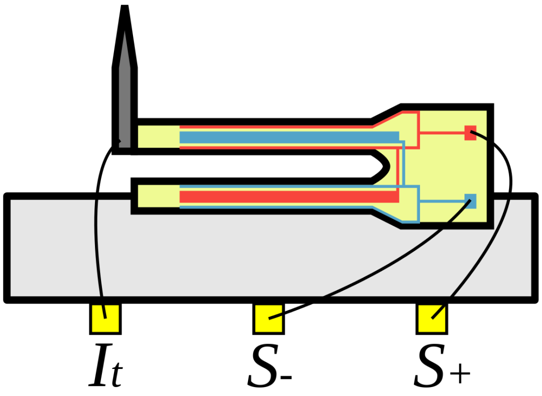


Figure 2.8: Schematic diagram of q-Pulse sensor.

directly, by always exciting the sensor on resonance. To maintain excitation on resonance the electronics must keep a 90° phase difference between the excitation and response of the sensor. This is either done by driving the sensor with the deflection signal phase shifted by 90°, or by using an advanced phase-locked loop which can lock to a specific phase. The microscope can then use the change in resonant frequency (δf) as the SPM reference channel, either in feedback mode or in constant height mode.

Amplitude Modulation: Amplitude modulation was one of the original modes of operation introduced by Binnig and Quate in their seminal 1986 AFM paper, [8] in this mode the sensor is excited just off resonance. By exciting the sensor just above its resonant frequency, it is possible to detect forces which change the resonant frequency by monitoring the amplitude of oscillation. An attractive force on the probe causes a decrease in the sensors resonant frequency, thus the driving frequency is further from resonance and the amplitude decreases, the opposite is true for a repulsive force. The microscopes control electronics can then use amplitude as the SPM reference channel. It can be also recorded either in feedback mode or in constant height mode.

Chapter 3

Theoretical Techniques

Due to some limitations with experimental techniques such as tip/cantilever preparation, scanned surface preparation, noise dumping and data interpretation, the SPM field is developing rapidly and new SPM theoretical techniques are proposed. As the complexity of the experimental SPM techniques are continuously increasing, the theoretical model becomes popular day by day. A number of reliable theoretical models of experiments are established which can provide an understanding of image contrast, and give an interpretation of particular experimental images. Although the sample surface always remains constant, the experimental images and simulated images are quiet different. A little bit change in the environment of STM or AFM may cause a great disorder in the surface structure. The same process has to be operated repeatedly to get the exact result. It is really time consuming and the experiment is too difficult to run properly. To overcome these shortcomings theoretical concept is applied which can produce images with bright spot and clarified network pattern. In this chapter, Hückel Molecular Orbital (HMO) theory for STM imaging [21] and probe particle model, developed by Prokop Hapala for AFM imaging [9] will be explained in details.

3.1 Modeling STM Images

Images obtained from STM are constructed by analyzing the tunneling current observed between the tip and sample. Different methods may be used to model the STM, these will only represent different ways of obtaining the electronic distribution within the system. Bardeen's tunneling theory, Chen's 'Derivative Rule', Hückel molecular orbital theory, extended Hückel molecular orbital theory are applicable to calculate the initial current at specific conditions. Among these theories, HMO theory is extensively used because of its simplicity and most accuracy.

3.1.1 Hückel Molecular Orbital Theory

Hückel theory was formulated by Erich Hückel in 1931 [21]. It has been used extensively in chemistry and physics to investigate the electronic properties of molecules. Hückel theory is primarily used to simulate the wavefunctions of planar molecules, though it can be used with other molecules that meet certain conditions. It is relatively simplistic in its formalism and makes assumptions that limit its scope. However, where it is applicable, it can accurately reproduce experimental results. An advantage it holds over competing techniques such as DFT is that it is many order of magnitudes faster. It is not an iterative procedure and does not need to compute any integrals. The HMO method is a simple but powerful approach toward explaining the stabilities, physical properties, and chemical reactivities of organic $\pi-$systems. The $\sigma-$electronic frameworks of these systems are relatively uninteresting in a theoretical sense since the properties of $\sigma-$bonds do not vary significantly from structure to structure [22].

HMO theory constructs the expressions for the MOs by considering a LCAO associated with each atom. Each of the atoms contributes a single electron to the $\pi-$ bonding network within the molecule, and as such the basis of atomic orbitals used to construct the linear combination is the set of $p-$ orbitals associated with each atom, pointing outwards from the molecule. A

Hückel Hamiltonian can then be constructed that acts on this basis, which incorporates the kinetic and potential energy of the electron on the diagonal elements, and the interaction between adjacent orbitals only, on the off diagonal terms. The matrix element can be represented as following:

$$\mathcal{H}_{ii} = \langle \psi_i | \mathcal{H} | \psi_i \rangle = \alpha$$

$$\mathcal{H}_{ij} = \langle \psi_i | \mathcal{H} | \psi_j \rangle = \beta, \text{ if the atoms are adjacent or 0, otherwise.}$$

The term α is referred to as the Coulomb integral, which represents the total potential and kinetic energy associated with the electron present in the $p-$ orbital of atom i. The β term is the resonance integral and represents the energy of an electron in the region between atoms where the atomic orbitals overlap. For a Hamiltonian of any form, the secular equation is defined as:

$$\mathcal{H}\ \vec{\Psi} = \varepsilon\ \vec{\Psi}$$

Here, ε is the energy, and is found from the eigenvalues of the Hamiltonian, $\mathcal{H}$ which is found from the eigenvectors and $\vec{\Psi}$ is the wavefunction, which can be represented as:

$$\vec{\Psi} = \sum_i c_i\ \psi_i$$

where i sums over all atoms, c_i is the coefficient of the relative proportion of the $\pi-$ orbital in $\vec{\Psi}$. Thus, to obtain the mathematical expressions that represent the MOs, and their relative energies, it is necessary to diagonalize the Hamiltonian to give the eigenvectors as a function of the $\pi-$ orbitals. In HMO theory, the Hamiltonian becomes a square matrix containing elements equal to either α on the diagonal elements or β on the non-zero off diagonal elements. However, to obtain the eigenvalues and eigenvectors it is not necessary to know the values for either α or β. Instead, the secular equation is divided through by β, resulting in a Hamiltonian that has the same unknown on each diagonal element [23].

We apply this HMO theory to calculate the eigenvalues and eigenvectors of benzene's molecular orbital. The first step is to plot the Hückel Hamiltonian in the matrix form as,

$$\mathcal{H} = \begin{bmatrix} \alpha & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha \end{bmatrix}$$

Inserting this in secular equation, we find:

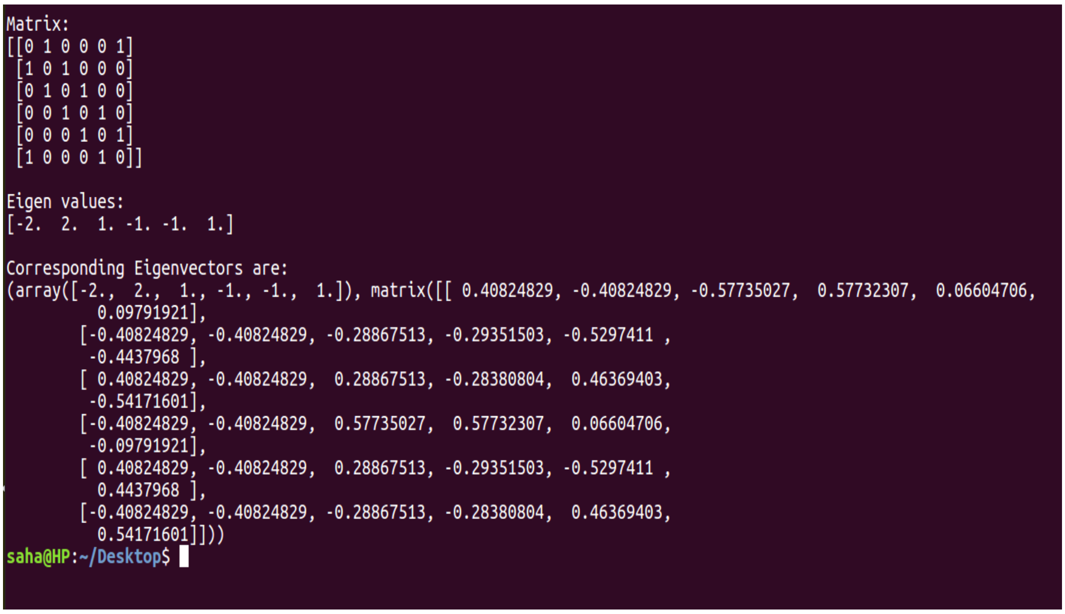
$$\begin{bmatrix} \alpha-\epsilon & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-\epsilon & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-\epsilon & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-\epsilon & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-\epsilon & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-\epsilon \end{bmatrix} \vec{\Psi} = 0$$

Assuming $E' = -\frac{\alpha-\epsilon}{\beta}$ we can rearrange the matrix element as,

$$\begin{bmatrix} -E' & 1 & 0 & 0 & 0 & 1 \\ 1 & -E' & 1 & 0 & 0 & 0 \\ 0 & 1 & -E' & 1 & 0 & 0 \\ 0 & 0 & 1 & -E' & 1 & 0 \\ 0 & 0 & 0 & 1 & -E' & 1 \\ 1 & 0 & 0 & 0 & 1 & -E' \end{bmatrix} \vec{\Psi} = 0$$

$$or, \quad \begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{bmatrix} \vec{\Psi} = E' \; \vec{\Psi}$$

Finally, from this simplified matrix we can calculate corresponding eigenvalues and eigenvectors of benzene's $\pi-$orbital. The eigenvalues indicate both HOMO and LUMO molecular orbitals.



```
Matrix:
[[0 1 0 0 0 1]
 [1 0 1 0 0 0]
 [0 1 0 1 0 0]
 [0 0 1 0 1 0]
 [0 0 0 1 0 1]
 [1 0 0 0 1 0]]

Eigen values:
[-2.  2.  1. -1. -1.  1.]

Corresponding Eigenvectors are:
(array([-2.,  2.,  1., -1., -1.,  1.]), matrix([[ 0.40824829, -0.40824829, -0.57735027,  0.57732307,  0.06604706,
          0.09791921],
        [-0.40824829, -0.40824829, -0.28867513, -0.29351503, -0.5297411 ,
         -0.4437968 ],
        [ 0.40824829, -0.40824829,  0.28867513, -0.28380804,  0.46369403,
         -0.54171601],
        [-0.40824829, -0.40824829,  0.57735027,  0.57732307,  0.06604706,
         -0.09791921],
        [ 0.40824829, -0.40824829,  0.28867513, -0.29351503, -0.5297411 ,
          0.4437968 ],
        [-0.40824829, -0.40824829, -0.28867513, -0.28380804,  0.46369403,
          0.54171601]]))
saha@HP:~/Desktop$ 
```

Figure 3.1: Eigenvalues and eigenvectors of Benzene's molecular orbital.

3.2 Modeling AFM Images

AFM image is formed basically depends on the atom-atom interactions between the tip and sample surface. Hence, we have to calculate the attractive and repulsive forces to obtain the AFM image. Our previously discussed HMO theory can also be applied in case of AFM imaging. But, the probe particle model is more convenient for this imaging process. Probe particle model can measure the Lennard-Jones potential and electrostatic force field over the sample and hence we get the surface structure with a good resolution. This model was proposed by Prokop Hapala in the year of 2014 [9].

3.2.1 Probe Particle Model

The main ingredient of this model is the geometric distortion of the soft apex of a functionalized tip due to the interaction with the surface [24]. The model allows soft apex as the outermost atom of the metal tip (tip base) and the probe particle that decorates it.

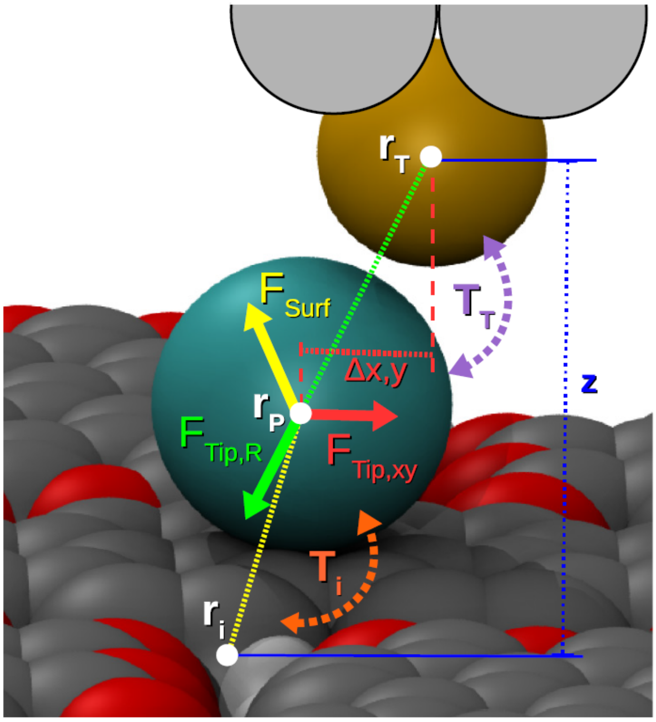


Figure 3.2: Schematic of intermolecular interaction [9].

To account for the interaction between the functionalized tip and a molecular layer (sample) on the surface Hapala *et al.* construct a force-field model of the junction using empirical potentials. In particular, they used a pairwise Lennard-Jones (LJ) potential to describe the weak interaction F_{surf} between the probe particle of the functionalized tip and the sample. F_{surf} is calculated as a sum of all pairwise LJ forces acting between the probe particle and the atoms constituting the molecular layer. Besides F_{surf} the probe particle experiences two additional forces: (i) a radial LJ force $F_{Tip,R}$, between the probe particle and the tip base which keeps the probe particle attached to the tip base at a particular distance and (ii) an additional lateral harmonic force $F_{Tip,xy}$ that stems from the cylindrically symmetric attractive potential of the tip base. Two different sets of LJ parameters, i.e. the binding energy ϵ_α and the equilibrium distance r_α of the $F_{Tip,R}$ interaction are associated with this mechanism. The variations of the image contrast are related with these two parameters. A lateral stiffness is experienced by the surrounded atoms and it is kept constant for all types of probe particles. The expression for Lennard-Jones potential is given by,

$$V_{LJ} = 4\epsilon \; [\frac{\sigma}{r}^{12} - \frac{\sigma}{r}^{6}]$$

Here, σ is the minimum interatomic separation where attractive and repulsive forces are equal and r is any separation between two atoms.

In our project work, we use the code which was implemented by Prokop Hapala in python module to obtain the AFM image of the sample. In his model, the probe was made of CO with multipole such that the charge could not be tilted. The effective charge of the probe particle is 0.5. The stiffness constant for x, y, R components are 0.5, 0.5 and 20.00 in N/m unit respectively. The x, y represent bending stiffness and R represents the particle-tip bond-length stiffness. The bond length is 4.00 $\mathring{A}$. The amplitude of the tip-sample is kept at $1.0\mathring{A}$ [9].

Chapter 4

Supplementary Figures

4.1 STM Images of Benzene

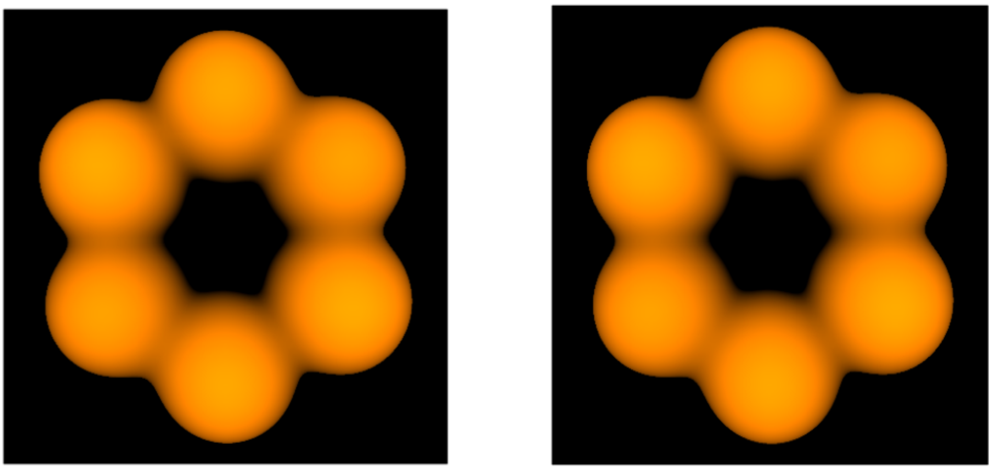


Figure 4.1: STM images of Benzene at different tip position using HMO theory [23].

4.2 STM Images of Porphine

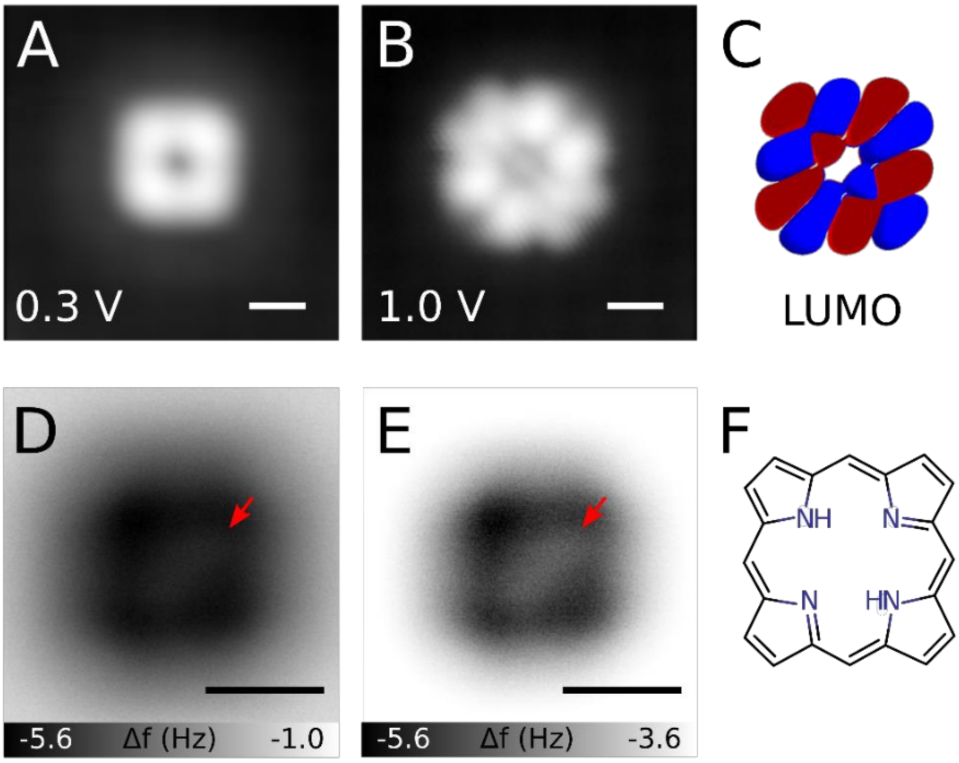


Figure 4.2: STM images of Porphine at different voltages [25].

4.3 AFM Images of Benzene

The structure file (.xyz) of benzene [23] as following is used to generate AFM images using Hapala Probe Particle Model under specific condition as mentioned in chapter 3.

01	C	0.00000	1.40272	0.00000
02	H	0.00000	2.49029	0.00000
03	C	-1.21479	0.70136	0.00000
04	H	-2.15666	1.24515	0.00000
05	C	-1.21479	-0.70136	0.00000
06	H	-2.15666	-1.24515	0.00000
07	C	0.00000	-1.40272	0.00000
08	H	0.00000	-2.49029	0.00000
09	C	1.21479	-0.70136	0.00000
10	H	2.15666	-1.24515	0.00000
11	C	1.21479	0.70136	0.00000
12	H	2.15666	1.24515	0.00000

4.4 AFM Images of Porphin

The structure file (.xyz) of porphine [25] as following is used to generate AFM images using Hapala Probe Particle Model under specific condition as mentioned in chapter 3.

01	N	5.0387	-1.3862	0.0000
02	N	6.5404	-0.0167	0.0000
03	N	3.5352	-0.0167	0.0000
04	N	5.0052	1.3527	0.0000
05	C	5.8406	-1.9873	0.0000
06	C	7.108	0.7852	0.0000
07	C	2.9677	-0.7852	0.0000

08	C	4.2032	1.9873	0.0000
09	C	4.2367	-2.0208	0.0000
10	C	7.1415	-0.7517	0.0000
11	C	2.9677	0.7517	0.0000
12	C	5.8406	2.0208	0.0000
13	C	6.8083	1.7194	0.0000
14	C	3.269	-1.7194	0.0000
15	C	6.8418	-1.7194	0.0000
16	C	3.2356	1.7194	0.0000
17	C	5.5393	-2.9550	0.0000
18	C	8.0773	0.5173	0.0000
19	C	2.0000	-0.5173	0.0000
20	C	4.5046	2.9550	0.0000
21	C	4.5381	-2.9550	0.0000
22	C	8.0773	-0.4838	0.0000
23	C	2.0000	0.4838	0.0000
24	C	5.5058	2.9550	0.0000
25	H	7.2448	2.1597	0.0000
26	H	2.8329	-2.1600	0.0000
27	H	7.2716	-2.1662	0.0000
28	H	2.7971	2.1578	0.0000
29	H	5.9068	-3.4543	0.0000
30	H	8.5707	0.8928	0.0000
31	H	1.5066	-0.8927	0.0000
32	H	4.1371	3.4543	0.0000
33	H	4.1731	-3.4562	0.0000
34	H	8.5724	-0.8571	0.0000
35	H	1.5066	0.8592	0.0000
36	H	5.8626	3.4620	0.0000

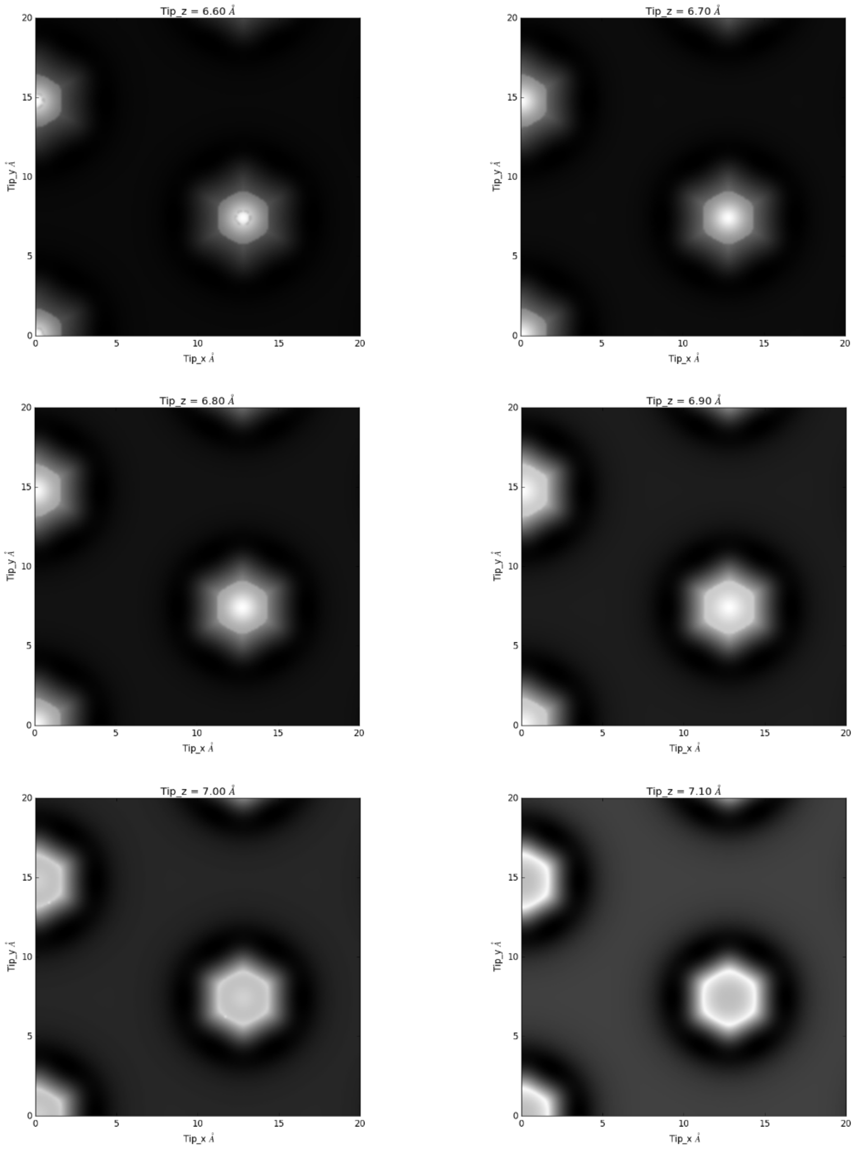


Figure 4.3: AFM images of Benzene at different tip position using probe particle model.

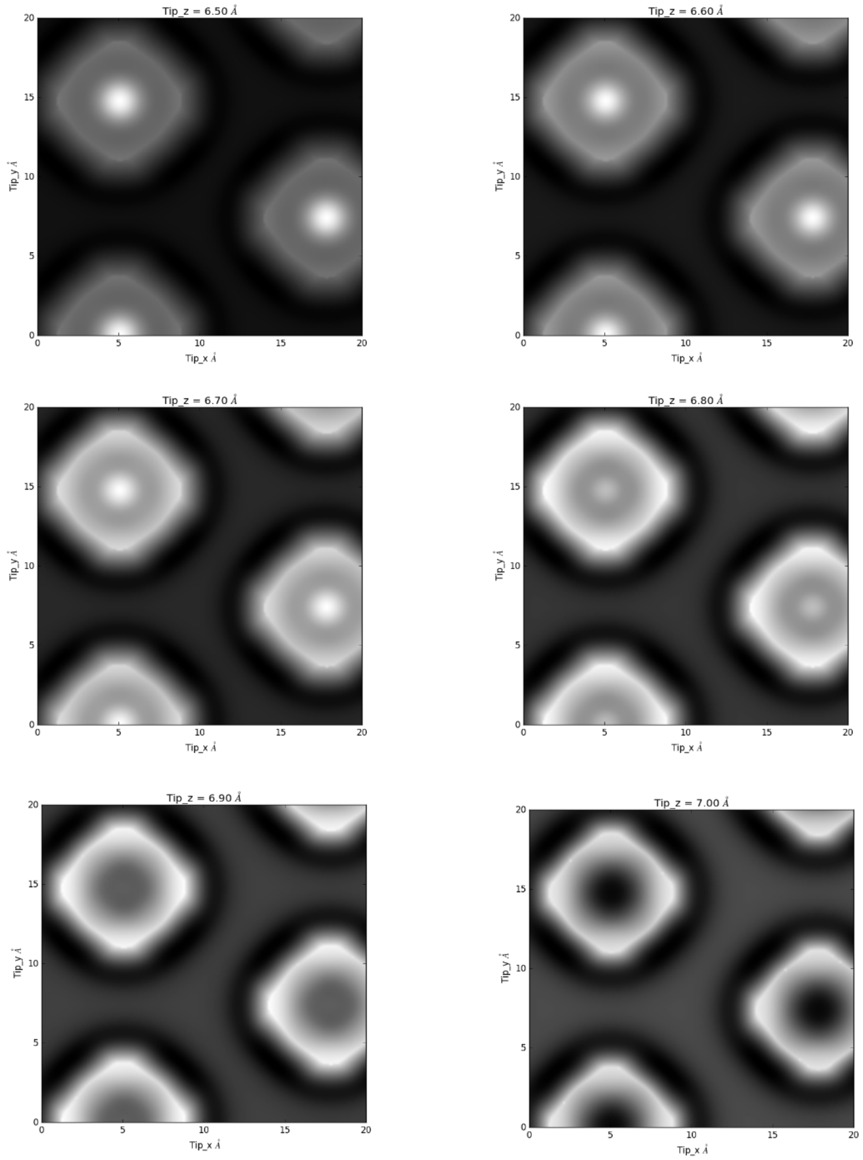


Figure 4.4: AFM images of Porphine at different tip position using probe particle model.

Chapter 5

Discussion and Conclusion

In our project work, we gather information about the experimental and theoretical techniques for STM and AFM. Our main focus has been on imaging benzene and porphine molecules in both STM and AFM according to H*ü*ckel Molecular Orbital theory and Hapala Probe Particle Model respectively. It was really difficult to to image these molecules physically within our short time. By studying the instrumental setup and the physics behind the imaging technique, it becomes possible to complete our work.

The report began with a brief introduction of different scanning techniques, then the experimental setup and different modes of operation has been discussed. In chapter three, the necessary theoretical concept and some calculations related to our work has been described. We have known about the advantages and disadvantages of both experimental and theoretical view and the reason why we choose the theoretical process. In HMO theory for STM imaging necessary calculations were performed in python programming language. Although this same technique could be applied for AFM imaging, because of simplicity we use the probe particle model developed by Prokop Hapala. I also use the code that was written by P. hapala for PTCDA [9] and Graphene molecule. After the modification in structure file for benzene and porphine, AFM simulated images are obtained. The environment and other parameters in this case was predetermined in Hapala's coding. He also wrote his code in python language. In chapter four, the output simulated images and the structure file have been mentioned. It is found that, the AFM imaging technique is more interesting than the STM as the STM is limited only in metals. Researchers are working non stop for the development of both processes. It has a great future which can contribute a lot in the field of modern science.

After completing this project work, I able to learn a lot about the surface science and atomic level imaging process. In future, I wish to extend my work in this field.

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