

Lab Week 1 – Module α_2

Visualizing Electron Wavefunctions in STM

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OBJECTIVES

- ✓ Refresh the concepts of electron wavefunction and tunneling
- ✓ Introduce the concept of scanning tunneling microscopy (STM)
- ✓ Understand the form of the wavefunction of various types of materials
- ✓ Understand the crystallographic and electronic structure of graphite
- ✓ Interpret STM images of materials as a function of their electronic properties

Questions

At the end of this laboratory experience you should be able to answer the following questions:

1. What is tunneling?
2. Why do STM images of materials vary depending on the electronic properties of the material?
3. Why does the STM image of graphite not contain all of the atoms?

INTRODUCTION

This laboratory module is designed to help solidify the concept of an electron wavefunction and to link it to observable materials properties. It is strongly linked to the discussions of wavefunctions and tunneling that you have studied recently in 3.012.

The goal of this laboratory experience is to demonstrate the fundamental role of wavefunctions in determining materials properties. To do so we will image (or attempt to image!) the wavefunctions on the surface of three different classes of materials:

- Gold, a metal (conductor)
- Graphite, a zero band gap semiconductor
- An octylthiol ($\text{CH}_3\text{-(CH}_2\text{)}_7\text{-SH}$) self-assembled monolayer (SAM) (insulator)

We will show that the relationship between the image of the surface obtained by a scanning tunneling microscope (STM) and the real atomic structure of the same surface varies depending on the nature of the electron wavefunction in that material.

An STM image represents the convolution of the wavefunction of the microscope tip with the wavefunction of the material being imaged. We can assume that the wavefunction of the tip is always the same; thus, we will attribute differences between various images to differences in the wavefunctions of the materials at the surface.

BACKGROUND

A few key concepts are needed to understand this laboratory.

Tunneling

Tunneling is a phenomenon that is a direct consequence of the wave nature of particles, and has no classical mechanics counterpart.

In quantum mechanics, tunneling describes that ability of a particle to access regions of space that would not be accessible if the particle were not a wave.

Put more clearly, let us consider a particle with total energy E and a potential barrier of height V , where $V > E$. In classical mechanics, the particle does not have enough energy to surmount this barrier. In quantum mechanics, however, there is a finite probability of finding the particle in or past the barrier. This is a direct consequence of the definition of a wavefunction and the requirement that a wavefunction and its first derivative must be everywhere continuous.

Let's look now at your 3.012 Lecture notes:

Metal Surfaces (I)

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \varphi(x) = E\varphi(x)$$

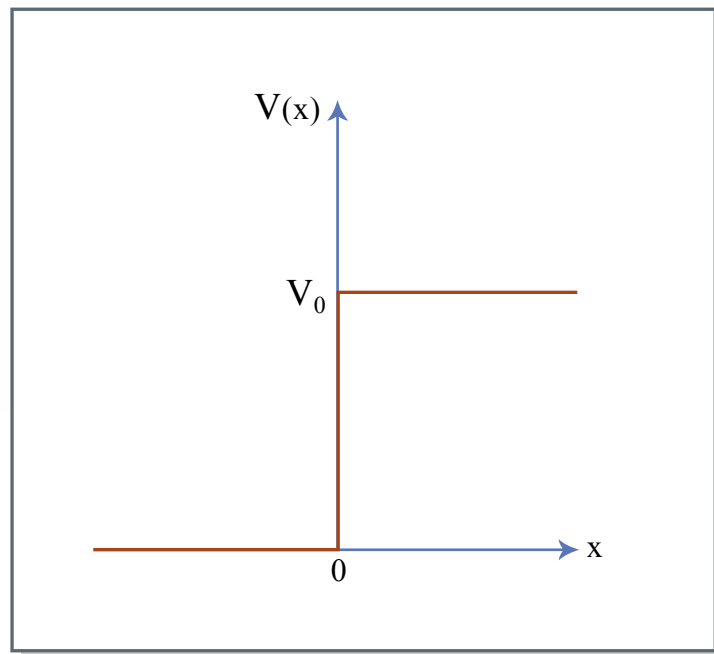


Figure by MIT OCW.

How does the wavefunction of an electron of energy $E < V_0$ look?

Why?

Metal Surfaces (II)

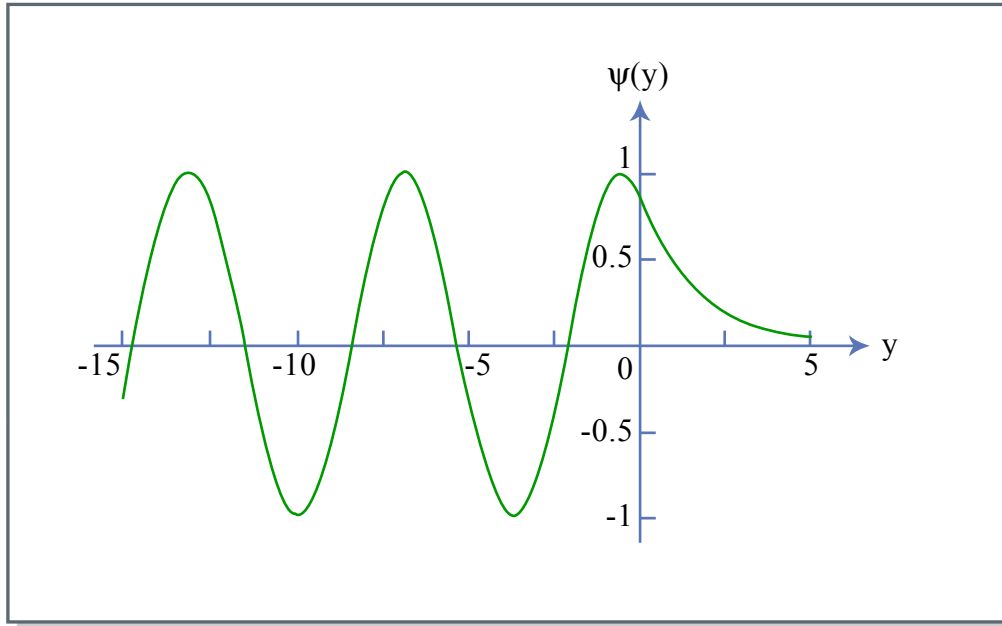
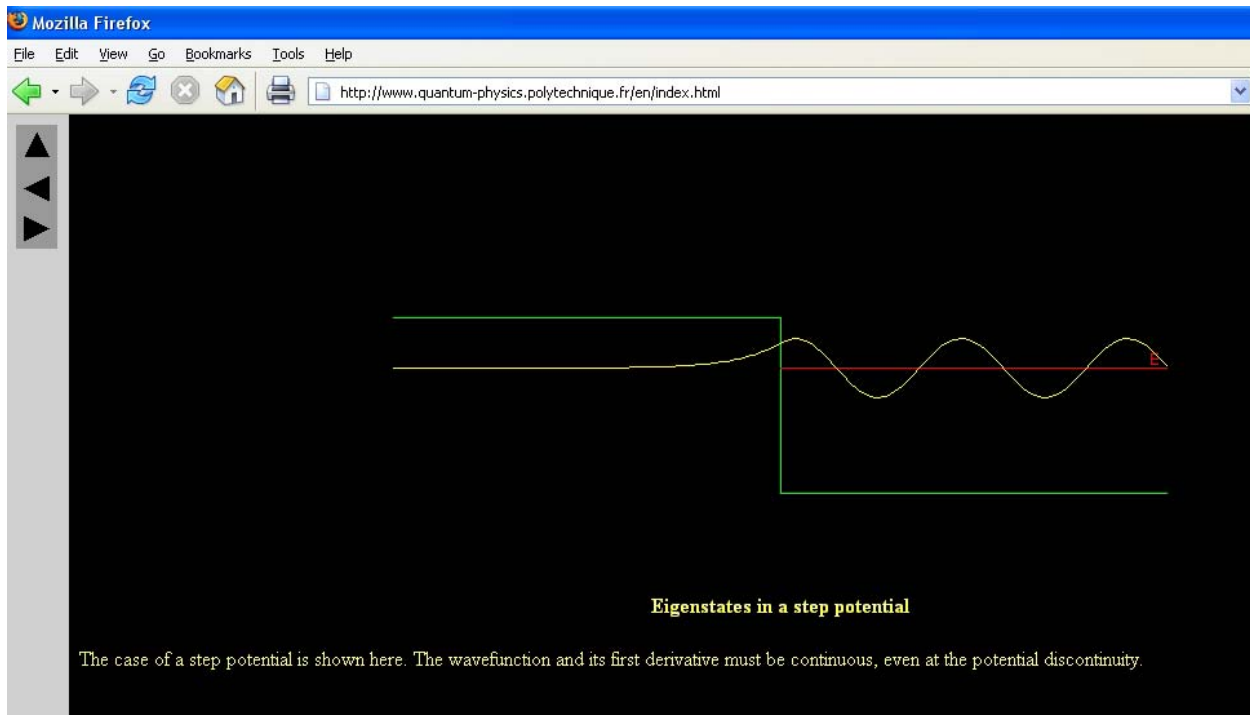


Figure by MIT OCW.

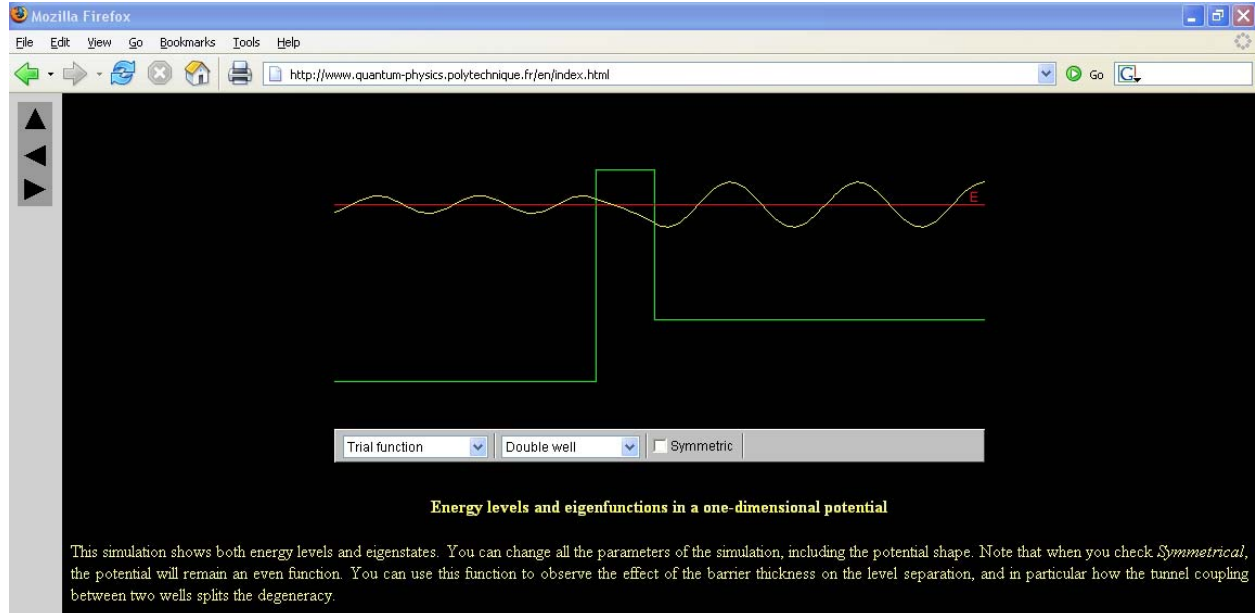
To help us understand tunneling, let us look at an applet that you were asked to use in Problem Set 1:

<http://www.quantum-physics.polytechnique.fr/en/index.html>



What is this telling you?

What happens if we have a barrier of finite thickness rather than a step potential?



Courtesy of Manuel Joffre. Used with permission.

This is tunneling through a barrier.

Tunneling may seem like an abstract concept with no realistic consequences. On the contrary, it has been used to generate one of the most amazing instruments in modern physics, the scanning tunneling microscope (STM).

Scanning Tunneling Microscopy

In STM, electrons tunnel from a metallic tip (typically made of either a Pt/Ir alloy or of W) into a *conductive* sample through an insulating gap (air, liquid, or vacuum). To relate to our schematics above, the insulating gap is the barrier through which the electrons must tunnel to get from tip to sample.

The microscope measures the current that flows between the tip and the sample as the tip scans along the surface, and

1. displays current vs. lateral tip position (constant height mode imaging), or
2. moves the tip up and down to adjust the current to a given current setpoint, and then displays an image of lateral tip position vs. vertical tip height (constant current mode)

From your 3.012 notes we learn:

Scanning Tunnelling Microscopy

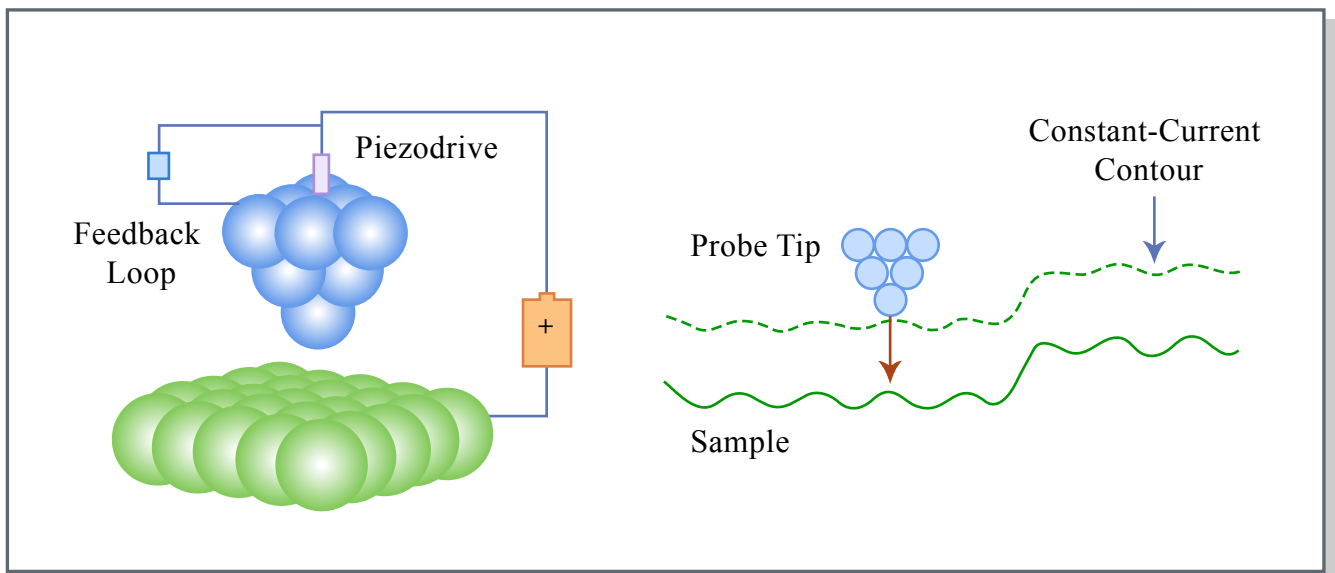


Figure by MIT OCW.

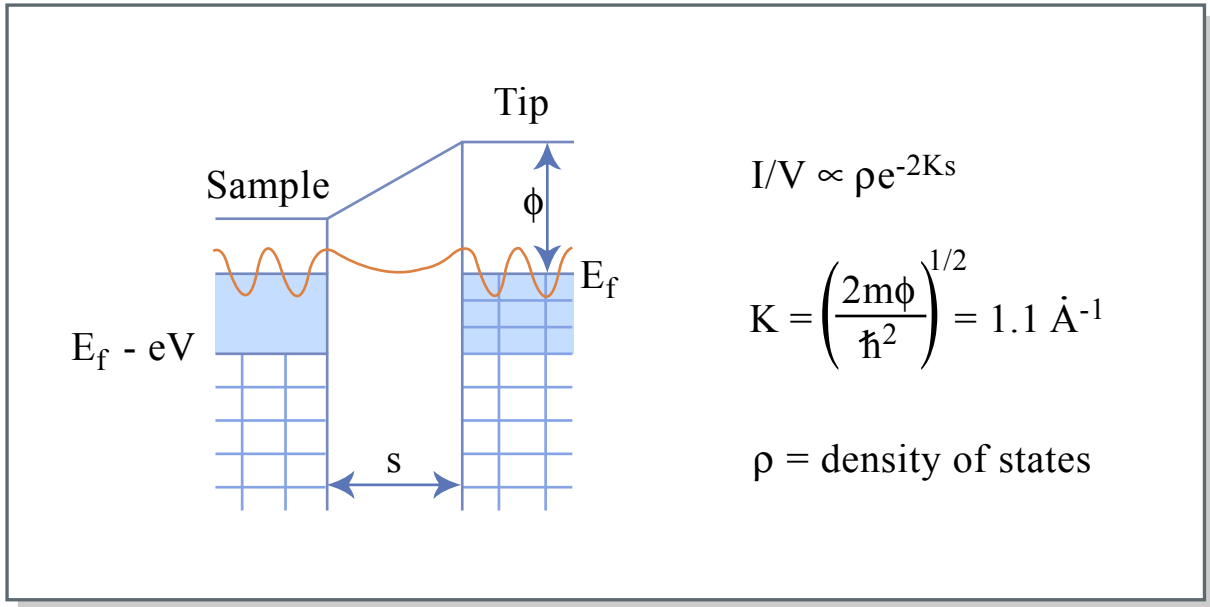


Figure by MIT OCW.

The current measured is proportional to the overlap between the wavefunction of the Fermi level electrons of the tip and that of the electrons in the sample. Why?

Since the wavefunction of the tip is constant, we can interpret our STM image as a map of the wavefunction of the electrons on the surface of the sample.

In this laboratory experience we will image the surfaces of three different materials.

One material is Au (111), a metal. The crystal structure (e.g. atomic positions) of Au is shown below.

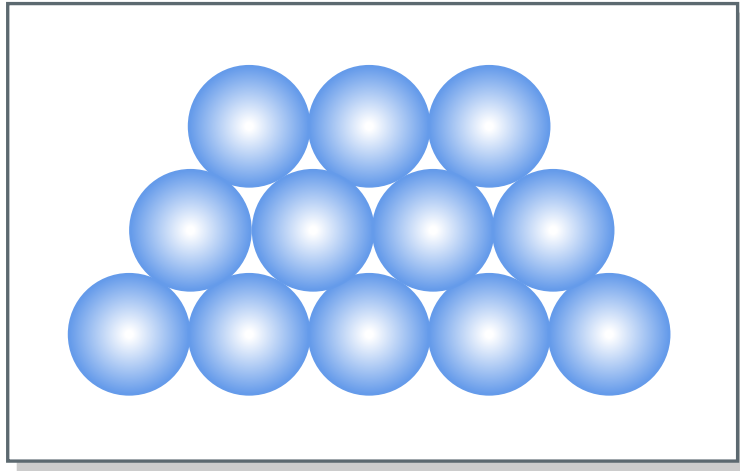


Figure by MIT OCW.

How do you expect the STM image of this surface to look? Recall that electrons in metals are delocalized rather than being associated with one particular atom.

The second material is graphite:

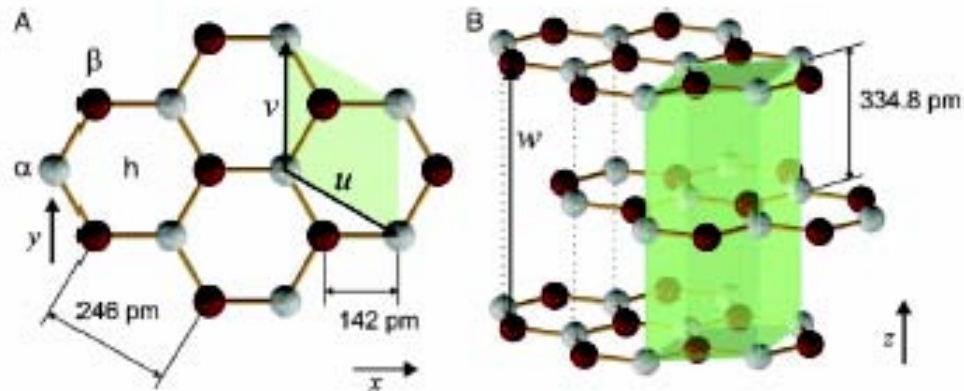


Fig. 1. Crystal structure of graphite. The unit cell is shaded in green. (A) Top view on the surface layer. The hexagonal surface lattice is defined by two unit vectors, α and β , in the xy plane with a length of 246 pm and an angle of 120° forming a honeycomb web of hexagonal rings. The basis of the lattice consists of two carbon atoms α (white) and β (red) with a distance of 142 pm. (B) Perspective view, showing the layered structure. The distance between layers is 2.36 times the next-neighbor distance of atoms within one layer, and the bond between layers is weak. The α atoms (white) are directly above an α atom in the layer directly underneath at a distance of 334.8 pm; the β atoms (red) are over a hollow site (h). The unit vector w is parallel to the z -axis with a length of 669.6 pm.

Courtesy of National Academy of Sciences, U. S. A. Used with permission.

Source: Hembacher, S., F. J. Giessibl, J. Mannhart, and C. F. Quate. Revealing the hidden atom in graphite by low-temperature atomic force microscopy." *PNAS* 100 (2003) 12539–12542.

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Figure from reference 4

How will this material appear in STM?

The third is an octyl-thiol self-assembled monolayer, bonded to the surface in a hexagonally packed arrangement.

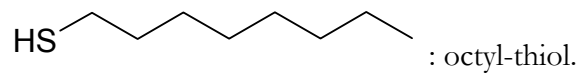


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Schematic representation of alkyl thiol molecules on a gold surface from reference 5.

The SAM behaves as a thin insulating layer. How do you expect this image to look?

Fourier Transforms

Fourier transforms are an important mathematical tool for the analysis of periodic phenomena.

Any function can be represented by a superposition of sine and cosine waves of different amplitudes and frequencies:

$$f(x) = \int_0^{\infty} [A(\omega) \cos \omega x + B(\omega) \sin \omega x] d\omega$$

By performing a Fourier transform on a function, we can represent it as a sum of sinusoidal waves of all possible frequencies. If our function has a periodic component, the Fourier transform will have a strong contribution from the sine (or cosine) wave at that periodic frequency (i.e., its amplitude will be large) and the amplitude at all other frequencies will be small.

Consider that our STM images are essentially functions on which we can perform a Fourier transform. What can this operation tell us about the surfaces we will study?

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