A New Theoretical Model for Inelastic Tunneling in Realistic Systems
Comparing STM Simulations with Experiments
Dit proefschrift is goedgekeurd door de promotor:

prof.dr.ir. R.A.J. Janssen

Copromotoren:
dr.ir. C.F.J. Flipse
en
dr. J.I. Cerdá

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**Glossary**

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<td>AO</td>
<td>Atomic orbital</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
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<td>DOS</td>
<td>Density of states</td>
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<td>(HR)EELS</td>
<td>(High resolution) electron energy loss spectroscopy</td>
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<tr>
<td>FT</td>
<td>Fourier transform</td>
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<tr>
<td>GGA</td>
<td>General gradient approximation</td>
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<tr>
<td>IETS</td>
<td>Inelastic electron tunneling spectroscopy</td>
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<td>LDA</td>
<td>Local density approximation</td>
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<td>LEED</td>
<td>Low energy electron diffraction</td>
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<td>LOIT</td>
<td>Lowest order in inelastic tunneling</td>
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<td>MP</td>
<td>Monkhorst-Pack</td>
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<td>MTJ</td>
<td>Molecular transport junction</td>
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<td>NEGF</td>
<td>Non equilibrium’s Green’s functions formalism</td>
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<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<td>PES</td>
<td>Photoemission spectroscopy</td>
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<td>PL</td>
<td>Principal layer</td>
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<td>SCBA</td>
<td>Self-consistent Born approximation</td>
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<td>SERS</td>
<td>Surface enhanced Raman spectroscopy</td>
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<td>SK</td>
<td>Slater-Koster</td>
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<td>STM</td>
<td>Scanning tunneling microscopy</td>
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<tr>
<td>STS</td>
<td>Scanning tunneling spectroscopy</td>
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<td>TP</td>
<td>Thiophenol</td>
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<tr>
<td>UHV</td>
<td>Ultrahigh vacuum</td>
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<td>vdW</td>
<td>Van-der-Waals</td>
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<tr>
<td>WBL</td>
<td>Wide band limit</td>
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<tr>
<td>(AR)XPS</td>
<td>(Angular resolved) X-ray photoemission spectroscopy</td>
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Chapter 1 – Introduction

Whether we call it vibration, shaking, trembling, quivering or oscillation, we all have our own imagination what a vibration is. It could be that shaky motion when you are cold, a regular periodic variation in value about a mean or that distinctive emotional feeling that you experience instinctively when your favorite music gives you a good *vibe*. We have all seen vibrations in action. But what about unseen vibrations? Vibrations so tiny that we cannot see them with the naked eye, or with the best optical microscopes? Vibrating molecules? What do we know about them? Most people picture a vibrating molecule as a few marbles – atoms – connected with elastic ropes, where the marbles can have any arbitrary amplitude. Because we are operating in the quantum world however, all excitations are quantized as well, resulting in a minimum energy required for a vibration to exist. Can we induce a vibration of a molecule by shaking it at its resonance frequency? In the classical sense: no. A typical molecular vibrational frequency is 10 THz, too fast for any macroscopic object to vibrate. However, in a quantum mechanical sense: yes! As long as a (quasi-)particle, be it a photon, a phonon or an electron, has enough energy and some selection rules are obeyed, it can excite a molecular vibration. This thesis covers the exciting subject of electrons inducing molecular vibrations on the nanoscale, or in other words, the subject of inelastic electron tunneling spectroscopy, IETS in short.

Why investigating IETS? The most immediate application is molecular recognition. Since each molecule has its own unique set of vibrations, they can be easily identified by measuring this set. Molecular recognition is of extreme importance in the human body. Why does sugar taste sweet? How does a white blood cell know which molecules to target? And why do rotten eggs smell that bad?! The human body has several mechanisms to distinguish between molecules, and vibrational recognition might be one of them. The sense of smell is so far not fully understood. While most people claim that the *shape* of the molecule is probed by proteins in the nose, some people claim that it might actually be the set of *vibrations* of the molecule that is measured inside our nose. To date, there is still no consensus about the actual mechanism.

This Chapter introduces the reader to this debate. The pros and cons of both methods are explained in Section 1.1 with examples of performed experiments. Section 1.2 introduces the concepts of IETS and discusses how this could explain how the nose could detect vibrations of molecules. To indicate a possible route for further research, Section 1.3 presents a roadmap of future experiments and theory to settle this debate. Finally, Section 1.4 makes clear where in this roadmap the work in this thesis can be placed and outlines the structure of the thesis. It should be noted that the application of IETS to the mechanism of smell serves here solely as an example. The connection between the theory to describe IETS and the mechanism of smell will not be made throughout the rest of the thesis. This introductory Chapter can therefore be omitted by the reader who is only interested in the IETS theory and not in a possible application.
1.1 Smell: shape or vibration?

Although Linda Buck and Richard Axel won the Nobel Prize in Physiology or Medicine in 2004 for cloning and identifying the olfactory receptors, the physical mechanism of smell is still not fully understood. There are two distinct theories explaining how certain molecules have their characteristic odors. One of them is called the odotope theory, which states that the receptors have a particular shape which would allow a particular shape of the odorant molecules to fit, as a key would fit to a lock. Buck and Axel showed that the olfactory receptors are G-proteins, and other G-proteins (e.g. in the immune system) recognize the shape of molecules as well. The other theory is known as the vibration theory, and it states that the receptors probe the energy of the vibrations of the odorant molecule, where a specific energy corresponds to a specific odor. To test both theories, several experiments have been performed and reviewed.1

1.1.1 Functional groups

The presence in a molecule of certain chemical groups like thiols, esters and ethers is frequently correlated with a particular odor. The example best known to non-specialists is the thiol functional group (SH) which gives any odorant molecule a unique “sulfuraceous” (rotten egg) odor character. The SH stretch frequency (316 meV) is also unique, not found in any other common group frequency.2 A boron-hydrogen (BH) group, while having a different shape as a SH,3 is the only group that has a similar stretch mode (322 meV).4 Remarkably, decaborane (B_{10}H_{14}) and other boranes smell sulfuraceous as well. In general, IR spectra have been reported to be good predictors of odor character.5 This would imply that the vibration theory is correct. On the other hand, the infrared spectrum of civetone, a macrocyclic ketone with a musk odor, is practically identical to that of its odorless acyclic analog.6,7 This would imply that the vibration theory is incorrect.

1.1.2 Isosteric molecules

Isosteric molecules are molecules similar in shape, but with different atoms comprising them. According to the odotope theory, they would smell similar, while according to the vibration theory, they could smell different. It has been reported8 that replacement of C atoms by Si, Ge and Sn in cyclohexane changes its odor, despite very similar geometries. Assuming no additional differences between the isosterics, e.g. boiling point, play a role, this would suggest that the odotope theory is incorrect.

1.1.3 Isotope replacements

Isotopes are species of an element, differing only in mass but not in chemical properties. According to the odotope theory, they would smell similar, while according to the vibration theory, they could smell different. Two examples are acetophenone and dimethyl sulfide. It is recently shown that fruitflies can differentiate between normal and deuterated acetophenone and even trained against either of them.9 Whether humans
can make this distinction too is debated. It is reported that deuterated acetophenone is fruitier and has less toluene-like character than acetophenone, and in addition has a much stronger bitter almonds character.\textsuperscript{1} Other studies show however that humans could not discriminate between acetophenone and deuterated acetophenone.\textsuperscript{10} The odor of dimethyl sulfide has been reported as “repulsive, sharp, green, cabbage-like” at high concentrations. Deuterated dimethyl sulfide clearly smells cleaner, more truffle-like without the gassy cabbage-like note of the parent compound.\textsuperscript{11} Assuming no additional differences between the isotopes, e.g. acidity,\textsuperscript{7} play a role, this would suggest that the odotope theory is incorrect.

1.1.4 Enantiomers

Enantiomers are mirror images of the same molecule. According to the vibration theory, they would smell similar, while according to the odotope theory, they could smell different. It has been reported that R and S-carvone smell very different.\textsuperscript{11} Assuming no additional differences between the enantiomers, e.g. binding mechanism, play a role, this would imply that the vibration theory is incorrect.

1.1.5 Odor intensity

Besides the odor character, also the odor intensity of molecules can vary orders of magnitude. In the odotope theory, this can be explained by assuming that different molecules have a different affinity (probability to bind to a receptor), or a different efficacy (probability that an event is transduced after the binding).\textsuperscript{12} Within the vibration theory, this can be explained by introducing the concept of sensor bands.\textsuperscript{1} If a frequency is too common in any event to distinguish molecules from another, it is likely that such a band is not represented in the spectrum. This would for instance explain the fact that methane (CH\textsubscript{4}) is odorless. This fact cannot discriminate between the two possible theories.

1.2 IETS as mechanism for smell?

A mechanism for the human body to recognize the shape of a molecule is the use of G-protein receptors, in which the binding of a ligand causes a conformational change in the receptor that will activate the corresponding G-protein through chemical means.\textsuperscript{13} For a long time, a mechanism for the human body to detect vibrations could not be indicated, until Turin suggested the possibility of IETS inside the nose.\textsuperscript{1} IETS was discovered in 1966 by Jaklevic and Lambe\textsuperscript{14} and is a technique in which the vibrational modes of molecules are probed by electrons which tunnel between two metal electrodes through a thin insulating barrier containing those molecular species. This will lead to antisymmetric peaks in the second derivative of the current with respect to the voltage at certain energies, as will be explained in Subsection 2.1.3. Metallic conductors are absent in the human body, but electron transfer in proteins is known for a long time\textsuperscript{15} and an estimate for the biological reducing power is given to be 500 mV,\textsuperscript{16} which is sufficient to measure molecular vibrations. Not the second derivative of the current would be
measured, but only the inelastic part of the current, i.e. tunneling only occurs when energy is conserved by emission of an odorant vibration of the correct energy, visualized in Ref 1. Sweeping the voltage would be replaced by a series of receptors each tuned to a different energy range. Simple modeling revealed that indeed it could be possible for humans to recognize odor using inelastic tunneling, provided the receptor has certain properties that are well within ranges known from other biomolecular systems.17

A receptor would hence detect the vibrations of a single molecule. Whether or not an electron is able to excite a vibration depends on the interaction between the two, which is termed the electron-vibration coupling. To measure this coupling, IETS experiments are necessary. Since 1998 single molecule IETS has been possible in the laboratory with the use of a scanning tunneling microscope (STM).18 Nowadays, the most used test beds for performing IETS on a single molecular level are mechanical break junctions19,20 and an STM.18,21,22,23,24,25,26 A typical ratio between inelastic and elastic current is 1-10% in systems with molecules chemisorbed onto metal electrodes. This rather low signal stems from a modest electron-vibration interaction compared with the interaction between electronic states in the molecule and in the electrodes.

There are two ways to increase this ratio. The first one is to increase the coupling between tunneling electrons and vibrations. An exact expression for coupling between vibrations and electronic states will be given in Chapter 3. Intuitively, the coupling is largest if the interaction between two states is influenced the most by the exciting of a certain vibration, and is fixed for most systems. If these electronic states do not contribute to a current-carrying state however, no inelastic effects are observed. In other words, the tunneling electron has to traverse the electronic states involved in the molecular vibration. By measuring which vibrations are excited one can deduce the tunneling path,27 and by actively changing the tunneling path one can tune which vibrations are excited mostly.

The second approach is by reducing the electronic interactions in the molecule. If for instance a system is chosen with a different adsorption mechanism or a very thin insulating oxide layer is added in between, there is a resonant level on the molecule in which the traversing electron resides for a relative long time, resulting in a larger electron-vibration coupling.28 The experimental fingerprint is no longer an antisymmetric peak in the second derivative, but satellite peaks in the first derivative of the resonant level, shifted by the vibrational energy.28,29

1.3 Physics to help settle debate?

To investigate the possible role of IETS in the mechanism for smell, several physical experiments are required, in conjunction with predictive theoretical modeling. One requirement is that the adsorption mechanism of the odorants to the receptors is known. To this end, surface enhanced Raman spectroscopy (SERS)30,31 can be used to measure the vibrational energies of single molecules.32,33 Nowadays, SERS can be performed inside the human body34,35 to measure the vibrations in the biological environment.
These can differ from the vibrations in the gas phase, and these shifts in energy can give hints about the adsorption mechanism of the molecule. The lowering of the vibrational energy for a certain functional group of the molecule is for instance an indicator for chemisorption of this group to the receptor, where the absence of any of the vibrations is an indicator for dissociation of the molecule. These measurements have to be backed up by *hybrid molecular dynamics*. Macroscopic-scale modeling applies methods from statistical mechanics to the system as a whole, ignoring details about how each atom responds. Atomic-scale modeling applies the laws of quantum mechanics that describe electrons, but because of the complex nature of the equations, these models can handle only a few atoms at a time. Hybrid molecular dynamics is a mixture of the two, where quantum mechanics is used to predict the behavior of blocks, which serves as the input for macroscopic modeling.\(^{36}\) From this, a stable binding mechanism can be deduced, which should confirm the SERS measurements.

As described in Section 1.2, there are several important parameters which determine the inelastic signal: electron-vibration coupling, tunneling path and electron residence time. With an STM, these parameters can be tuned and the influence can be systematically investigated. Furthermore, once the adsorption mechanism of the odorants in the nose is known, systems can be chosen with similar adsorption to mimic the biological environment. To this end, functionalized tips\(^ {24}\) are most likely required to copy this environment. A better understanding of the role of the tip is required to predict IETS intensities.

**Figure 1.1** Roadmap of the required experiments and calculations to prove or disprove the vibrational theory as the mechanism of sense of smell.

If the vibrational theory is correct, and with the adsorption mechanism known and the influence of the rest of the parameters well investigated theoretically, one should be able to predict smell intensities and possibly characters of new odorants. With this knowledge, one should devise a conclusive experiment to prove that either the
vibrational theory, the odotope theory, or a hybrid theory of these two is the correct theory to describe our sense of smell. The chain of required experiments and calculations is summarized in the block diagram in Fig. 1.1.

1.4 IETS in this thesis

Section 1.3 explains why IETS is a necessary step to investigate the mechanism of the nose. There are however many other interesting possibilities with IETS. In a world with ever smaller electronics, single molecular electronics in which the active region consists of only one molecule might be an alternative to the current semiconductor devices made with a lithography process. These single molecular devices are called molecular transport junctions (MTJs). For characterizing the molecular species in the junction, IETS is a powerful tool for chemical identification. On the other hand, in a real MTJ, the excitation of vibrations is linked to losses and should be avoided as much as possible. Therefore it is necessary to know the interplay between the electrons and the vibrations in a given system. The main question to answer in this thesis is: can the inelastic signal of any vibrational mode in any tunnel junction be predicted? Although the transport can take place in many regimes, this thesis only focuses on transport in the tunneling regime. Galperin et al. reviewed thoroughly the vibrational effects on electron transport through MTJs in Ref. 29.

As already mentioned in Section 1.2, the IETS signal strength depends crucially on the tunneling path of the electron through the junction, which in turn depends on the details of the tunnel junction. Predicting inelastic intensities taking full junction details into account is a branch of research which is currently investigated theoretically by several groups. The main limiting factors of the approaches so far are that full junction details are only partly taken into account, the change of tunneling probabilities due to excitations of vibrations is not taken into account, or that the whole junction is treated as a black box, taking too much into account, and such making calculations with realistic structures intractable.

In this thesis, the lowest order in inelastic tunneling (LOIT) model will be introduced to calculate the inelastic effects in a tunnel junction. With this model, one is able to simulate IETS curves in any given tunnel junction. The approach allows taking the full details of the junction into account and is still efficient enough to obtain results in a reasonable amount of time. The LOIT model will be applied to calculate the inelastic current through an STM setup for different systems, and the results will be compared with the experimental available data.

This thesis is organized as follows. Chapter 2 introduces the concepts of STM and IETS, and states the details of the performed STM experiments. After this, an elaborate model is presented in Chapter 3 to calculate the elastic current in an STM, which is a necessary requirement to use the LOIT model in any realistic calculation. Inelastic effects are not introduced until Chapter 4, in which the LOIT model will be motivated and explained in detail. This model is then applied to two different simple structures: a single CO molecule adsorbed on Ag(110) in Chapter 5, and an NO monolayer adsorbed...
on Rh(111) in Chapter 6. The final two Chapters investigate the more complex system of a thiophenol monolayer adsorbed on Ag(111). Since the details of the tunnel junctions are crucial, Chapter 7 is solely devoted to the geometry of a thiophenol on Ag(111) monolayer, while the inelastic effects are investigated in Chapter 8. The application of the LOIT model in this last Chapter is part of an explanation for the zero-bias anomaly, a feature that is introduced in this Chapter in which a few possible explanations are explored.

1.5 Bibliography

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Chapter 2 – Scanning tunneling microscopy

Chapter 1 introduced the concept and the need of IETS. All IETS experiments reported in this thesis have been performed using a scanning tunneling microscope (STM).\textsuperscript{1,2,3,4} Instead of giving a detailed description of this technique, a number of approximations is made in Section 2.1 to explain the processes of STM, scanning tunneling spectroscopy (STS) and IETS in simple terms, although a word of warning using these approximations is given as well. Section 2.2 provides more details about the experimental setup used in Chapters 6, 7 and 8.

2.1 Basic STM description

A scanning tunneling microscope (STM) is a non-optical microscope in which (semi-)conductive surfaces can be imaged at the atomic level. Besides imaging the surface, the same technique can also be used to probe the density of states of a sample with scanning tunneling spectroscopy (STS) and to probe excitations of the surface (e.g. vibrational modes of an adsorbate on the surface) with inelastic electron tunneling spectroscopy (IETS). In an STM, a sample surface is probed with a tip, as schematically sketched in Fig. 2.1. It is based on the concept of tunneling: when a conducting tip is brought in the proximity of the surface and a bias voltage is applied between the tip and the surface, electrons can tunnel from the tip to the surface or vice versa. The magnitude of this tunneling current is given in the Bardeen formalism\textsuperscript{5,6,7} by:

\[ I = \frac{e}{\pi \hbar} \sum_{\alpha \beta} n_{FD}(E_{\alpha}) \left[ 1 - n_{FD}(E_{\beta} + eV) \right] \times \left| H_{\alpha \beta} \right|^2 \delta(E_{\alpha} - E_{\beta}). \tag{2.1} \]

Here, \( e \) is the electronic charge, \( n_{FD}(E) \) is the Fermi-Dirac distribution, \( V \) is the applied voltage, \( H_{\alpha \beta} \) is the tunneling matrix element between states \( |\alpha\rangle \) of the surface and \( |\beta\rangle \) of the tip and \( E_{\alpha} \) is the energy of state \( |\alpha\rangle \) in the absence of tunneling. The delta function in Eq. 2.1 ensures energy conservation of the tunneling process.
The sum over states can be rewritten as an integral over energy as:

\[
I = \frac{e}{\pi\hbar} \int_{-\infty}^{\infty} dE \ g(E, V, R) \left[ n_{FD}(E - \mu_s) - n_{FD}(E - \mu_t) \right].
\]

Here, \( \mu_s = E_F + \frac{1}{2}eV \) and \( \mu_t = E_F - \frac{1}{2}eV \) are the chemical potentials of the sample and tip respectively with \( E_F \) the common Fermi level and the transmission function \( g \) depends on energy \( E \), applied bias \( V \) and tip-sample separation \( R \).

To explain in simple terms how STM, STS and IETS work, Eq. 2.2 will be examined under certain assumptions in Subsections 2.1.1 (STM), 2.1.2 (STS) and 2.1.3 (IETS). Subsection 2.1.4 warns for overinterpretation of experimental data using these simplified explanations. One assumption in all cases is that the surface and tip conduct perfectly internally. This implies that every electron which tunnels from tip to surface or vice versa contributes to the tunneling current and that the entire bias voltage drop is at the vacuum gap.

2.1.1 STM

In STM imaging, the bias voltage is fixed, and the tip is scanned across the surface while measuring the current. To describe STM imaging, it is assumed that the interaction between surface and tip states is proportional to the overlap of the respective states:

\[
g(E, V, R) \propto \int d\bar{r} \ \rho_s(E - eV, \bar{r}) \rho_t(E, \bar{r}).
\]

Here, \( \rho_s(t, \bar{r}) \) is the local density of states (LDOS) of the sample and tip respectively. At a sufficiently large distance, the wavefunctions of the electronic states (and hence the LDOS) decay exponentially into the vacuum. Let the wavefunctions of
the surface and tip decay with decay constant $\kappa_s$ and $\kappa_t$, respectively. The transmission function between the two states, separated by a distance $R = |\vec{R}|$, can now be written for any energy $E$ as:

$$g(\vec{R}) \propto \int_0^R dr \exp[-\kappa_s r] \exp[-\kappa_t (R - r)]$$

$$= \frac{\exp[-\kappa_s R] - \exp[-\kappa_t R]}{\kappa_t - \kappa_s} \text{ if } \kappa_s \neq \kappa_t$$

$$= \frac{\exp[-\kappa_{s/t} R]}{\kappa_{t/s}} \text{ if } \kappa_{s/t} \ll \kappa_{t/s}$$

$$= R \exp[-\kappa_s R] \text{ if } \kappa_s = \kappa_t,$$

where $r$ denotes the coordinate along the separation vector $\vec{R}$. Eq. 2.4 shows that the current depends exponentially on the separation distance between sample and tip. Due to the exponential dependence on distance, the resolution in the vertical direction can be very high, in the order of $\sim 10$ pm. Besides this exponential behavior in the normal direction, the transmission function also depends on the lateral position of the tip above the surface. For a spherical, metallic tip, the lateral resolution is estimated by $\sqrt{2\lambda(R + R_t)}$, where $R_t$ is the tip radius. This formula leads to a resolution of $\sim 5\text{Å}$.

There are two modes of scanning: i) one can keep the height of the tip constant and record the current, which is called a current map, or ii) one can adjust the height with a feedback loop to keep the current constant in order to ensure that the separation distance is also constant, which is called a constant current or topography map. All STM images presented in this thesis, both the experimental and the theoretical ones, are topography maps.

### 2.1.2 STS

In STS, the tip is fixed at a certain position above the surface and the bias voltage is swept in the range of interest while measuring the current. To describe STS, Eq. 2.3 is assumed to hold again. For fixed $\vec{r}$, substitution of Eq. 2.3 into Eq. 2.2 leads to:

$$I(V) \propto \int_{-\infty}^{\infty} dE \left[ \rho_s(E - E_F - \frac{1}{2} eV) \rho_t(E - E_F + \frac{1}{2} eV) \right]$$

$$\times \left[ n_{FD}(E - E_F - \frac{1}{2} eV) - n_{FD}(E - E_F + \frac{1}{2} eV) \right].$$

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Figure 2.2 Schematic energy diagram of an STM setup. The tunneling current is proportional to the DOS integrated over the energy window (light shaded area) determined by the applied bias voltage. Hence the derivative of the current is proportional to the sample DOS at energy $E = E_F + |e| V$.

To continue, the following two additional assumptions are made: i) the tip states are in the wide band limit (WBL) and ii) the temperature $T = 0$ K. The definition of the WBL is that the DOS is constant in energy and therefore $\rho_t$ can be taken out of the integral. At $T = 0$ K, the Fermi-Dirac distributions are replaced with Heaviside step functions. Eq. 2.5 is now further simplified to:

$$ I(V) \propto \int_{0}^{|e|V} dE \rho_s (E - E_F), $$

which is depicted in Fig. 2.2. The derivative of the current with respect to the voltage gives information about $\rho_s (E)$ according to:

$$ \frac{dI}{dV} (V) \propto \rho_s (E - E_F) \bigg|_{E=|e|V}. $$

The absolute value of the DOS is however not extractable with this method. In practice, the derivative of the current is measured directly with a lock-in technique, which is described in Subsection 2.2.7.
2.1.3 IETS

To perform IETS, the same experimental procedure is used as to perform STS. However, IETS relies on the fact that the transmission function can also couple states which differ in energy. The tunneling electron then absorbs or emits the energy of a (vibrational) excitation, denoted by $h\Omega$, and the delta function in Eq. 2.1 should be replaced with $\delta(E_\alpha - E_\beta \pm h\Omega)$.

Figure 2.3 Energy diagrams of the four possible inelastic processes.

Fig. 2.3 shows the energy diagrams of the four different processes of inelastic tunneling. Fig. 2.3a shows tunneling from sample to tip, absorbing a vibration, Fig. 2.3b shows tunneling from sample to tip, exciting a vibration, Fig. 2.3c shows tunneling from tip to sample, absorbing a vibration and Fig. 2.3d shows tunneling from tip to sample, exciting a vibration. To ensure the final state is an unoccupied state, the argument of the Fermi-Dirac distribution changes compared with Eq. 2.5. The inelastic tunneling current between the two states can now be written as:

$$I^{inel} \propto \int_{-\infty}^{\infty} dE \, g^{inel}(E,V) \left[ n_{FD}(E - E_F - \frac{1}{2}eV) - n_{FD}(E - E_F + \frac{1}{2}eV \pm h\Omega) \right].$$

To further simplify the description, the following two additional assumptions are made i) the transmission function $g^{inel}$ is energy independent and ii) the temperature $T = 0$ K. This means that below the threshold value $eV = \pm h\Omega$ there is no inelastic tunneling possible, and above the threshold value, the inelastic current is proportional to the bias voltage. In the STM setup, both elastic and inelastic processes occur, resulting in a current which is the sum of these two individual currents. This leads to a sudden change of slope in the current vs. voltage curve ($IV$ curve) and antisymmetric peaks and dips in the second derivative at precisely the threshold value, as shown in Fig. 2.4. In practice, the second derivative of the current is measured directly with a lock-in technique, which is described in Subsection 2.2.7. Each antisymmetric peak is a fingerprint for an excitation and is assigned to a vibrational mode.
Figure 2.4 The opening of an inelastic channel at a specific energy corresponds to a) a change of slope in the current, b) a step in the first derivative and c) an antisymmetric peak in the second derivative of the current with respect to the voltage.

2.1.4 Full STM description

In a real STM setup, the surface and tip states are not in the WBL, the interaction between them is not just proportional to their overlap, the temperature $T > 0$ K and the tip and sample do not conduct perfectly. Besides quantitative differences, this could even lead to results which cannot be explained qualitatively using the theory in this Section, like interference effects in STM images, apparent absence of DOS in STS measurements, and elastic backscattering in IETS experiments. Therefore care should be taken when using the simplified explanations in this Section to interpret experimental STM images and spectroscopy results! It can be imagined that several electronic configurations can lead to the same current, and hence the measurement of the current can, even in principle, not give full details about the system of interest.

To properly describe the tunneling current, one needs to know all electronic states under bias, all coupling elements between electronic states, including inelastic ones, and be able to compute all possible electron paths between the bulk of the tip to the bulk of the surface. Such a description will be given in Chapter 3, although still approximations have to be made to be able to calculate the current.

2.2 Experimental setup

The STM used in all experiments in this thesis is a low temperature (LT) STM, operated in ultrahigh vacuum (UHV). This Section will describe the vacuum system, the preparation tools and the STM proper which are used to perform the STM experiments in Chapters 6, 7 and 8 of this thesis. More specific details for each performed experiment are given in each corresponding Chapter.

2.2.1 Sample and tip introduction

The UHV system consists of three connected chambers which can be closed from each other with valves. The first chamber, where samples and tips enter, is called the fast entry chamber. The base pressure of this chamber is $10^{-7}$ mbar. To introduce samples to the fast entry, they are placed in a very small volume connected to the outside of the
entrance valve and this volume is evacuated before opening the valve to the fast entry. In this way the pressure in the fast entry rises to maximally $10^{-4}$ mbar, and is recovered to $10^{-7}$ mbar within 5 minutes.

### 2.2.2 Sample preparation

The second chamber is called the *preparation chamber*, and has a base pressure between $10^{-10}$ and $10^{-9}$ mbar. Pressures are measured with an ionization gauge (Bayard-Alpert ionization gauge, Granville Phillips 350 ion gauge controller). This chamber is used to clean the used surfaces and is furthermore equipped with a low energy electron diffraction (LEED, VG Scientific AEP 8011) apparatus. Samples are attached to a stainless steel sample plate with tantalum wires through a slit at the side of the sample, which are spot welded to the sample plate. The surface is cleaned by repeated cycles of Ar$^+$ ion bombardment (Leybold Heraeus ion gun 12/38, 1.5 kV, 2 µA sputter current) and annealing, achieved by electron bombardment (Vacuum Generators EBHC) of the back side of the sample plate and monitored by a thermocouple at the sample plate holder.

### 2.2.3 Cryostat

The third chamber houses the STM proper, and is therefore called the *STM chamber*. The base pressure is $10^{-10}$ mbar at room temperature. The STM is placed inside a gold-plated, double walled cryostat. The outer cryostat is filled with liquid nitrogen (LN) and serves for shielding. When the outer cryostat is filled with LN the base pressure drops below $10^{-11}$ mbar. The inner cryostat can be filled with either LN or liquid helium (LHe) and serves for cooling the STM. The STM stage sits below the inner cryostat inside a copper cup which is screwed tight to the cryostat. Therefore the STM is surrounded by cold surfaces. The lowest operating temperature inside the STM is 77.8 K when using LN or 4.8 K when using LHe. This temperature is measured using a diode temperature monitor (Lakeshore 321 temperature controller), attached to the stainless steel housing which encases the sample.

### 2.2.4 Vibration reduction

For successful high-resolution STM, a high quality vibration decoupling system is essential. The STM stage is suspended by three springs directly mounted to the inner cryostat. Vibrations of the suspension system are suppressed using an eddy current damping mechanism. For this the LT STM stage is surrounded by a ring of copper plates which come down between permanent magnets, fixed at the copper container at the bottom of the inner cryostat. To minimize vibrations further, the entire UHV setup is supported on four active damping blocks (Table Stable, AVI-400-M), which detect and counteract any vibration of the setup as a whole. The setup is built on an island, which is a block of 3 m by 2.5 m with its foundations disconnected from the building’s foundations. While measuring, all turbomolecular and rotary vane pumps are switched
off, while the UHV is maintained by ionization pumps (Perkin-Elmer). With these measures, an average drift of $< 0.2$ nm/hour can be reached.\textsuperscript{14}

2.2.5 STM

The STM used in this work is a commercial LT STM from Omicron GmbH. It uses a single tube scanner with four electrodes around the piezo-tube to move the tip in the $x$- and $y$-direction and a single electrode around the piezo-tube for extension and contraction in the $z$-direction. The tip is held in place by a magnet. For coarse movement in the $x$- and $y$-direction, the stage is placed on two sets of rails, for coarse movement in the $z$-direction, the piezo tube is moved up and down the tube holder using the principle of piezoelectric stick-slip motion.\textsuperscript{15}

2.2.6 STM electronics

The electronics operating the STM is an SPM100 from RHK Electronics. The bias voltage, current setpoint, and the time constant and gain of the feedback loop are set manually by knobs at the front end. The SPM100 has just one integrator. Both the time constant and gain do the same thing but in different ways. The gain physically changes the gain of an amplifier, and the time constant changes the resistance in front of the integrator. The gain of the integrator is a combination of both the gain and time constant. The sampling rate of the STM is 50 kHz, although the 3 dB point of the used IV-converter (RHK IVP-300) including all cables is 13 kHz. If the dwell time per pixel is longer than the sampling time, the software averages the data over the entire dwell time. The coarse piezos are operated using the PMC 100 from RHK Electronics.

2.2.7 Lock-in measurements

The first and second derivative of the current with respect to the voltage are measured using lock-in amplifiers (Stanford Research Systems, SR830 DSP Lock-In Amplifier). With this technique, an AC modulation voltage with amplitude $V_\omega$ and frequency $\omega$ is added to the DC bias voltage $V_b$. A Taylor expansion around $V_b$ gives the following relations between the derivatives and the components of the measured current with frequencies $\omega$ and $2\omega$ ($I_\omega$ and $I_{2\omega}$):\textsuperscript{3}

$$\frac{dI}{dV}\bigg|_{V=V_b} = \sqrt{2} \frac{I_\omega(V_b)}{V_\omega},$$

$$\frac{d^2I}{dV^2}\bigg|_{V=V_b} = 4\sqrt{2} \frac{I_{2\omega}(V_b)}{V_{\omega}^2}.$$  \hspace{1cm} 2.9

The lock-in amplifier uses a technique known as phase-sensitive detection to single out this component of the signal, while noise signals at frequencies other than the reference frequency are rejected and do not affect the measurement. The basics and advanced concepts of the lock-in amplifier are described clearly in Ref. 16.
For fast measurements, $\omega$ should be chosen as high as possible. However, the capacitance of the system limits the transmission of signals for higher frequencies. Since the IV-converter cutoff is at 13 kHz and for the second derivative the current component with frequency $2\omega$ is required, $\omega$ is always chosen less than 6 kHz. The amount of noise measured by the lock-in is determined by the integration time $t_c$. Since this amount varies from measurement to measurement, an optimal value for $t_c$ is decided per measurement by trial-and-error, balancing noise reduction with measurement time. The digital low pass filter used to single out the desired frequency is set to a transmission slope of 24 dB/octave. The drawback of this steep slope is that the pre-sample-delay, which is the time between setting the bias voltage and reading the signal, should be chosen high. In this case, the pre-sample-delay is set to 10 times $t_c$, after which the signal has reached 99% of the final signal.\textsuperscript{16}

Although in principle the exact prefactors in Eq. 2.9 are known, care must be taken to measure only the signal due to the STM current and not due to the capacitance of the system, which lags 90 degrees in phase. This can be done by first measuring the phase of the signal when not in contact and then measuring only the signal which is perpendicular to this in phase. In practice however, it is found to be easier and more exact to determine the offset and multiplication factor of the final signal by fitting it to the simultaneously recorded $IV$ curve. The sampling time per voltage point is set to a multiple of the reference time period in order to avoid beating in the DC current signal.

### 2.2.8 Tip preparation

Platinum iridium (PtIr) tips have been cut using an extremely sharp cutter from a 90% Pt / 10% Ir wire with a diameter of 0.25 mm. Tungsten (W) tips have been etched\textsuperscript{17} from a polycrystalline W wire with a diameter of 0.25 mm, using a 1 molar NaOH solution and a Pt counter electrode. The used voltage is 6.25 V. A partition wall has been placed in the liquid between the Pt electrode and the W tip to avoid hydrogen gas to cause vibrations near the meniscus at the W electrode side. Just before breaking the wire, the meniscus is refreshed by retracting the tip and making new contact. The final shape of both PtIr and W tips are checked using an optical microscope. PtIr tips are used as prepared, W tips are first heated in the preparation chamber until they start to glow, to remove the native oxide layer.\textsuperscript{3} Both kind of tips can be further modified/improved by i) generating a high electric field at the apex by applying voltage pulses up to 10 V between tip and sample or ii) by dipping the tip into the metal sample, transferring atoms of the substrate material onto the tip. No clear differences between PtIr and W tips have been observed, neither in stability nor in image quality. Therefore PtIr tips are preferred due to the easier preparation process.
2.3 Bibliography

Chapter 3 – Theoretical background

All calculations presented in this thesis have as a final goal the simulation of STM images and/or STS and IETS spectra which can be directly compared with their experimental counterparts. This requires ab initio calculations of the geometric structure of both the surface and the tip in the ground state, interactions inside the tip and surface and interactions between the tip and the surface under application of a bias voltage. Furthermore, interactions of electronic states with vibrations are taken into account. For calculating ground state properties, density functional theory (DFT) is the most widely used method nowadays, which is reviewed in Section 3.1. To calculate transport properties, several approaches can be taken, depending on which approximations one wishes to make. The first choice is which Hamiltonian to take, for instance a tight binding Hamiltonian or a DFT Hamiltonian. The second choice is how to incorporate the bias voltage. There are several options to do this:

1. Calculate the system Hamiltonian self-consistently under the applied electric field, although this is computationally very demanding.
2. Define the voltage drop across the junction \textit{a priori}, which can be done in different fashions, for instance linear over the junction or a sudden drop at a certain point.
3. Neglect the bias voltage and assume that the conductance of the junction is bias independent. This approach is called the linear response approach.

In this thesis, the voltage is assumed to make a sudden drop at the vacuum gap between the tip and the sample, and the non equilibrium Green's function (NEGF) formalism is used. This approach is reviewed in Section 3.2. The inclusion of inelastic effects in the calculations is introduced in Chapter 4.

3.1 Density functional theory

Density functional theory is a framework used by both the physics and the chemistry community to investigate the geometry and electronic structure of the ground state of atoms, molecules and condensed matter. It is based on two theorems, proven by Hohenberg and Kohn\textsuperscript{4} in 1964, and reduced to a set of self-consistent equations by Kohn and Sham\textsuperscript{5} in 1965 by introducing an approximation for the exchange and correlation interactions. The concepts are briefly reviewed in Subsection 3.1.1. The representation of the wavefunctions can in principle be done in any basis set. All DFT calculations presented in this thesis are performed with the code VASP,\textsuperscript{6,7} which uses a plane wave (PW) basis set, or with the code SIESTA,\textsuperscript{8} which uses a linear combination of atomic orbitals (LCAO) basis set. The differences between these basis sets and an overview of DFT in matrix representation are given in Subsection 3.1.2. The various outputs of DFT are presented in Subsection 3.1.3, after which Subsections 3.1.4 and 3.1.5 describe how the vibrational modes and the electron-vibration couplings are calculated using DFT. Van-der-Waals interactions are not commonly taken into account.
in DFT, although recent developments make corrections possible. The used corrections throughout this thesis are introduced in Subsection 3.1.6.

### 3.1.1 DFT formalism

A material is a collection of atoms, consisting of nuclei and electrons that interact with each other through the Coulomb forces. In principle any measurable property of a system can be derived from the many-body wavefunctions \( \{\Psi\} \) describing the entire system. Each wavefunction \( \Psi \) is an eigenfunction of the Hamiltonian operator \( \hat{H} \) describing all interactions, with the energy \( E \) as the corresponding eigenvalue. The general many-body Hamiltonian is given by:

\[
\hat{H} = \hat{H}_{ee} + \hat{H}_{ll} + \hat{H}_{el},
\]

where

\[
\hat{H}_{ee} = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|},
\]

\[
\hat{H}_{ll} = -\sum_i \frac{\hbar^2}{2M_i} \nabla_{\vec{R}_i}^2 + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|\vec{R}_i - \vec{R}_j|},
\]

\[
\hat{H}_{el} = -\sum_{i,l} \frac{Z_i e^2}{|\vec{r}_i - \vec{R}_l|}.
\]

In Eq. 3.2 \( Z_i |e|, M_i \) and \( \vec{R}_i \) are the charge, mass and coordinates of ion \( I \), respectively. The symbol \( \nabla^2_{\vec{R}_i} \) indicates the Laplacian with respect to the ionic coordinates.

Since the electrons move much faster than the ions due to their much smaller mass, they have enough time to respond immediately to moving atoms and hence the electronic part of the Hamiltonian can be solved at fixed ionic positions, the latter treated as parameters. This is called the \textit{adiabatic} or \textit{Born-Oppenheimer approximation}.\(^8\) This approximation decouples the electronic part of the Hamiltonian from the total Hamiltonian 3.2:

\[
\hat{H}_{el} = \hat{T} + \hat{W} + \hat{V}_{ext},
\]

3.3
where
\[ \hat{T} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2, \]
\[ \hat{W} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}, \]
\[ \hat{V}_{ext} = -\sum_i \sum_j \frac{Z_j e^2}{|\vec{r}_i - \vec{R}_j|}. \]

In Eq. 3.4 \( \hat{T} \) is called the kinetic operator, \( \hat{W} \) is the electron-electron interaction operator and the operator \( \hat{V}_{ext} \) describes any local static external potential, in this case only the electron-ion potential. The first Hohenberg-Kohn theorem now states that there is one-to-one correspondence between the external potential and the ground state density. A proof can be found in the original paper \(^4\) or in any textbook about DFT. \(^{10,11}\)

A corollary of this theorem is that a universal functional for the total energy in terms of the density can be defined. The second theorem states that the exact ground state of the system is the global minimum value of this functional. Again, a proof of this can be found in the original paper.\(^5\) This functional can be written as:

\[ E[n] = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \]
\[ = \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}_{ext} | \Psi_0 \rangle \]
\[ = F[n] + \int d\vec{r} \ V_{ext}(\vec{r})n(\vec{r}), \]

where \( |\Psi_0 \rangle \) is a ground state wavefunction and \( n(\vec{r}) \) is the corresponding electron density. The key idea is that \( F[n] \) is the same for all electron systems and can be decomposed into three parts:

\[ F[n] = T[n] + \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{XC}[n] \]
\[ = T[n] + E_H[n] + E_{XC}[n], \]

where \( T[n] \) is the kinetic energy of a fictitious non-interacting system with the same ground state density \( n(\vec{r}) \) as the interacting one, \( E_H[n] \) is the Hartree energy, or the mean-field part of the Coulomb energy and \( E_{XC}[n] \) is the exchange-correlation part of the Coulomb energy, which is by definition the rest. After defining the Hartree potential \( V_H(\vec{r}) \) as the functional derivative of \( E_H[n] \) with respect to the density and the exchange-correlation potential \( V_{XC}(\vec{r}) \) as the functional derivative of \( E_{XC}[n] \) with
respect to the density, the functional $F[n]$ can be minimized by variational means to obtain the Kohn-Sham equations:\(^5\)

$$\left[-\frac{h^2}{2m}\nabla^2 + V_H(\vec{r}) + V_{XC}(\vec{r}) + V_{\text{ext}}(\vec{r})\right] \phi_{n}^{KS}(\vec{r}) = \varepsilon_{,n}\phi_{n}^{KS}(\vec{r}).$$

3.7

The band index $n$ labels the solutions of these equations. The solutions of Eqs. 3.7 yield the ground state density:

$$n(\vec{r}) = \sum_{n=1}^{N_\alpha} n_{FD}(E_{n})|\phi_{n}^{KS}(\vec{r})|^2,$$

3.8

where $N_\alpha$ is the number of bands taken into account. There are three problems with this approach, for which certain approximations have been developed in the last decades. The first one is that in order to solve Eqs. 3.7 one needs to know the exact exchange-correlation functional. This is however an unknown functional and approximations are thus necessary. Well-known approximations are the local density approximation (LDA)\(^12\) and the generalized gradient approximation (GGA),\(^13\) but also hybrid functionals exist which combine the two.\(^14\) Authors performing DFT calculations always have to specify the used exchange-correlation functional. The exchange-correlation functional used throughout this thesis is of the GGA-PBE type.\(^13\)

The second problem is that the electron wavefunctions around the core have rapid oscillations, so many basis functions have to be taken into account to accurately describe the electron wavefunctions in the core region (more about basis functions will follow in Subsection 3.1.2). A common approximation to work around this problem is to disregard the core electrons, since they hardly contribute to the bonding, and to introduce pseudopotentials for the valence electrons, which are identical to all-electron potentials beyond a fixed radius from the core, but are smooth inside this radius and contain the interactions with the nucleus, screened by the core electrons. Without entering into details, norm-conserving pseudopotentials constructed following the Troullier-Martins scheme\(^15\) are employed in the SIESTA calculations, while the more accurate plane augmented wave (PAW) method is used in VASP instead. The third problem is that the Kohn-Sham orbitals $\phi_{n}^{KS}(\vec{r})$ depend on the ground state density $n(\vec{r})$ and the ground state density $n(\vec{r})$ depends on the Kohn-Sham orbitals $\phi_{n}^{KS}(\vec{r})$. In practice, given an exchange-correlation potential, Eqs. 3.7 are solved iteratively until self-consistency in density, potential or total energy is achieved within a fixed tolerance level.

### 3.1.2 DFT iteration scheme in matrix representation

In this Subsection, the DFT iteration scheme is presented in matrix representation. To this end, first the employed basis sets are defined and the notation how operators act on these basis functions is introduced.
Basis functions

The solutions of the Kohn Sham equations are wavefunctions which are vectors inside a Hilbert space. A Hilbert space has a precise mathematical definition, but the definition for physicists, used here, is just a linear space with all possible electron wavefunctions. Since it is a linear space, all wavefunctions can be written as a linear combination of certain basis functions from a basis set. In practice, one has to choose a finite basis set, which means that the Hilbert space is not complete anymore. The chosen basis sets in this thesis contain either plane waves (PWs) or atomic orbitals (AOs) as basis functions. The differences between these two have been reviewed in literature. In general AOs (PWs) are better suited for systems with mainly (de)localized electron character. With either basis set the iterative DFT scheme can be written down as a set of matrix equations. This Section takes the AO basis set as an example how this is done, but the same holds for any other basis set.

Consider a molecule or group of atoms, isolated in space, schematically drawn in Fig. 3.1. \( N_I \) denotes the number of atoms, which are labeled with the index \( I \in \{1, \ldots, N_I\} \). Each atom has a certain amount of AOs, denoted by \( N^I_{\alpha} \) which can be different for each species. There are \( N_{\alpha} := \sum_{I=1}^{N_I} N^I_{\alpha} \) AOs, which are labeled with the index \( \alpha_I \), where the subscript \( I \) indicates the atom which is the center of the AO. The subscript is omitted whenever the corresponding atom is irrelevant. The position of the atom \( I \) is given by \( \vec{R}_I \). Each AO is assumed to be strictly localized, which means that the AO is precisely 0 outside a certain cutoff radius \( R_c (\alpha) \):

\[
\forall \alpha : |\vec{r} - \vec{R}_I| > R_c (\alpha) \Rightarrow \langle \vec{r} | \alpha \rangle = 0.
\]
These AOs are also called *contracted* AOs. The basis set employed in the SIESTA calculations correspond to the so-called double zeta polarized scheme, whereby each occupied \( l \) shell is split into two separate functions while empty shells are generated *polarizing* the \( l-1 \) occupied shell.\(^8\) The cutoff radius of the first zeta orbitals is determined from the confinement energy, thus the larger this energy, the more contracted the AO is. In this work the confinement energy is fixed to 100 meV. The second zeta orbitals are generated using the split valence scheme, in which the radius is defined according to the amount of norm that this second zeta orbital has to carry; in this work this norm is fixed to 0.15. In VASP, no AOs are used, but plane waves form the basis set. The plane waves with a smaller kinetic energy typically have a more important role than those with a very high kinetic energy. The introduction of a plane wave energy cutoff reduces the basis set to a finite size; in this thesis this cutoff energy is set to 400 eV for each chemical species. Convergence in the basis set can be checked in VASP by simply increasing the cutoff energy, whereas in SIESTA this is much more problematic since there is no systematic way to improve the AO basis set.

The physical interpretation of the electron wavefunction is the probability amplitude to find an electron at a certain point in space, hence \( |a\rangle : \mathbb{R}^3 \rightarrow \mathbb{C} \). This means that all points in space also span the same Hilbert space and hence form a basis set. These points in space are denoted by \( \{|\vec{r}\rangle\} \), and any wavefunction \( |a\rangle \) can be written in either basis set as:

\[
|a\rangle = \sum_{\alpha=1}^{N_a} a_{\alpha} |\alpha\rangle = \int d\vec{r} \ c(\vec{r}) |\vec{r}\rangle. \quad 3.10
\]

Any AO can be written down in the spatial basis set as \( |\alpha\rangle = \int d\vec{r} \varphi_\alpha(\vec{r}) |\vec{r}\rangle \), where the coefficients \( \varphi_\alpha := \langle \vec{r} |\alpha\rangle \). In practice, both the AO representation and the real space representations truncate the Hilbert space; the former due to the finite basis set size and the latter because the basis functions are only defined for discrete points forming a 3D grid.

**Operators**

A linear operator \( \hat{O} \) transforms a wavefunction \( |a\rangle \) into another wavefunction \( |a'\rangle \). Once it is known how \( \hat{O} \) operates on the basis functions, the entire operator is given. Since the \( |\alpha\rangle \) and the \( |\vec{r}\rangle \) representation will be used, the operator \( \hat{O} \) can either be given by a matrix with coefficients \( O_{\alpha\beta} \) or a function \( O(\vec{r},\vec{r}') \), where:

\[
O_{\alpha\beta} := \langle \alpha |\hat{O}|\beta\rangle, \\
O(\vec{r},\vec{r}') := \langle \vec{r} |\hat{O}|\vec{r}'\rangle. \quad 3.11
\]
In the rest of this Section, only local operators are treated, i.e. 
$$O(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}') \langle \vec{r}' | \hat{O} | \vec{r} \rangle,$$
which are written as $O(\vec{r})$. Once $O(\vec{r})$ is known, $O_{\alpha\beta}$ can be found with:

$$O_{\alpha\beta} = \int d\vec{r} \phi_\beta^*(\vec{r}) \phi_\alpha(\vec{r}) O(\vec{r}).$$

3.12

Similarly, once $O_{\alpha\beta}$ is known, $O(\vec{r})$ can be found with:

$$O(\vec{r}) = \sum_{\alpha, \beta} \phi_\beta^*(\vec{r}) \phi_\alpha(\vec{r}) O_{\alpha\beta}.$$  

3.13

The statistical operator or density operator is defined as:

$$\hat{\rho} := \sum_\alpha p_\alpha |\alpha\rangle \langle \alpha|,$$  

3.14

where $p_\alpha$ gives the occupancy of state $|\alpha\rangle$, in practice given by the Fermi-Dirac distribution. This density operator is characterized by the density matrix $\rho_{\alpha\beta} := \langle \alpha | \hat{\rho} | \beta \rangle$. Another important operator is the overlap operator $\hat{S}$, which is characterized by the matrix $S_{\alpha\beta} := \langle \alpha | \beta \rangle$. If an orthogonal set of basis functions would be used, the overlap operator is equal to the identity operator.

**Periodicity**

Now consider a group of atoms, which is periodically repeated in one or more spatial dimensions, schematically drawn in Fig. 3.2. This repeating cluster is called the unit cell. The infinite number of AOs can now be written down as $|\alpha_\vec{R}\rangle$, where $\alpha$ labels the AOs within the unit cell, just as in the non-periodic case, and $\vec{R}$ indicates in which unit cell the AO resides. Since the external potential is periodic with any translational symmetry vector $\vec{R}$, so are the wavefunctions. The AO basis $|\alpha_{i,\vec{R}}\rangle$ can therefore be transformed into the Bloch AO basis $|\alpha_{i,\vec{k}}\rangle$ by a Fourier transform:

$$|\alpha_{i,\vec{k}}\rangle := \frac{1}{\sqrt{N_{\vec{R}}}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} |\alpha_{i,\vec{R}}\rangle,$$  

3.15

where $N_{\vec{R}}$ is the number of unit cells over which is summed.
Figure 3.2 Graphical representation of a group of atoms, periodic in space. The vector $\vec{R}$ shows one possible translational symmetry vector.

Instead of an infinite number of wavefunction labeled with $\vec{R}$, the Bloch AO basis contains an infinite number of wavefunctions labeled with $\vec{k}$. Due to periodicity, all Bloch AO basis functions are periodic in $\vec{G}$, where $\vec{G}$ is any reciprocal lattice vector. Therefore, only the k-points in the first Brillouin zone need to be considered. In practice, k-space is discretized by a sampling grid with $N_k$ sampling k-points, where the number of k-points is systematically increased until convergence is reached. Monkhorst and Pack\textsuperscript{17} introduced an algorithm to produce the set of sampling k-points. The required density of this grid depends strongly on the system under investigation. If the bands are rather flat, a few sampling k-points suffice to describe all wavefunctions, but if there is a large dispersion present, a fine sampling grid is required to include all details. With this discretization of k-space, the Bloch AO basis set has a finite number of basis functions, equal to $N_k \cdot N_\alpha$, where $N_k$ is the number of sampling k-points and $N_\alpha$ is the number of AOs taken into account within one unit cell.

When metallic systems are involved, one must integrate a discontinuous function over the first Brillouin zone due to the partial filling of the bands. For numerical integration methods, this requires a large number of k-points to achieve convergence in the number of k-points. To reduce the required number of k-points, smearing is employed, in which the step function occupation is replaced by the Fermi-Dirac\textsuperscript{18} distribution or a more sophisticated occupation function using the Methfessel and Paxton method,\textsuperscript{19} both with a certain width defined by the thermal energy $kT$. Throughout this thesis, a Fermi smearing of 100 meV is used in the SIESTA calculations and a first order MP smearing of 200 meV in the VASP calculations.
Within this Bloch AO basis, the Hamiltonian matrix elements are:

\[ H_{\alpha\beta}(\vec{k}, \vec{k}') = \delta(\vec{k}, \vec{k} + \vec{G}) \cdot \sum_{\vec{R}} e^{i\vec{R}\cdot\vec{k}} H_{\alpha\beta}(\vec{R}), \quad 3.16 \]

where \( \vec{R} \) is the vector between the unit cells in which AOs \( \alpha \) and \( \beta \) reside. Because of the \( \delta \)-function and since only k-points within the first Brillouin zone are sampled, there is no k-mixing and the Hamiltonian can be labeled with a single k-point: \( H_{\alpha\beta}(\vec{k}) = \langle \alpha_{\vec{k}} | \hat{H} | \beta_{\vec{k}} \rangle \). In fact, Eq. 3.16 and its implication hold for any operator \( \hat{O} \) acting solely on the states \( |\alpha_{\vec{k}}\rangle \). The sum over \( \vec{R} \) in Eq. 3.16 runs only over a small number of terms, since the matrix elements \( H_{\alpha\beta}(\vec{R}) \rightarrow 0 \) for large values of \( |\vec{R}| \).

**DFT iteration scheme**

The DFT iteration scheme can now be written down in the language explained above.

1. Start with a chosen geometry, i.e. choose the initial ionic coordinates.
2. Choose the pseudopotential \( V_{pp}(\vec{r}) \) and the functional form for the exchange-correlation potential \( V_{XC}[n] \).
3. Start from the charge density \( n(\vec{r}) \) which is the ground state density for isolated atoms.
4. Use the density \( n(\vec{r}) \), the functional forms for \( V_H[n] \) and \( V_{XC}[n] \), and \( V_{pp}(\vec{r}) \) to create the DFT Hamiltonian \( H(\vec{r}) \) and transform it first to AO basis and next to the Bloch AO basis:

\[ H_{\alpha\beta}(\vec{R}) = \int d\vec{r} \varphi_\alpha^*(\vec{r} - \vec{R}) \varphi_\beta(\vec{r} - \vec{R}) H(\vec{r}), \quad 3.17 \]

\[ H_{\alpha\beta}(\vec{k}) = \frac{1}{\sqrt{N_{\vec{k}}}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} H_{\alpha\beta}(\vec{R}). \quad 3.18 \]

If the Hamiltonian matrices already exist, the new matrices are mixed in into the existing ones. The mixing parameter, which is the ratio between new and old matrix elements, is typically very small (<5%) for increased stability.

5. Solve for every sampling k-point the Kohn-Sham equations individually. For non-orthogonal basis functions, these equations read:

\[ \left( \hat{H} - E_{n,k} \hat{S} \right) |\Psi_{n,k}^{\text{new}}\rangle = 0. \quad 3.19 \]

6. Find the Fermi level \( E_F \) by filling the states, starting with those with the lowest energy until the exact number of electrons in the system is obtained.
7. Construct the density matrix per k-point:

\[ \rho_{\alpha\beta}(\vec{k}) := \sum_n p_{n,k} \langle \beta | \Psi_{n,k}^{*} \rangle \langle \Psi_{n,k}^{*} | \alpha \rangle. \quad 3.20 \]

From these, the real space density matrix is constructed by summing over the k-points and stored. It is also possible to mix the density matrix instead of the Hamiltonian matrices, but that approach is not taken in this work.

8. Extract the charge density in real space from the density matrices defined in step 7:

\[ n(\vec{r}) = \sum_{\alpha,\beta,k} \phi_{\alpha,\vec{k}}^{*}(\vec{r}) \phi_{\beta,\vec{k}}(\vec{r}) \rho_{\alpha\beta}(\vec{k}). \quad 3.21 \]

9. Repeat steps 4-8 until the difference between any two subsequent Hamiltonian matrix elements is below a certain threshold value.

### 3.1.3 Output of DFT

The output of the DFT calculations presented in this thesis is:

1. electronic structure;
   - the self-consistent Hamiltonian matrix elements;
   - band structure: \( E \) vs. \( \vec{k} \) relation;
   - (local) DOS: number of states per energy (projected onto spatial coordinates);
2. geometry of ionic ground state;
3. vibrational frequencies and modes;
4. electron-vibration coupling elements.

This and subsequent Subsections describes how these quantities are extracted using DFT.

#### Electronic structure

After the procedure presented in Subsection 3.1.2 is finished, the output is a set of wavefunctions \( \Psi_{n,k} \), called Kohn-Sham orbitals, the corresponding eigenvalues \( E_{n,k} \), the Fermi energy \( E_F \) and the Hamiltonian matrix \( H \) with the interactions between any two basis functions. The band structure is defined as the relation between \( E_{n,k} \) and \( \vec{k} \) and is mostly plotted along the high symmetry directions. The density of states operator \( \hat{D}(E) \) is defined as:

\[ \hat{D}(E) := \frac{1}{N_{\vec{k}}} \sum_{n,k} \left| \Psi_{n,k} \right> \delta \left( E - E_{n,k} \right) \left< \Psi_{n,k} \right| \quad 3.22 \]

and can be evaluated in any given basis. Note that this operator is closely related to the density operator defined in Eq. 3.14, but explicitly takes the energy dependence into account and does not take the occupation of a state into account. The trace of this
operator, denoted by \( D(E) \), is called the density of states (DOS) and represents the number of states per unit energy. When evaluated in the position basis, it is termed the local density of states (LDOS):

\[
D(E, \vec{r}) = \langle \vec{r} | \hat{D}(E) | \vec{r} \rangle = \frac{1}{N} \sum_{k} \sum_{\alpha, \beta} a_{\beta, n, \mathbf{k}} a_{\alpha, n, \mathbf{k}}^{*} \varphi_{\alpha, \mathbf{k}}^{*} \varphi_{\alpha, \mathbf{k}} \delta \left( E - E_{n, \mathbf{k}} \right)
\]

3.23

Note that the last line is an inequality which makes interference effects possible. When the DOS is evaluated in the AO basis, it is termed the projected density of states (PDOS). When evaluating the DOS in practice, the delta functions are broadened by 100 meV or less, depending on the desired peak resolution in the DOS plots.

**Ionic ground state**

With the ionic coordinates fixed and the electron density known, the force on each atom can be calculated. How this is done is shown in the next Subsection. The ionic ground state is defined as the set of ionic coordinates for which all forces on all nuclei are zero, or equivalently, the set of ionic coordinates which results in the lowest energy in the electronic ground state. Since one of the goals of DFT is to find this ground state, the iteration scheme in Subsection 3.1.2 is repeated for several ionic coordinates until all forces are below a fixed threshold value; in this thesis this threshold value is 10 meV/Å for the SIESTA calculations, unless otherwise stated, and 2 meV/Å for the VASP calculations. To minimize the number of DFT iterations, the conjugate gradient algorithm\(^{20,21}\) is adopted, for which the forces on the atoms are required for each geometric structure.

### 3.1.4 Vibrational modes

Once the ionic ground state is known, the normal mode vibrations can be calculated.\(^{22}\) A normal mode vibration, termed a vibrational mode throughout this thesis, is a vibration wherein all atoms vibrate with the same phase and frequency. Let \( \zeta \) be the column vector with length \( 3N_{a} \), with elements \( \zeta_{I, \nu} \) being the displacements coordinates, defined as the displacement of atom \( I \) from equilibrium in direction \( \nu \), where index \( I \) runs over all dynamic nuclei and \( \nu = x, y, z \) over all spatial dimensions. These coordinates are first transformed into the mass-weighted displacement coordinates, defined as:

\[
q_{I, \nu} = \sqrt{m_{I}} \cdot \zeta_{I, \nu},
\]

3.24
where \( m_I \) is the mass of atom \( I \) and the vector \( \tilde{q} := \{q_{I,v}\} \). The Taylor expansion of the potential energy around the ground state coordinates can be written in terms of these displacement coordinates up to second order as:

\[
V = V_0 + \sum_{I,v} \left( \frac{\partial V}{\partial q_{I,v}} \right) \cdot q_{I,v}' + \frac{1}{2} \sum_{I,v,v',v''} \left( \frac{\partial^2 V}{\partial q_{I,v} \partial q_{I,v'}} \right) \cdot q_{I,v}' q_{I,v''}',
\]

where the derivatives are evaluated at \( q_{I,v} = q_{I,v}' = 0 \). Since higher orders are neglected, this is called the harmonic approximation. The total energy can be chosen such that \( V_0 = 0 \) and in the ionic ground state, the forces \( \partial V/\partial q_{I,v} = 0 \) for all \( \{I,v\} \).

The terms \( \partial^2 V/\partial q_{I,v} \partial q_{I,v'} \) can be interpreted as the differential change in the force on atom \( I \) in the direction \( v \) if atom \( I' \) is moved infinitesimally in the direction \( v' \) and will be collected in the matrix \( D \) termed the force matrix, dynamical matrix or Hessian matrix. In practice, the elements of \( D \) are calculated by moving atom \( I \) a finite distance \( \delta \) from its equilibrium position along the directions \( v \) and \( -v \) and subsequently calculating the force \( F_{I,v'} \) on atom \( I' \) in direction \( v' \):

\[
D_{I,v,I',v'} = \frac{1}{2\delta} \left[ F_{I',v'} \left( \tilde{q} = \delta \tilde{e}_{I,v} \right) - F_{I',v'} \left( \tilde{q} = -\delta \tilde{e}_{I,v} \right) \right],
\]

where \( \tilde{e}_{I,v} \) is the vector with elements \( [\tilde{e}_{I,v}]_{I,v'} = \delta_{II'} \delta_{vv'} \). Therefore, calculating \( D \) requires at least \( 6N_a \) electronic relaxations. The \( 3N_a \) eigenvalues of the Hessian matrix are the squares of the vibrational frequencies \( \omega^2 \), which are labeled with the index \( \lambda \). The corresponding eigenvectors are written for each \( \lambda \) as \( \tilde{v}^\lambda := \{v^\lambda_{I,v}\} \), and normalized such that \( \tilde{v}^\lambda \cdot \tilde{v}^\lambda = 1 \). Now, the normal mode coordinates \( Q^\lambda \), defined as:

\[
Q^\lambda := \sum_{I,v} v^\lambda_{I,v} q_{I,v} = \tilde{v}^\lambda \cdot \tilde{q},
\]

give the displacements of each atom around the equilibrium position for a specific vibrational mode \( \lambda \).

### 3.1.5 Electron-vibration coupling

Once the vibrational frequencies \( \Omega^2 \) and corresponding normal mode coordinates \( Q^\lambda \) are calculated, the influence of these vibrations on the electrons, known as electron-vibration coupling, can be calculated. This will be used later in Chapter 4 to include inelastic effects in STM modeling. The electron-vibration coupling elements \( M^\lambda_{\alpha \beta} \) are defined for every vibrational mode as:

\[
M^\lambda_{\alpha \beta} := \sum_{I,v} \langle \beta | \frac{\partial H}{\partial q^\alpha_{I,v}} | \alpha \rangle \bigg|_{q=0} \frac{\hbar}{2m_I\omega^\lambda},
\]
and can be interpreted as the interaction between states $|\alpha\rangle$ and $|\beta\rangle$ under an infinitesimal displacement of the atoms along the vibrational mode $\lambda$. The derivative in Eq. 3.28 can be written as:

$$\langle \beta | \hat{\partial} \frac{\partial H}{\partial \zeta_{1,v}} | \alpha \rangle = \frac{\partial}{\partial \zeta_{1,v}} \langle \beta | \hat{H} | \alpha \rangle - \langle \beta | \hat{H} | \alpha \rangle - \langle \beta | \hat{H} | \alpha' \rangle,$$

where $|\alpha'\rangle = \partial |\alpha\rangle / \partial \zeta_{1,v}$ represents the change in AOs with displacements. In Ref. 23 is explained how the last two terms in Eq. 3.29 can be calculated, however in this work, these terms have been neglected.

If the Hamiltonian element only depends on the states $|\alpha\rangle$ and $|\beta\rangle$ and the state $|\beta\rangle$ is not moving in the vibrational mode $\lambda$, the electron-vibration couplings are calculated in practice with:

$$M_{\alpha \beta}^\lambda = \sum_\nu \frac{1}{2\delta} \left( H_{\alpha \beta} \left( \zeta = \delta \vec{e}_{1,v} \right) - H_{\alpha \beta} \left( \zeta = -\delta \vec{e}_{1,v} \right) \right) \sqrt{\frac{\hbar}{2m_1\Omega^\lambda}},$$

where only atom $I$ to which AO $|\alpha\rangle$ belongs is moved and $\delta$ is the size of the displacements. However, if the Hamiltonian is calculated in a self-consistent way, for instance with DFT, the calculation of the electron-vibration couplings is performed by displacing all atoms along the directions $Q^\lambda$ simultaneously:

$$M_{\alpha \beta}^\lambda = \frac{1}{2\delta} \left( \left( H_{\alpha \beta} - E_F S_{\alpha \beta} \right) \left( q = \delta Q^\lambda \right) - \left( H_{\alpha \beta} - E_F S_{\alpha \beta} \right) \left( q = -\delta Q^\lambda \right) \right) \sqrt{\frac{\hbar}{2m_1\Omega^\lambda}}. \quad 3.31$$

The terms in Eq. 3.31 involving the overlap matrix are introduced as a correction for a possible Fermi energy shift in a finite cell. 3.1.6 Van-der-Waals interactions in DFT

Both LDA and GGA are approximations to the real exchange-correlation functional involving only local functionals: correlation effects between charge densities separated in space are neglected. In all systems however, an instantaneous charge fluctuation in one region in space can induce an instantaneous dipole in a neighboring region in space, resulting in an attractive dipole-dipole interaction called the Van-der-Waals (vdW) force. These vdW bonds are in general weaker than metallic, ionic or covalent bonds, which are properly described in DFT, and hence these vdW interactions are usually neglected. However, in certain systems one may find components for which these three kinds of bonds are absent or very small, and the vdW bonds play a dominant role and should therefore be included in the DFT calculations. The vdW force at one point
depends on charge fluctuations in another region and is hence a nonlocal (i.e. beyond mean field theory) correlation effect. There are two ways to take these interactions into account: semi-empirical and \textit{ab initio}. Both methods are used in Chapter 7 to calculate the ground state properties of a thiophenol monolayer on Ag(111) and the differences in this particular system are discussed there. This Subsection briefly describes these two methods.

\textbf{Semi-empirical corrections}

The total energy can be corrected by adding an additional attractive energy between each pair of atoms $I$ and $J$:

$$E_{\text{vdW}}^{IJ} = -f_{IJ}(R)\frac{C_6^{IJ}}{R_6^{IJ}},$$

where $R_{IJ} = |\vec{R}_I - \vec{R}_J|$ and the damping factor $f_{IJ}(R)$ goes to 1 for large values of $R_{IJ}$ and to 0 for small values of $R_{IJ}$. The virial coefficient $C_6^{IJ}$ depends on the ionization potentials and the polarizability of the atoms. This correction has been recently implemented in the GREEN-SIESTA interface, which is used throughout this work, providing good results.\textsuperscript{25}

\textbf{Ab initio functional}

The exact density functional\textsuperscript{4,5} contains the vdW interactions, but as pointed out in Subsection 3.1.1 this exact functional is unknown and approximate functionals (like LDA and GGA) are used in practice. The vdW-functional\textsuperscript{26,27} is a correction to the GGA functional, and is written as:

$$E_{\text{xc}}[n] = E_{\text{x}}^{\text{GGA}}[n] + E_{\text{c}}^{\text{nl}}[n].$$

An appropriate GGA exchange functional is selected and a fully \textit{nonlocal} correlation functional is developed that includes an account of vdW forces. This nonlocal correlation part in its most simple form is:

$$E_{\text{c}}^{\text{nl}} = \int d^3\vec{r}\int d^3\vec{r}'\ n(\vec{r})\phi(\vec{r},\vec{r}'\ n(\vec{r}'),$$

where $\phi(\vec{r},\vec{r}')$ is some given, general function depending on $\vec{r} - \vec{r}'$ with $\phi(\vec{r},\vec{r}) = 0$ to make it truly nonlocal and $\phi(\vec{r},\vec{r}') \rightarrow |\vec{r} - \vec{r}'|^{-6}$ for large $|\vec{r} - \vec{r}'|$ to correctly describe the dipole-dipole interaction. By using the functional derivative of $E_{\text{c}}^{\text{nl}}$ with respect to the density $n(\vec{r})$ as a component in the Kohn-Sham Eqs. 3.7, the vdW interactions can be solved fully self-consistently.\textsuperscript{27} This functional, including an efficient implementation to calculate the double spatial integral,\textsuperscript{28} is implemented in the SIESTA code.
3.2 Elastic STM simulations

After the DFT calculations described in Section 3.1 have been performed, the ionic and electronic ground state of the system is known. The charge density matrix as well as the Hamiltonian matrix, describing the interactions between the different electronic states, is known, and one could intuitively think that the conductance of such a system can be deduced from it by summing up the interactions of the bulk atoms of the tip with the bulk atoms of the sample.

However, the Hamiltonian matrix element between two states tends to decrease rapidly for increasing distance between them, so this approach would always lead to a zero conductance. An electron can however travel from one state to another state, even if the Hamiltonian matrix element between them is zero, if it travels via other states which do have interaction with the initial and final state and with each other. This is called multiple scattering, and is clarified in Fig. 3.3.

![Figure 3.3 Schematic drawing of the difference between the Hamiltonian matrix and the Green’s function matrix. Each single arrow represents a direct transition from one electronic state to another and is stored in the Hamiltonian matrix \( H \). Each path of multiple arrows represents a path consisting of many consecutive direct transitions and the sum of all possible paths is stored in the Green’s function matrix \( G \).](image)

A direct transition from one electronic state to another has a probability amplitude given by a combination of the respective overlap matrix and Hamiltonian matrix element. If an electron makes many transitions, it is possible to create a path between any two states, where the probability amplitude of this path is given by the product of the probability amplitudes of the individual transitions. In fact, there are infinitely many
paths between two given states, and the probability amplitude for an electron to travel from one state to another is given by the sum of the probability amplitudes of all paths connecting the two states. The probability amplitude between each pair of states is contained in the *Green's function* matrix $G$, and with this information one is able to extract the conductance of the system, as will be demonstrated in this Section.

The goal of this Section is not to give a full explanation of the Green's function formalism; for this the reader is referred to any textbook on transport through nanosystems.\textsuperscript{29,30,31,32} Instead, this Section presents the equations which are necessary to be able to obtain the matrix $G$ and hence the current through the system. In Subsection 3.2.1 the Green's function matrix for the entire system is defined and a scheme is given to be able to calculate this matrix and subsequently the tunneling current. Subsections 3.2.2 to 3.2.6 explain the details of this scheme to efficiently calculate an STM image and at last Subsection 3.2.7 clarifies how the Slater-Koster parameterization is used to efficiently calculate the coupling between the surface and the tip apex. Inelastic effects will not be incorporated until Chapter 4.

The theory presented in this Section to calculate the Green's functions follows Ref. 34, whereas the current calculation scheme is taken from Ref. 35. The entire scheme is implemented in the GREEN code,\textsuperscript{33} which includes a GREEN-SIESTA interface to perform the DFT calculations under the SIESTA framework and to use these results for the evaluation of the Green's functions.

### 3.2.1 Green's function of the STM system

![Figure 3.4](image)  
**Figure 3.4** Schematic of the STM system, with four different regions: bulk of the sample $s$, (reconstructed) surface of the sample $r$, bulk of the tip $t$ and tip apex $a$. The bulk blocks $s$ and $t$ are considered to be in equilibrium with electron reservoirs at chemical potentials $\mu_s$ and $\mu_t$ respectively.

Fig. 3.4 shows the STM system, which is described by two semi-infinite bulk blocks, the sample and the tip. The sample block is constructed from an infinite stack of bulk layers, labeled with $s$, and is terminated by a (reconstructed) surface, labeled with $r$.  

40
The tip block is also constructed from an infinite stack of bulk layers, labeled with $t$, and is terminated by the tip apex, labeled with $a$. The two blocks may have different chemical elements and/or lattices and the tip may be translated with respect to the sample in all directions or rotated over any axis. Each semi-infinite bulk block is divided into principal layers (PLs), which are chosen thick enough to be allowed to neglect interactions between any nonadjacent PLs, i.e. $S_{ij} := \langle \alpha_n | \hat{S} | \alpha_{n'} \rangle = 0$ and $H_{ij} := \langle \alpha_n | \hat{H} | \alpha_{n'} \rangle = 0$ for $|i - j| > 1$, where $S$ is the overlap matrix, $H$ is the Hamiltonian matrix and $|\alpha_n\rangle$ is any AO in PL $n$. For any given complex energy, the Green’s function matrix $G$ is defined by:

$$G(E) F(E) = F(E) G(E) = I,$$

where $I$ is the identity matrix and $F(E)$ is the secular matrix defined as:

$$F(E) := ES - H,$$

$S$ being the overlap matrix defined in Subsection 3.1.2 and $H$ the Hamiltonian matrix defined in Eq. 3.16. The elements of $F$ are the outcome of the DFT calculations, presented in Section 3.1. Note that all elements of $F$ and $G$ are energy dependent, although this explicit dependence is omitted for clarity from now on. The interaction between the tip and the sample depends strongly on the position and orientation of the tip with respect to the sample and hence should be calculated for each tip position separately. The calculation of these elements is discussed in Subsection 3.2.7.

![Figure 3.5](image)

**Figure 3.5** Schematics and notation for the matrix blocks corresponding to a) the secular matrix $F$ and b) the Green’s function matrix $G$, where each block is a submatrix linking two PLs.

Fig. 3.5 shows the schematics for the matrix blocks corresponding to $F$ and $G$. The secular matrix is block tridiagonal because only nearest-neighbor-PL interactions are...
taken into account. The projection of $F$ on block $n'n'$, denoted with the submatrix $F_{n'n'}$, is a $\left(N_{k'} \cdot N_{\alpha'}\right) \times \left(N_{k'} \cdot N_{\alpha'}\right)$ matrix, where $N_{k'}$ and $N_{\alpha'}$ are the number of k-points and of AOs used in block $n$. The interlayer submatrix where only one specific k-point per PL is taken into account is written as $F_{n'n'}\left(\tilde{k}_n, \tilde{k}'_n\right)$. Since the size of $F$ is in principle infinite, a direct calculation of the inverse is not possible. Instead, the calculation of the Green’s function matrix $G$, the self energy matrix $\Sigma$ (defined later) and the current $I$ consists of the following steps:

1. Calculation of the bulk-related matrices $G_{ss}^0$ and $\Sigma_{ss \pm 1s}$ for the sample and $G_{tt}^0$ and $\Sigma_{tt \pm l}$ for the tip. The superscript 0 is used to indicate that surface-apex interaction is not taken into account.

2. Calculation of the surface-related matrices $G_{rr}^0$ and $\Sigma_{rr}$ for the sample and $G_{aa}^0$ and $\Sigma_{aa}$ for the tip, in the absence of coupling between surface and apex.

3. Calculation of the matrix block $G_{ar}$ by coupling the two independent blocks.

4. Calculation of the current $I$ from $G_{ar}$, $\Sigma_{rr}$ and $\Sigma_{aa}$.

**3.2.2 Step 1: Calculation of GF and SE for isolated bulk**

![Diagram](image)

**Figure 3.6 a)** An infinite one-dimensional chain of atomic blocks, divided into PLs such that there is only nearest-neighbor PL interaction. **b)** The block tridiagonal matrix $F$ and **c)** the matrix $G^0$ corresponding to the system in (a).

Consider the infinite 1D chain depicted in Fig. 3.6. The corresponding secular matrix $F$ is the outcome of a bulk DFT calculation. Due to translation symmetry, the blocks of
$G^0$ depend only on the difference between $n$ and $n'$ and is hence labeled as $G^0_{s\pm ns}$.

Projecting Eq. 3.35 onto the diagonal block $ss$ leads to:

$$I = F_{ss-1}G^0_{s-1s} + F_{ss}G^0_{ss} + F_{ss+1}G^0_{s+1s},$$

3.37

To proceed, the following transfer matrix $T_{n'n}$ is defined by:

$$T_{n'n} := G^0_{nn'} \left( G^0_{nn} \right)^{-1}.$$

3.38

Taking into account that $T_{n'n}$ also only depends on the difference $n' - n$, Eq. 3.37 can be rewritten as:

$$I = \left\{ F_{ss-1}T_{s-1s} + F_{ss} + F_{ss+1}T_{s+1s} \right\} G^0_{ss}.$$

3.39

To obtain the bulk transfer matrices $T_{s\pm 1s}$, an iterative procedure is developed in Refs. 36 and 37, leading to the expressions:

$$T_{s+1s} = t_0 + h_0 t_1 + \ldots + h_0 h_1 \ldots h_{m-1} t_m = \sum_{i=0}^{m} \prod_{j=0}^{i-1} h_j t_i,$$  

3.40

$$T_{s-1s} = h_0 + t_0 h_1 + \ldots + t_0 t_1 \ldots t_{m-1} h_m = \sum_{i=0}^{m} \prod_{j=0}^{i-1} t_j h_i,$$

where $m$ is the maximum iteration step used. The procedure is initialized through:

$$t_0 := - \left( F_{ss} \right)^{-1} F_{s+1s},$$

3.41

$$h_0 := - \left( F_{ss} \right)^{-1} F_{s-1s},$$

and the rest of the matrices $t_i$ and $h_i$ are obtained with:

$$t_i := - \left( I - t_{i-1} h_{i-1} - h_{i-1} t_{i-1} \right)^{-1} t_{i-1}^2,$$

3.42

$$h_i := - \left( I - t_{i-1} h_{i-1} - h_{i-1} t_{i-1} \right)^{-1} h_{i-1}^2,$$

The algorithm is applied until convergence is achieved. A small imaginary part added to the energy $E$ will ensure this convergence. The self energy $\Sigma_{ss\pm 1s}$ of block $s$, due to interactions with neighboring bulk blocks, is defined as:

$$\Sigma_{ss\pm 1s} := F_{ss\pm 1} T_{s\pm 1s}.$$  

3.43

With this definition and Eq. 3.39, the bulk Green’s function matrix $G^0_{ss}$ can be expressed as:

$$G^0_{ss} = \left\{ F_{ss} + \Sigma_{ss-1s} + \Sigma_{ss+1s} \right\}^{-1}.$$  

3.44

Similar expressions can be obtained for the bulk tip self energy and Green’s function matrix by simply replacing $r$ by $a$ and $s$ by $t$. 

43
Figure 3.7 Infinite chain in three dimensions. The principal layers are still only defined in one dimension, in this example the horizontal direction. For the infinite planes perpendicular to the chain, a 2D Brillouin zone is defined.

If the 1D chain is replaced by a periodic 3D chain, as sketched in Fig. 3.7, a 2D Brillouin zone can be defined for the plane normal to the propagation direction, with given k-points. Due to Eq. 3.16, the matrix $F$ is block diagonal in k-blocks. Therefore, also the inverse, matrix $G^0$, is block diagonal in k-blocks. The entire procedure of the 1D chain can now be repeated for each k-point individually, resulting in an expression for the transfer matrices $T_{ss}(\vec{k}_s)$, for the self energy $\Sigma_{ss}(\vec{k}_s)$ and the bulk Green’s function $G^0_{ss}(\vec{k}_s)$, where $\vec{k}_s$ is any sampling k-point defined for block $s$.

3.2.3 Step 2: Calculation of GF and SE for isolated surface

Now consider the semi-infinite 1D chain depicted in Fig. 3.8. The corresponding secular matrix $F$ is the outcome of a slab DFT calculation. Since translation symmetry is broken, the blocks of $G^0$ depend not only on the difference between $n$ and $n'$. Projecting Eq. 3.35 onto the blocks $rr$ and $rs$ leads to respectively:

$$I = F_{rs}G^0_{sr} + F_{rr}G^0_{rr} = \{F_{rs}T_{sr} + F_{rr}\}G^0_{rr} \quad 3.45$$

and:

$$0 = F_{sr}G^0_{rr} + F_{ss}G^0_{sr} + F_{ss-1}G^0_{s-1r}$$
$$= F_{sr}G^0_{rr} + \{F_{ss} + F_{ss-1}T_{s-1r}\}G^0_{rr} \quad 3.46$$
Figure 3.8 a) A semi-infinite one-dimensional chain of atomic blocks, divided into PLs such that there is only nearest-neighbor PL interaction. b) The block tridiagonal matrix $F$ and c) the matrix $G^0$ corresponding to the system in (a).

The matrix $T_{s-1s}$ is identified with the bulk transfer matrix, given in Eq. 3.40. This identification is allowed if the coupling between these PLs is already bulk-like. In practice, this is checked by the difference between the onsite energy of the states for atoms in a bulk calculation and center atoms in a slab calculation, which should be at least below 50 meV. Substituting Eq. 3.46 into Eq. 3.38, leads to an explicit expression for $T_{sr}$:

$$T_{sr} = -\left\{ F_{ss} + F_{ss-1}T_{s-1s} \right\}^{-1} F_{sr}, \quad 3.47$$

The self energy $\Sigma_{rsr}$ of block $r$ due to interactions with block $s$, is defined as:

$$\Sigma_{rsr} := F_{rs}T_{sr}. \quad 3.48$$

With this definition and Eq. 3.45 the surface Green’s function matrix $G^0_{rr}$ can be expressed as:

$$G^0_{rr} = \left\{ F_{rr} + \Sigma_{rsr} \right\}^{-1}. \quad 3.49$$

Again, similar expressions can be obtained for the tip apex self energies and Green’s function by simply replacing $r$ by $a$ and $s$ by $t$. 

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Figure 3.9 The 1D chain, depicted in Fig. 3.8 can be replaced by a periodic 3D chain. In this Figure, the ratio $M$ between the size of block $r$ and the size of block $s$ is 6.

Now suppose that the 1D chain is replaced by a periodic 3D chain, as depicted in Fig. 3.9, where block $r$ is commensurate with block $s$. The ratio between the size of block $r$ and the size of block $s$ is labeled by $M$. Within each block or between two bulk blocks, there is still no k-mixing:

$$F_{rr}(\vec{k}_r, \vec{k}'_r) = \delta_{\vec{k}_r, \vec{k}'_r} F_{rr}(\vec{k}_r),$$

$$F_{ss}(\vec{k}_s, \vec{k}'_s) = \delta_{\vec{k}_s, \vec{k}'_s} F_{ss}(\vec{k}_s),$$

$$F_{ss-1}(\vec{k}_s, \vec{k}'_s) = \delta_{\vec{k}_s, \vec{k}'_s} F_{ss-1}(\vec{k}_s),$$

but each surface k-point $\vec{k}_r$ will couple to bulk k-points $\vec{k}_s = \vec{k}_r + \vec{G}_{rs}$, where $\vec{G}_{rs}$ is any of the $M$ surface reciprocal lattice vectors contained in the bulk first Brillouin zone:

$$F_{rs}(\vec{k}_r, \vec{k}_s) = \delta_{\vec{k}_s, \vec{k}_r + \vec{G}_{rs}} F_{rs}(\vec{k}_r, \vec{k}_r + \vec{G}_{rs}).$$

The projection of Eq. 3.35 now involves a summation over $\vec{G}_{rs}$:

$$I = \sum_{G_{rs}} F_{rs}(\vec{k}_r, \vec{k}_r + \vec{G}_{rs}) T_{sr}(\vec{k}_r + \vec{G}_{rs}, \vec{k}_r)$$

$$+ F_{rr}(\vec{k}_r) G_{rr}^{0}(\vec{k}_r),$$

where the transfer matrix $T_{sr}(\vec{k}_r + \vec{G}_{rs}, \vec{k}_r)$ is obtained with Eq. 3.47:

$$T_{sr}(\vec{k}_r + \vec{G}_{rs}, \vec{k}_r) = -\left( F_{ss}(\vec{k}_r + \vec{G}_{rs}) + F_{ss-1}(\vec{k}_r + \vec{G}_{rs}) \right)$$

$$\times T_{s-1s}(\vec{k}_r + \vec{G}_{rs})^{-1} F_{sr}(\vec{k}_r + \vec{G}_{rs}, \vec{k}_r).$$

With the definition for the k-dependent self-energy $\Sigma_{rsr}(\vec{k}_r)$:
\[
\Sigma_{rsr}(\vec{k}_r) := \sum_{G_{rs}} F_{rs}(\vec{k}_r, \vec{k}_r + \vec{G}_{rs}) T_{sr}(\vec{k}_r + \vec{G}_{rs}, \vec{k}_r),
\]

the surface Green's function \( G_{rr}^0(\vec{k}_r) \) can now be written as:

\[
G_{rr}^0(\vec{k}_r) = \left\{ F_{rr}(\vec{k}_r) + \Sigma_{rsr}(\vec{k}_r) \right\}^{-1}.
\]

### 3.2.4 Step 3: Calculation of coupled GF

After the calculation of the Green's functions and self energies of the isolated blocks, the sample block and tip block are coupled with each other by introducing interactions between PLs \( r \) and \( a \), denoted by \( \Delta F := F_{ar} + F_{ra} \). The Green's function of the total system \( G \) can then be obtained by solving the Dyson equation:

\[
G = G^0 - G^0 \Delta F G.
\]

Projecting Eq. 3.56 onto the interface \( ar \) leads to the following four expressions for the interface Green's functions:

\[
G_{rr} = \left[ \left( G_{rr}^0 \right)^{-1} + F_{ra} G_{aa}^0 F_{ar} \right]^{-1},
\]

\[
G_{aa} = \left[ \left( G_{aa}^0 \right)^{-1} + F_{ar} G_{rr}^0 F_{aa} \right]^{-1},
\]

\[
G_{ar} = G_{aa}^0 F_{ar} G_{rr},
\]

\[
G_{ra} = G_{rr}^0 F_{ra} G_{aa}.
\]

In the calculation of \( G_{rr} \), k-mixing is induced at \( r \) by the interaction with the apex, i.e. an electron with initial momentum \( \vec{k}_r \) can tunnel to \( a \), where it loses the parallel momentum and then tunnel back to \( r \) picking up momentum \( \vec{k}_r' \). Therefore \( G_{rr} \) is not block diagonal in k-points and the matrix to be inverted contains all blocks \( (\vec{k}_r, \vec{k}_r') \). Its dimensions can become too large (larger than \( 10^3 \times 10^3 \)) to render the method efficient. One may circumvent this drawback by exploiting the fact that the STM typically works under the tunneling regime, in which case the tip-sample interactions \( F_{ar} \) become exponentially small and one may expand the Dyson equation only up to first order in \( F_{ar} \):

\[
G = G^0 + G^0 \Delta F G^0 + G^0 \Delta F G^0 \Delta F G^0 + \cdots \approx G^0 + G^0 \Delta F G^0.
\]

This approximation removes any multiple scattering in the vacuum region and implies that the electrons tunnel only once, having no probability of subsequent tunneling back and forth. As long as the transport takes place in the tunneling regime, this approximation is perfectly valid.\(^{34}\) Indeed this is crucial in the STM formalism and in
the LOIT method, explained in Chapter 4. It leads, when projected onto the interface \( ar \), to the following four simple and inversion-free expressions:

\[
G_{rr} \left( \vec{k}_r, \vec{k}_r' \right) = \delta_{\vec{k}_r, \vec{k}_r'} G_{rr}^0 \left( \vec{k}_r \right),
\]

\[
G_{aa} \left( \vec{k}_a, \vec{k}_a' \right) = \delta_{\vec{k}_a, \vec{k}_a'} G_{aa}^0 \left( \vec{k}_a \right),
\]

\[
G_{ar} \left( \vec{k}_a, \vec{k}_r \right) = G_{aa}^0 \left( \vec{k}_a \right) F_{ar} \left( \vec{k}_a, \vec{k}_r \right) G_{rr}^0 \left( \vec{k}_r \right),
\]

\[
G_{ra} \left( \vec{k}_r, \vec{k}_a \right) = G_{rr}^0 \left( \vec{k}_r \right) F_{ra} \left( \vec{k}_r, \vec{k}_a \right) G_{aa}^0 \left( \vec{k}_a \right),
\]

where k-dependence is explicitly taken into account for completeness.

3.2.5 Step 4: Calculation of the current

To calculate the current through the system, the Landauer-Büttiker picture\(^{38}\) is adopted and hence it is assumed that the bulk of the sample and the bulk of the tip are each in equilibrium with chemical potentials \( \mu_s \) and \( \mu_t \), respectively, which are shifted with respect to each other by applying an external bias \( V \) such that \( eV = \mu_s - \mu_t \) with \( e < 0 \). When \( V < 0 \), then \( \mu_s > \mu_t \) and electron flow is directed from sample to tip, while when \( V > 0 \), the empty states of the sample are probed. The elastic tunneling current \( I(V, \vec{r}) \) for any relative tip-sample position \( \vec{r} \) is given by Eq. 2.2. If the energies are given in eV, as is often used in these type of calculations, the prefactor contains an additional factor \( |e| \). The transmission function \( g(E, V, \vec{R}) \) is given by:\(^{23,32,35}\)

\[
g = \text{Tr} \left[ \Gamma_r G_{ra} \Gamma_a G_{ra}^\dagger \right],
\]

where \( \Gamma_r \) is the coupling matrix of the sample. It is a measure for the coupling strength between the surface block \( r \) and the bulk block of the sample \( s \), and is defined as:

\[
\Gamma_r := - \left[ \Sigma_{rsr} - \Sigma_{sr}^\dagger \right] = - 2 \text{Im} \left[ \Sigma_{rsr} \right],
\]

where \( \Sigma_{rsr} \) is the self energy defined in Eq. 3.48. A similar definition holds for the tip contact matrix \( \Gamma_a \). Substituting Eq. 3.59 into Eq. 3.60, the first order transmission function can be written as:

\[
g \left( E, V, \vec{R} \right) = \text{Tr} \left[ \Gamma_r \left( G_{rr}^0 F_{ra} G_{aa}^0 \right) \Gamma_a \left( G_{aa}^0 F_{ar} G_{rr}^0 \right) \right]
\]

\[
= \text{Tr} \left[ \rho_r^0 \left( E - \mu_s \right) F_{ar} \left( \vec{R} \right) \rho_s^0 \left( E - \mu_t \right) F_{ra} \left( \vec{R} \right) \right],
\]

where the density of scattering states matrices \( \rho_r^0 \) and \( \rho_a^0 \) are defined as:

\[
\rho_r^0 \left( E \right) := G_{rr}^0 \left( E \right) \Gamma_r \left( E \right) G_{rr}^0 \left( E \right),
\]

\[
\rho_a^0 \left( E \right) := G_{aa}^0 \left( E \right) \Gamma_a \left( E \right) G_{aa}^0 \left( E \right),
\]

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and where the cyclic property of the trace is used. These contact matrices are independent of the relative tip-sample position \( \vec{R} \) and the applied bias \( V \) and can hence be calculated independently for the surface and the apex for a fine energy grid around their respective Fermi energies and then stored to disk. Eq. 3.62 shows that the only matrix to be updated for each \( \vec{R} \) is \( \rho_{ar} \).

In order to minimize disk space, the large contact matrices are diagonalized and their spectral representation is used:

\[
\begin{align*}
\rho_r^0 &= \sum_{m_r} \left| \left\langle u_{\rho_r^0}^m \right| \left| u_{\rho_r^0}^m \right\rangle \right|^2, \\
\rho_a^0 &= \sum_{m_a} \left| \left\langle u_{\rho_a^0}^m \right| \left| u_{\rho_a^0}^m \right\rangle \right|^2,
\end{align*}
\]

where the eigenvectors \( \left| u_{\rho_r^0}^m \right\rangle \) are scaled by the square root of the corresponding eigenvalue and the summation runs over all \( m \) with an eigenvalue larger than a small predefined tolerance limit. With this representation, the transmission function can be written as:

\[
g = \sum_{m_r,m_a} \left| \left\langle u_{\rho_r^0}^m \left| F_{ar} \left( \vec{R} \right) \right| u_{\rho_a^0}^m \right\rangle \right|^2.
\]

### 3.2.6 STM simulations

An STM image is now calculated as follows:

1. Perform DFT calculations for the bulk of the sample and tip to obtain bulk Hamiltonian and overlap matrices and obtain \( F_{ss}, F_{ss\pm1}, F_{st}, \) and \( F_{st\pm1}. \)

2. Perform DFT calculations for the isolated surface and tip apex to obtain surface Hamiltonian and overlap matrices and obtain \( F_{rr}, F_{rs}, F_{sr}, F_{aa}, F_{at}, \) and \( F_{ta}. \)

   This is done for a slab with extra layers in order to ensure self-consistency.

3. Run steps 1 and 2, described in this Section, to obtain the isolated Green's functions \( G_{rr}^0 \) and \( G_{aa}^0 \) and self energies due to coupling with their respective electrodes \( \Sigma_{rst} \) and \( \Sigma_{ata}. \)

4. Diagonalize \( \rho_r^0 \) and \( \rho_a^0 \), defined in Eq. 3.63, and save the eigenvectors to disk.

5. Per pixel:

   - Choose an initial tip-sample position \( z \).
   - Calculate \( F_{ar} \), described in Subsection 3.2.7.
   - Calculate \( g(E,V,\vec{R}) \) with Eq. 3.65 and with it the current \( I \) with Eq. 2.2.
   - Update \( z \) and recalculate \( I \) until the current equals a predefined current setpoint.
For a second STM image, e.g. with a different bias $V$, or for an additional $IV$ curve, steps 1-4 do not have to be repeated.

### 3.2.7 Slater-Koster parameterization

As pointed out in Subsection 3.2.1, the interaction $F_{ar}$ between surface and tip apex depends strongly on the relative tip-sample position $\tilde{R}$ and it would be too time consuming to recalculate these matrix elements with DFT for each tip displacement. Therefore another method is required to obtain these matrix elements. Early attempts adopted the Extended Hückel Theory, in which the interaction between any two surface and tip AOs is approximated by setting them proportional to the overlap according to:

$$H_{\alpha\beta} = K_{EHT} \frac{E_{\alpha} + E_{\beta}}{2} S_{\alpha\beta}, \quad 3.66$$

where $K_{EHT}$ is a dimensionless scalar. The onsite energies $E_{i}$ are obtained by fitting the obtained band structures with this method to ab initio band structure calculations. The fitted EHT parameters were then applied to the entire system, i.e. bulk electrodes and STM interface. For large cells however, this fitting procedure is computationally too expensive and the method is not efficient anymore.

An alternative way is to keep the *ab initio* description of the decoupled surface and tip semi-infinite blocks, as explained in Subsection 3.2.1, and adopt a Slater-Koster (SK) parameterization scheme for the surface-tip interactions only. The SK formulas provide a simple way to approximate the interactions between any two AOs via:

$$H_{\alpha\beta} = \sum_{\mu} R_{\mu} (R_{\alpha\beta}) f_{\mu}^{SK} (\tilde{R}_{\alpha\beta}), \quad 3.67$$

where $R_{\alpha\beta} = |\tilde{R}_{\alpha\beta}|$ and $\mu$ denotes the quantum numbers $\{l_{\alpha}, l_{\beta}, m_{\alpha}, m_{\beta}\}$ of the AOs $|\alpha\rangle$ and $|\beta\rangle$. $f_{\mu}^{SK}$ are the SK formulas that depend only on the quantum numbers $\mu$ and the orientation of the vector linking the AOs, $\tilde{R}_{\alpha\beta}$, while $R_{\mu}$ are radial functions that only depend on the distance between the two AOs. The overlap matrix elements are parameterized as well with SK formulas, similar to Eq. 3.67. Since for any realistic tip-sample distance the interactions correspond to the tunneling regime, the radial functions are assumed to decay exponentially with $R_{\alpha\beta}$ according to:

$$R_{\mu} (R_{\alpha\beta}) = A_{\mu} \exp \left[ -\kappa_{\mu} R_{\alpha\beta} \right]. \quad 3.68$$
To obtain the SK parameters $A_\mu$ and $\kappa_\mu$, they are fitted to DFT calculations. This Subsection presents three schemes to perform this fitting procedure, summarized in Fig. 3.10. In the first scheme, the decay factors $\kappa_\mu$ are fixed to 1.0 Å$^{-1}$ for all $\mu$ to reproduce the expected experimental decay. This leaves only the coefficients $A_\mu$ as free parameters. For the DFT calculations, a slab consisting of the first surface layer plus any adsorbates and the tip apex atoms is constructed, with the atomic positions fixed. The tip apex is placed at several tens of different sites and heights from the surface and the Hamiltonian and overlap matrix elements are obtained from DFT employing the same basis set as for the geometry optimization. The parameters $A_\mu$ are then fitted to these matrix elements. With this scheme, the DFT calculated interactions are more contracted than the fitted ones, implying that their decay constant is larger than 1.0 Å$^{-1}$. This is caused by the localized nature of the AOs generated by SIESTA; employing a confinement energy of 100 meV in their generation yields contracted AOs which decay too fast. This is not a serious problem in condensed systems, but for surfaces it does not reproduce correctly the decay of the wavefunctions into vacuum.

In the second scheme, the decay factors are not fixed, and interactions and overlaps between any two states are derived from fits to DFT calculations with extended basis sets. In practice the confinement energy is set to a much lower value of 10 meV, for which already a reasonable asymptotic decay is found in the Hamiltonian matrix elements. The disadvantage of this scheme is that, since these calculations are computationally expensive due to the long range of the AOs, only two atoms are taken into account in the DFT calculations. The parameters $A_\mu$ and $\kappa_\mu$ are then fitted to the obtained matrix elements. An advantage of this scheme is that one may construct a database between any two species for all interatomic interactions.

Figure 3.10 Properties of the three schemes to fit the SK parameters to DFT derived results.
The third scheme mixes the first two schemes. The decay factors are not fixed and extended basis sets are used, again with a confinement energy of 10 meV. The fits are done to DFT results in which atoms of molecules such as CO or NO (to be used in Chapters 6 and 7) are in their molecular environment. The thus obtained interactions are expected to better agree with the real interactions, while extended orbitals can still be used. Fits for three representative pairs of orbitals are shown in Fig. 3.11 for the parameterization scheme 2 and 3. The exact details of this Figure are unimportant here, only the matching between the DFT derived interactions (dark circles) and the Slater-Koster interactions (light circles). It can be seen that the decay rate of the SK-interactions follow the DFT-interactions, and the general fit quality is good.

These two sets of SK parameters will be used in subsequent Chapters to obtain the tip-sample interactions. With these interactions and the theory described in this Chapter, the elastic current through the STM junction can be calculated. Before this theory is applied to realistic systems however, the inelastic effects are incorporated into the theory as well. How this is done will be explained in the next Chapter.
3.3 Bibliography

Chapter 4 – Lowest order in inelastic tunneling in a one dimensional model

Electrical current is affected by the interaction between electrons and ions, and consequently electrons may undergo inelastic transitions between states of different energy, even if the electrons are considered non-interacting with each other. The importance of these inelastic effects in electronic transport in molecular junctions is widely recognized and reviewed in literature.\textsuperscript{1,2} When trying to describe these processes theoretically, there are two main approaches to include these inelastic effects. The first approach is to include this interaction in the DFT procedure, generalizing it to time dependent DFT (TDDFT),\textsuperscript{3,4} which has indeed been used to model the conductance of molecular wires.\textsuperscript{5,6} The most widely used approach however, and also the approach taken in this work, uses a combination of ground state DFT with non-equilibrium Green's functions (NEGF).\textsuperscript{7} No formal derivation of the formalism will be given in this Chapter; this can be found in many textbooks.\textsuperscript{8,9,10,11,12}

Within the NEGF formalism, there are still many approximations to make. The purpose of this Chapter is to present and validate a main approximation developed in this thesis in order to efficiently calculate inelastic tunneling in an STM setup. This approximation is demonstrated by using a simple 1D model, in which the surface of the sample and the apex of the tip are each modeled as a single electronic level, skipping the need of \textit{ab initio} DFT calculations.

In Section 4.1, the general 1D model and the adapted 1D model are defined, after which a general solving procedure at the self-consistent Born approximation (SCBA) level is given in Section 4.2. After it is shown in this Section that inelastic tunneling must be taken into account, the \textit{lowest order in inelastic tunneling} (LOIT) approach is introduced and explained in detail in Section 4.3. In Section 4.4 this method is compared with the SCBA approach, and Section 4.5 describes how the LOIT method is implemented in the GREEN program, which is described in Section 3.2. In the end, the main conclusions of the Chapter are summarized in Section 4.6.

4.1 One dimensional model

A simple 1D model is often used in literature to investigate the influence of several input parameters on transport and heating properties of a molecular transport junction (MTJ), like a break junction or an STM.\textsuperscript{2} To gain a deeper insight into the importance of the different parameters on the transport in the realistic 3D calculations, the 1D model has been slightly modified in this work to include two levels, representing the surface and the tip. This Section defines the two models and presents the different regimes in which transport can take place and approximations which can be made.
4.1.1 One-level system: 1LS

Figure 4.1 A schematic view of a transport junction. a) The dashed rectangle defines the central region of the junction. b) The ingredients of the 1LS, represented in an energy diagram.

The 1D model used in general is schematically drawn in Fig. 4.1, and is referred to as the one-level system (1LS) throughout this Chapter. It consists of a single electronic level (called bridge) with given energy $\epsilon_0$, coupled to a left and right electrode with respective coupling strengths $\Gamma_L$ and $\Gamma_R$. The injection gap $E_G$ is defined as the energy difference between $\epsilon_0$ and the closest electrode Fermi energy. There are one or more vibrational modes $\lambda$ active at the bridge, with vibrational energy $\Omega^\lambda$ and coupling strength $M^\lambda$ to the bridge level. The electrodes are considered to be in thermal equilibrium with respective chemical potentials $\mu_L$ and $\mu_R$, where $\mu_L - \mu_R = eV$. They are in the wide band limit (WBL) and have no interactions with any vibrations. The single level treats the entire central region of the junction, indicated by the dashed box in Fig. 4.1a, as a black box, neglecting any details within this region. The effect of all these parameters are thoroughly investigated and reviewed in literature. Here, a brief overview is given to indicate which parameters define the tunneling regime, which is always assumed in this thesis. The regimes in which the electron transport occurs can be distinguished by several energy scales, which are sketched in Fig. 4.2. In Fig. 4.2a, the regimes are classified by the size of the energy gap $E_G$ and the coupling to the electrodes $\Gamma_{L/R}$. If both $E_G$ and $\Gamma_{L/R}$ are small (regime I in Fig. 4.2a), a Coulomb blockade could occur, which is found both experimentally and theoretically. This Coulomb blocking does not occur if the coupling of the level to the electrodes is increased. In this regime (regime II in Fig. 4.2a) hysteresis effects and polaronic transport dominate the transport properties, also observed both in experiments and theory. The regions III and IV in Fig. 4.2a are characterized by a bridge level far away from the Fermi levels of the electrodes, i.e. large $E_G$. 

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Figure 4.2  

**a)** Different transport regimes for a molecular junction, depending on the injection gap $E_G$ and on the coupling strengths $\Gamma_{L,R}$ with the electrodes. Figure taken from Ref. 19.  

**b)** Different transport regimes for a molecular junction, depending on the asymmetry between the coupling strengths $\Gamma_L$ and $\Gamma_R$ and the transmission $\tau$ through the junction. Figure taken from Ref. 20.

At low voltages, the $IV$ curves in these regimes look similar. Vibrational effects can only be seen in the $d^2I/dV^2$ curves. Since $E_G$ is large in these regimes, transport has to take place via tunneling. An STM typically operates in these regimes (under low voltage). In Fig. 4.2b, the regimes are classified by the size of asymmetry in coupling strength $\alpha = \Gamma_R/\Gamma_L$ and the transmission $\tau$ at the Fermi energy, which is a measure for the conductivity of the junction and is similarly defined as the transmission function $g(E,V,\vec{R})$ in Eq. 2.2. The maximum transmission depends on the asymmetry, and is indicated by the black line. For small transmission, the inelastic effects are typically seen as peaks in the $d^2I/dV^2$ curves at positive voltages, while they are seen as dips for bigger transmissions. For symmetric devices, this crossover is found experimentally$^{17}$ and theoretically$^{18}$ to be at $\tau = 0.5$. For asymmetric devices, the red dashed line in Fig. 4.2b indicates this crossover. An STM setup is characterized by a big asymmetry in the two contact strengths and a small transmission, so this regime is found in the bottom left corner of the Figure. If the level is on resonance (i.e. between the two Fermi energies of the electrodes), dips are observed at positive voltages in the $d^2I/dV^2$ curves, which become peaks if the level is off resonance.

The most general solution of this model is obtained by using the self-consistent Born approximation (SCBA) to update the Green's functions of the electrons and the vibrations.$^{21,22}$ Approximations to be made are i) not updating the vibrational Green's functions,$^{23}$ ii) updating the electron Green's function only once, which is referred to as the Born approximation (BA)$^{22}$ or not at all, which is referred to as the lowest order perturbation theory (LOPT)$^{22}$ and iii) evaluating the electron Green's function only at the Fermi energy $E_F$, which is referred to as the lowest order expansion (LOE)$^{18}$

Approximation i is valid if the vibration excitation rate is small with respect to the vibrational damping rate, and is made throughout this thesis. Approximation ii indicates
low probability for multivibration processes and is valid for small electron-vibration couplings with respect to coupling to the electrodes, which is the case for small electron traversal times when compared to the vibration scattering time.\(^2\) Approximation iii is valid for slowly varying DOS of the bridge over a few vibrational energies around the Fermi energy.\(^{18}\)

4.1.2 Two-level system: 2LS

![Figure 4.3](image.png)

**Figure 4.3** A schematic view of an STM junction. a) The dashed rectangle defines the central region of the STM junction. b) The ingredients of the 2LS, represented in an energy diagram.

The main motivation to introduce an additional level to the system is the assumption that each level is tightly bound to one of the electrodes, while the interactions among them are small. This leads to a big asymmetry in the electron-vibration coupling inside one level on the one hand and between the two levels on the other hand. To this end, and to gain a better insight into the black box of the junction, the 1LS is modified in this Section. The new model, displayed in Fig. 4.3, is referred to as the two-level system (2LS) throughout this Chapter. The bridge electronic level has been replaced with two levels: a single electronic level, labeled \(L\) at energy \(\varepsilon_L\) and with coupling \(\Gamma_L\) to the left electrode and no direct coupling to the right electrode and a single electronic level, labeled \(R\) at energy \(\varepsilon_R\) and with coupling \(\Gamma_R\) to the right electrode and no direct coupling to the left electrode. These two levels represent the surface of the sample and the apex of the tip, while the two electrodes represent the bulk of the sample and tip. The tip and surface are assumed to be perfectly conducting, which means that the levels \(L\) and \(R\) are in thermal equilibrium with their respective electrodes and the entire vacuum drop is at the vacuum region. Coupling between the two levels is enabled through the elastic tunneling matrix element \(t_{LR}\) and the electron-vibration coupling matrix elements \(M_{\alpha\beta}^\lambda\) enable inelastic coupling between the states \(\alpha\) and \(\beta\), where \(\alpha,\beta = L,R\). The key difference with the 1LS is the explicit distinction between the
electron-vibration coupling inside a single level \( M_{LL/RR} \) and the coupling between the two states on either side of the vacuum gap \( M_{LR} \). Furthermore, this model gives a more intuitive insight in the various physical parameters and closer resembles the final implementation in the GREEN program.

### 4.2 Solving strategies

To extract the current through the 2LS with the given parameters, the NEGF formalism is employed. In this Section, first the problem of how to calculate the current through the system is defined, and definitions used throughout this Chapter are introduced in Subsection 4.2.1. After this, the approach with the least approximation, the SCBA approach, is explained and exemplified in Subsection 4.2.2, after which an attempt for simplification is made in Subsection 4.2.3 by neglecting all inelastic tunneling terms.

#### 4.2.1 Problem statement and definitions

The definitions of the used functions are presented in Table 4.1. To simplify the notation, the energy dependence is often omitted in this Chapter; the definitions of the used energy dependences are presented in Table 4.2.

**Table 4.1 Definitions of functions used in this Chapter. The superscript \( \gamma \) can be any label to distinguish several types of Green's functions / self energies.**

<table>
<thead>
<tr>
<th>Function</th>
<th>Definition / description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{FD}(E) )</td>
<td>Fermi-Dirac distribution</td>
</tr>
<tr>
<td>( n'_{FD}(E) )</td>
<td>( n_{FD}(E) - 1 )</td>
</tr>
<tr>
<td>( n_B(\omega) )</td>
<td>Bose-Einstein distribution</td>
</tr>
<tr>
<td>( n'B(\omega) )</td>
<td>( n_B(\omega) + 1 )</td>
</tr>
<tr>
<td>( G_{\alpha\beta}^{\gamma}(E) )</td>
<td>Green’s function between states ( \alpha ) and ( \beta ) with label ( \gamma )</td>
</tr>
<tr>
<td>( \Sigma_{\alpha\beta}^{\gamma}(E) )</td>
<td>Self energy between states ( \alpha ) and ( \beta ) with label ( \gamma )</td>
</tr>
<tr>
<td>( \Gamma_{\alpha}^{\gamma}(E) )</td>
<td>Contact matrix of state ( \alpha ) with label ( \gamma )</td>
</tr>
<tr>
<td>( g_{\alpha}^{\gamma}(E) )</td>
<td>Transmission function at electrode ( \alpha ) with label ( \gamma )</td>
</tr>
</tbody>
</table>
Table 4.2 Definitions of energy dependences used in this Chapter. Here, $\Omega^\lambda$ is the energy of a vibrational mode with label $\lambda$. The superscript $\gamma$ represents any label defined throughout the text (e.g. eph, 0, <, etc.).

<table>
<thead>
<tr>
<th>Function</th>
<th>Energy dependence</th>
<th>Function</th>
<th>Energy dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_\alpha$</td>
<td>$n_{FD}^\alpha (E - \mu_\alpha)$</td>
<td>$n'_\alpha$</td>
<td>$n'<em>{FD}^\alpha (E - \mu</em>\alpha)$</td>
</tr>
<tr>
<td>$n^\lambda_B$</td>
<td>$n_B^\lambda (\Omega^\lambda)$</td>
<td>$n'_B^\lambda$</td>
<td>$n'_{B}^\lambda (\Omega^\lambda)$</td>
</tr>
<tr>
<td>$G_{aa}^\gamma$</td>
<td>$G_{aa}^\gamma (E - \mu_\alpha)$</td>
<td>$G_{aa}^{\gamma \pm \lambda}$</td>
<td>$G_{aa}^{\gamma \pm \lambda} (E - \mu_\alpha \pm \Omega^\lambda)$</td>
</tr>
<tr>
<td>$\Sigma_{aa}^\gamma$</td>
<td>$\Sigma_{aa}^\gamma (E - \mu_\alpha)$</td>
<td>$\Sigma_{aa}^{\gamma \pm \lambda}$</td>
<td>$\Sigma_{aa}^{\gamma \pm \lambda} (E - \mu_\alpha \pm \Omega^\lambda)$</td>
</tr>
<tr>
<td>$\Gamma^\gamma_\alpha$</td>
<td>$\Gamma^\gamma_\alpha (E - \mu_\alpha)$</td>
<td>$\Gamma^{\gamma \pm \lambda}_\alpha$</td>
<td>$\Gamma^{\gamma \pm \lambda}<em>\alpha (E - \mu</em>\alpha \pm \Omega^\lambda)$</td>
</tr>
<tr>
<td>$g_{\alpha}^\gamma$</td>
<td>$g_{\alpha}^\gamma (E)$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The current at lead $\alpha = L, R$ is calculated with the Wingreen-Meir formula:\textsuperscript{22}

$$I_\alpha = \frac{e}{\pi \hbar} \left( dE \left\{ \sum_{aa}^{\alpha <} G_{aa}^{\text{eph}, >} - \sum_{aa}^{\alpha >} G_{aa}^{\text{eph}, <} \right\} \right). \quad 4.1$$

The superscripts $<$ and $>$ indicate lesser and greater Green's functions or self energies respectively. The main difference with the approach from Chapter 3 is that the Green's functions to be used are dressed with electron-vibration interactions, indicated by the superscript eph. In the absence of electron-vibration coupling, this formula is equivalent to the Landauer-Büttiker formula, Eq. 3.60. The challenge is now to calculate the dressed lesser and greater Green's functions. There are several approaches possible to calculate these, with a variety of interactions taken into account. Two of them are presented here. The first one takes the considered interactions up to full order into account and is presented in Subsection 4.2.2. The second one takes the interactions between $L$ and $R$ only up to lowest order into account and is presented in Section 4.3. Both approaches start with the following steps to couple the levels to the electrodes for every bias point $V$:

1. The chemical potentials are defined as:

$$\mu_L = \frac{1}{2} eV,$$

$$\mu_R = -\frac{1}{2} eV.$$ \quad 4.2

Note that $e$ is negative. These definitions satisfy the STM convention that if $V < 0$, electrons flow from sample to tip, in this case from $L$ to $R$. 

60
2. The self energy due to coupling of the electronic levels to the electrodes is given by:

\[ \Sigma^a_{aa} = -\frac{i}{2} \Gamma^a, \]

\[ \Sigma^{a,<}_{aa} = i n^a \Gamma^a, \]

\[ \Sigma^{a,>}_{aa} = i n^a \Gamma^a. \]

Green's functions and self energies without superscript denote the retarded versions. Throughout this Chapter, and in order to ease the formalism, the electrodes are assumed to be in the WBL, so that the contact matrices \( \Gamma^a \) are energy independent. However, this approximation can be very simply lifted without altering the final equations and indeed for the realistic 3D modeling presented in Section 4.5 the WBL is dropped.

3. With the following definition:

\[ F_{aa} := E - \varepsilon_a - \varepsilon_i - \Sigma_{aa}, \]

where \( \varepsilon_i \) is a fixed, small imaginary energy, the zero-order (in electron-vibration coupling) Green’s functions are written as:

\[ G = F^{-1}, \]

\[ G^< = G \left\{ \Sigma^{<,L} + \Sigma^{R,<} \right\} G^\dagger, \]

\[ G^> = G \left\{ \Sigma^{L,>} + \Sigma^{R,>} \right\} G^\dagger. \]

Without any coupling between the two levels, i.e. \( t_{LR} = M_{LR} = 0 \), the diagonal elements of these 2×2 Green's function matrices can be calculated separately with:

\[ G_{aa} = F_{aa}^{-1}, \]

\[ G_{aa}^< = G_{aa} \Sigma_{aa}^a G_{aa}^\dagger, \]

\[ G_{aa}^> = G_{aa} \Sigma_{aa}^{a,a>} G_{aa}^\dagger, \]

while the off-diagonal elements are zero. If level \( a \) is considered in the WBL, Eq. 4.4 is modified to read:

\[ F_{aa} = -\varepsilon_a - \varepsilon_i - \Sigma_{aa} \quad \text{(wide band limit)}. \]

Note that while the electrodes are always assumed to be in the WBL, the levels are only in the WBL if explicitly mentioned.
4. To update the Green's functions with the electron-vibration interactions, the phonon Green's functions $D^{i,<} (\omega)$ and $D^{i,>} (\omega)$ are required. In this work, they are not updated; instead the unperturbed Green's functions are used, defined as:\textsuperscript{7,22}

$$D^{i,<} (\omega) := -2\pi i \left\{ n^i_\beta \delta \left( \omega - \Omega^i \right) + n^i_\beta \delta \left( \omega + \Omega^i \right) \right\},$$

$$D^{i,>} (\omega) := -2\pi i \left\{ n^i_\beta \delta \left( \omega + \Omega^i \right) + n^i_\beta \delta \left( \omega - \Omega^i \right) \right\}.$$  

4.2.2 SCBA solving procedure

This Subsection describes the SCBA approach, which for the 2LS is the one with the least number of approximations. The SCBA approach consists of the following steps to calculate the current for every bias point $V$:

5. The elastic tunneling is taken into account up to full order. In order to do this, the off-diagonal terms in $F$ are written as:

$$F_{LR} = F_{RL} = -t_{LR}.$$  

The Green's functions are still defined by Eq. 4.5, but since the levels are coupled now, Eq. 4.6 does not hold anymore but should be replaced with:

$$G_{aa} = \left( F_{aa} - F_{ab} F_{\beta \beta}^{-1} F_{\beta a} \right)^{-1},$$

$$G_{a\beta} = -F_{aa}^{-1} F_{a\beta} G_{\beta \beta} \quad \text{if } \alpha \neq \beta,$$

$$G_{a\beta}^{<} = \sum_{\gamma, \delta = L, R} G_{a\gamma} \left\{ \Sigma_{\gamma \delta}^{L,<} + \Sigma_{\gamma \delta}^{R,<} \right\} \left[ G^+ \right]_{\delta \beta},$$

$$G_{a\beta}^{>} = \sum_{\gamma, \delta = L, R} G_{a\gamma} \left\{ \Sigma_{\gamma \delta}^{L,>} + \Sigma_{\gamma \delta}^{R,>} \right\} \left[ G^+ \right]_{\delta \beta}.$$  

6. Here starts the SCBA approach for the vibrations. The Green's functions with electron-vibration coupling taken into account, labeled by the superscript $eph$, are initialized as the zero-order Green's functions:

$$G^{eph} = G,$$

$$G^{eph,<} = G^{<},$$

$$G^{eph,>} = G^{>}.$$
7. The self energy due to electron-vibration coupling is calculated by taking only the Fock diagram into account:

\[
\Sigma_{\alpha\beta}^{eph,\ <} (E) = i \int_{0}^{\infty} \frac{d\omega}{2\pi} \sum_{\lambda} \sum_{\gamma,\delta=L,R} \left\{ M_{\alpha\gamma}^{\lambda} \right\},
\]

\[
D^{\lambda,\ <} (\omega) G_{\gamma\delta}^{eph,\ <} (E - \omega) M_{\delta\beta}^{\lambda},
\]

\[
\Sigma_{\alpha\beta}^{eph,\ >} (E) = i \int_{0}^{\infty} \frac{d\omega}{2\pi} \sum_{\lambda} \sum_{\gamma,\delta=L,R} \left\{ M_{\alpha\gamma}^{\lambda} \right\},
\]

\[
D^{\lambda,\ >} (\omega) G_{\gamma\delta}^{eph,\ >} (E - \omega) M_{\delta\beta}^{\lambda},
\]

\[
\Sigma_{\alpha\beta}^{eph} (E) = \frac{1}{2} \left[ \Sigma_{\alpha\beta}^{eph,\ >} (E) - \Sigma_{\alpha\beta}^{eph,\ <} (E) \right] - \frac{i}{2} \mathcal{H}_{E'} \left\{ \Sigma_{\alpha\beta}^{eph,\ >} (E') - \Sigma_{\alpha\beta}^{eph,\ <} (E') \right\} (E).
\]

Here the functional \( \mathcal{H}_{E} \) represents the Hilbert transform and is a simple linear operation. The Hartree diagram is neglected, since it only induces a static shift in the retarded self energy and hence does not lead to a signal at the vibrational threshold voltage.

8. The Green’s functions are updated with the self energies from Eq. 4.12.

\[
G_{\alpha\beta}^{eph,\ <} = \left( F - \Sigma_{\alpha\beta}^{eph} \right)^{-1},
\]

\[
G_{\alpha\beta}^{eph,\ >} = G_{\alpha\beta}^{eph} \left\{ \Sigma_{\alpha\beta}^{L,\ <} + \Sigma_{\alpha\beta}^{R,\ <} + \Sigma_{\alpha\beta}^{eph,\ <} \right\} G_{\gamma\delta}^{eph,\ ^{\dagger}},
\]

\[
G_{\alpha\beta}^{eph,\ >} = G_{\alpha\beta}^{eph} \left\{ \Sigma_{\alpha\beta}^{L,\ >} + \Sigma_{\alpha\beta}^{R,\ >} + \Sigma_{\alpha\beta}^{eph,\ >} \right\} G_{\gamma\delta}^{eph,\ ^{\dagger}}.
\]

9. Steps 7 and 8 are repeated until the difference between any two subsequent Green’s functions is less than a predefined tolerance limit for all energies, in this Chapter set to \( 10^{-16} \) meV.

10. The current at electrode \( \alpha \) is calculated using the Wingreen-Meir formula, Eq. 4.1.

Using the 2LS, the different tunneling transport regimes presented in Fig. 4.2 have been explored using this SCBA approach. The additional approximation made for these calculations is that one of the levels is considered to be in the WBL. The results for regime I in Fig. 4.2a are shown in Fig. 4.4, whereas the results for the regimes in the blow-up in Fig. 4.2b are shown in Fig. 4.5. As already pointed out in Section 1.2, the vibrational fingerprints in regime I in Fig. 4.2a are not peaks and dips in the \( d^2I/dV^2 \) spectrum, but satellite peaks in the \( dI/dV \) spectrum around the main resonant peak. It is shown that both the intensity of the satellite peaks and the renormalization energy, defined as the shift of the main resonant peak, grow as the electron-vibration coupling strength is increased. There are no satellite peaks for \( |e|V < \varepsilon_L \) due to the chosen low
value of $kT$, making absorption processes highly unlikely. There is still a non-resonant contribution visible in the IETS curve, which is defined as $\left(\frac{d^2I}{dV^2}\right)/\left(\frac{dI}{dV}\right)$. These small peaks show up at multiples of the vibrational energy (200 meV, 400 meV, etc.). Fig. 4.5 illustrates that vibrational fingerprints are seen as peaks in the $d^2I/dV^2$ spectrum at positive voltages for off resonance tunneling (blue line) and as dips for on resonance tunneling (black line).

**Figure 4.4** a) $dI/dV$ and b) IETS curves for a narrow resonant level (i.e. small $\Gamma$ and $E_G$) coupled with a single vibrational mode: regime I in Fig. 4.2a. The used parameters in meV are: $\varepsilon_L = 300$, $\varepsilon_R = 500$, $\Gamma_L = 25$, $\Gamma_R = 500$, level $R$ is in the WBL, $1_{LR} = 1$, $M_{LR} = M_{RR} = 0$, $\Omega^2 = 200$, $kT = 1$, $E_i = 1$, energy range is 3001 points from -1500 to 1500, voltage range is 451 points from -100 to 800 mV. $M_{LL}$ is varied per calculation and is shown in the legend.

### 4.2.3 Neglect of inelastic tunneling processes

As indicated in Subsection 4.1.2, approximations have to be made to make efficient inelastic current calculations feasible. A vibrational mode localized at the surface will couple more strongly to Hamiltonian matrix elements within the surface ($M_{LL}$) than to matrix elements in the other electrode ($M_{RR}$) or to those linking surface and tip states ($M_{LR}$). Therefore the elements $M_{LR}$ and $M_{RR}$ are expected to be small compared with the elements $M_{LL}$ and one would tend to neglect them. A similar reasoning holds for vibrational modes localized at the tip. Then, if the one-time tunneling approximation introduced in Subsection 3.2.4 is made, the vibrational modes would change only the Green's functions of the isolated levels where they are localized. However, it is found here that the approximation of neglecting inelastic tunneling cannot be made!
**Figure 4.5 a)** $\frac{dI}{dV}$ and **b)** IETS curves for a broad level (i.e. large $\Gamma$) on and off resonance (i.e. small and large $E_G$): regimes in blow-up of Fig. 4.2b. Note that the on resonance STM regime of Fig. 4.2b is not regime II displayed in Fig. 4.2a, since the small tunneling parameter $t_{LR}$ in this model is to be compared with a small $\Gamma_R$ in the original 1D model. In fact, this regime is not displayed in Fig. 4.2a. The used parameters in meV are: $\epsilon_R = 1000$, $\Gamma_L = 400$, $\Gamma_R = 400$, levels $L$ and $R$ are both in the WBL, $t_{LR} = 1$, $M_{LL} = M_{RR} = 100$, $M_{LR} = 0$, $Q^2 = 200$, $kT = 1$, $E_i = 1$, energy range is 3001 points from -1500 to 1500, voltage range is 501 points from -500 to 500 mV. $\epsilon_L$ is varied per calculation and is shown in the legend.

Fig. 4.6 shows $\frac{dI}{dV}$ and $\frac{d^2I}{dV^2}$ curves which are obtained using the SCBA procedure with $M_{LL}$ varying from 0 to 100 meV and $M_{LR} = 0$ (rows 1 and 3) or a finite value (rows 2 and 4). The ratio $t_{LR}/\Gamma_{L/R}$ is kept fixed to 0.01 in order to ensure the tunneling regime. With $M_{LR} = 0$, the inelastic contributions cause a reduction in conductance, resulting in dips for positive voltages in the $\frac{d^2I}{dV^2}$ curves. This is in contrast to what is seen in STM experiments. Furthermore, the calculated features are very small, even for unrealistic ratios of $M_{LL}/\Gamma_L = 0.1$ (not shown here). Introducing a small value for $M_{LR}$ transforms the decrease in conductance beyond the threshold voltage (Figs. 4.6a and e) to an increase in conductance (4.6c and g) of ~1%, which is a realistic number. From this it is concluded that the observed STM-IETS peaks cannot be understood from just taking $M_{LL}$ into account, but inclusion of inelastic tunneling is crucial. The next Section introduces an approach in which this term is taken into account up to first order.
Figure 4.6 $dI/dV$ and $d^2I/dV^2$ curves, obtained with the SCBA procedure with various values of $M_{LL}$, given in the legends. In (a-b) and (e-f) $M_{LR} = 0$, while in (c-d) and (g-h) $M_{LR} = 0.1 \cdot M_{LL}$. The WBL is employed in (a-d), the full Green’s functions in (e-h). The used parameters in meV are: $\epsilon_L = 500$, $\epsilon_R = 500$, $\Gamma_L = \Gamma_R = 10000$, $t_{LR} = 100$, $M_{RR} = 0$, $\Omega^\lambda = 130$, $kT = 1$, $E_i = 1$, energy range is 2001 points from -1000 to 1000, voltage range is 501 points from -500 to 500 mV.
4.3 Lowest order in inelastic tunneling (LOIT)

The reason why the inelastic tunneling matrix elements ($M_{LR}$) cannot be disregarded is that they should not be compared with the electron-vibration couplings within one level ($M_{LL}$), but with the elastic tunneling matrix elements ($t_{LR}$). This can be seen as follows. The tunneling process is the current limiting step in the transport mechanism. If a matrix element $M_{LR}$ changes the probability of tunneling, it has a large effect on the final tunneling current, and since these processes are only possible beyond a certain threshold voltage, it has an even larger effect on the $d^2I/dV^2$ spectra. The matrix elements $M_{LL/RR}$ change the conductance within the electrodes and hence have to be compared with the Hamiltonian elements within the electrode, which in the 2LS are represented by the contact matrices $\Gamma_{L/R}$. As can be seen in Eq. 3.28, the calculation of the inelastic tunneling matrix elements involve the derivative of the elastic tunneling matrix elements, and can therefore be expected to have the same order of magnitude. Subsection 4.3.4 gives a more accurate estimate for these inelastic tunneling matrix elements.

The approach described in Section 3.2 for elastic tunneling, which is based on the assumption that tunneling only happens once since the probability is very low, can be transferred to the inelastic case. In the proposed approach, the effect of $M_{LR}$ is only taken into account up to first order, as is the effect of $t_{LR}$. This approach, termed the lowest order in inelastic tunneling (LOIT) approach throughout this thesis, saves the need of performing a full iteration in $t_{LR}$ and $M_{LR}$, and, more importantly, prevents in the realistic calculations k-mixing, as explained in Subsection 3.2.4. Furthermore, due to the small tunneling probabilities, it is still assumed that the entire voltage drop is in the vacuum gap, and therefore the Green's functions for the isolated electrode + level block can be calculated in equilibrium and simply shifted in energy when a bias voltage is applied. This saves the need of calculating the Green's functions for every bias voltage point. If the coupling to the vibrations inside the levels is neglected, the method is termed the LOIT approach, if they are taken into account up to the SCBA level, the method is termed the LOIT+SCBA approach.

In summary, the main approximation of the LOIT(+SCBA) approach is:

1. If a vibration $\lambda$ is localized on $L$, then $M_{LL}^\lambda \gg M_{LR}^\lambda$, and similar for a vibration localized on $R$. Still, $M_{LR}$ is not neglected. It is shown in Subsection 4.2.3 that it is crucial to predict the correct IETS signal.

Furthermore, the same approximations as for the elastic STM simulations, described in Chapter 3, are made here as well:

2. Electrons only tunnel once. All multiple tunneling events are disregarded.
3. State \( L \) is at the same potential \( \mu_L \) as the left electrode and state \( R \) is at the same potential \( \mu_R \) as the right electrode. The entire voltage drop is in the vacuum gap.

The LOIT(+SCBA) approach for the 2LS can be summarized in the following three steps:

1. Coupling of the levels \( L \) and \( R \) to their respective electrodes at zero bias. (Subsection 4.3.1)
2. For the LOIT+SCBA approach: coupling of the levels \( L \) and \( R \) to the vibrations at zero bias. (Subsection 4.3.2)
3. Coupling of the states \( L \) and \( R \) to each other through elastic and inelastic processes only up to first order and calculation of the current using the Wingreen-Meir formula. (Subsection 4.3.3)

### 4.3.1 Coupling levels to electrodes

The coupling of the levels to the electrodes in the LOIT approach is similar to the coupling to the electrodes in the SCBA approach, steps 1 to 3 in Subsection 4.2.2. Since the two levels are not coupled yet, all Green's functions and self energies up to this point are labeled with the superscript 0. For future reference, the density of scattering states matrix, defined in Eq. 3.63, is written for the isolated, unperturbed levels as:

\[
\rho_0^0 = G_{aa}^0 \Gamma_{aa}^0 G_{aa}^{0,\dagger}.
\]

### 4.3.2 Coupling levels to vibrations

Next, for the LOIT+SCBA approach, the levels \( L \) and \( R \) are coupled to their respective vibrations in a self-consistent way (SCBA) at zero bias. For the LOIT approach, this step is omitted. Steps 5 to 9 of the SCBA approach in Subsection 4.2.2 are carried out for each electrode independently and hence the original 2×2 problem is reduced to two simpler 1×1 problems. The resulting isolated Green’s functions are written as \( G_{LL}^{0,\text{eph}} \) and \( G_{RR}^{0,\text{eph}} \), where the superscript \( \text{eph} \) denotes that vibrations have been taken into account up to the SCBA level. Since the calculation of \( \Sigma_s^0 < \Sigma_s^L + \Sigma_s^R + \Sigma_s^{\text{eph}} \) and \( \Sigma_s^0 > \) is done for the isolated electrodes, which are at zero bias, these lesser and greater self energies can be related to the retarded and advanced self energies via the fluctuation-dissipation theorem:

\[
\Sigma_{aa}^s < = -2i\mu_a \text{ Im} \left[ \Sigma_{aa}^s \right] = i\mu_a \Gamma_{aa}^{\text{eph}},
\]

\[
\Sigma_{aa}^s > = -2i\mu_a' \text{ Im} \left[ \Sigma_{aa}^s \right] = i\mu_a' \Gamma_{aa}^{\text{eph}},
\]

where the coupling matrix defined as \( \Gamma_{aa}^{\text{eph}} := -2 \text{ Im} \left[ \Sigma_{aa}^s \right] \) not only includes coupling to the electrodes, but also to the vibrations. For future reference, the density of scattering states matrices are written for the isolated electrodes as:
These quantities can be calculated once for each electrode over a wide energy range around the Fermi level, independent of the bias voltage and of the other electrode.

### 4.3.3 Coupling levels to each other

The final step is to introduce coupling between $L$ and $R$, to apply a bias voltage between the two electrodes (i.e. shifting the respective chemical potentials) and to calculate the elastic and inelastic contributions to the tunneling current. The current is calculated using the Wingreen-Meir formula, Eq. 4.1, which is written here for electrode $\alpha$ as:

$$ I_\alpha = \frac{e}{\pi \hbar} \int_{-\infty}^{\infty} dE \, g_\alpha, $$

where the transmission function $g_\alpha$ is defined as:

$$ g_\alpha := \text{Tr} \left[ \Sigma_{aa}^{<,G_{\text{eph},>}} - \Sigma_{aa}^{>,G_{\text{eph},<}} \right]. $$

Here, $\text{Tr}$ denotes the trace, and the energy dependences defined in Table 4.2 are taken into account. Since the assumption is made that tunneling can only happen once, the Dyson equation is expanded only up to first order, similar to Eq. 3.58, but this time including the electron-vibration interactions in the self-energy as well:

$$ G_{aa}^{\text{eph},<} = G_{aa}^{0,\text{eph}} \Sigma_{aa}^{<,\text{tot},G_{\text{eph},>}}, $$

$$ G_{aa}^{\text{eph},>} = G_{aa}^{0,\text{eph}} \Sigma_{aa}^{>,\text{tot},G_{\text{eph},<}}. $$

This means that the retarded and advanced Green’s functions are not updated, but the isolated retarded and advanced Green’s functions (with superscript $0$) are used to calculate the non-isolated lesser and greater Green’s functions. The total self energy is defined as:

$$ \Sigma_{aa}^{\text{tot}} := \Sigma_{aa}^{s} + \Sigma_{aa}^{el} + \Sigma_{aa}^{\text{inel}} + \Sigma_{aa}^{if}. $$

The subscripts $el$, $inel$ and $if$ denote interactions between $L$ and $R$ due to elastic tunneling, inelastic tunneling and interference effects respectively. The transmission function is split into the following four functions, taking into account the four terms in Eq. 4.20:

$$ g_\alpha = g_\alpha^{s} + g_\alpha^{el} + g_\alpha^{inel} + g_\alpha^{if}, $$

$$ g_\alpha^{if} := \text{Tr} \left[ \Sigma_{aa}^{<,G_{\text{eph},>}} G_{aa}^{0,\text{eph}} \Sigma_{aa}^{>,G_{\text{eph},<}} - \Sigma_{aa}^{<,G_{\text{eph},>}} G_{aa}^{0,\text{eph}} \Sigma_{aa}^{>,G_{\text{eph},<}} \right]. $$

These four contributions will be investigated separately below.
Intraelectrode tunneling, $\gamma = s$

For $\gamma = s$, Eq. 4.21 becomes:

$$g^s_\alpha = \text{Tr}\left[ \sum_{a} \left\{ G^{0,\text{eph}}_{aa} \sum_{a} G^{0,\text{eph},\dagger}_{aa} \right\} ight]$$

$$- \sum_{a} \left\{ G^{0,\text{eph}}_{aa} \sum_{a} G^{0,\text{eph},\dagger}_{aa} \right\}$$

$$+ \sum_{a} \left\{ G^{0,\text{eph}}_{aa} \sum_{a} G^{0,\text{eph},\dagger}_{aa} \right\}$$

$$- \sum_{a} \left\{ G^{0,\text{eph}}_{aa} \sum_{a} G^{0,\text{eph},\dagger}_{aa} \right\}$$

$$= 0.$$  

The first two terms in this equation cancel each other for all energies $E$. The last two terms give only zero when traced and integrated over energy $E$. The resulting transmission function is zero, which is a proof for the fact that the SCBA approach is current conserving.

Elastic tunneling, $\gamma = el$

![Feynman diagrams for a) elastic tunneling, b) inelastic tunneling and c) and d) interference effects.](image)

Figure 4.7 Feynman diagrams for a) elastic tunneling, b) inelastic tunneling and c) and d) interference effects.
For elastic tunneling the self energy $\Sigma_{\alpha\alpha}^t$ can be written down with the Feynman diagram shown in Fig. 4.7a, resulting in:

$$\Sigma_{\alpha\alpha}^{t,\,<} = t_{\alpha\beta} G_{\beta\beta}^{0,\text{eph},\,<} t_{\beta\alpha},$$

$$\Sigma_{\alpha\alpha}^{t,\,>} = t_{\alpha\beta} G_{\beta\beta}^{0,\text{eph},\,>} t_{\beta\alpha},$$

where $\beta = R$ if $\alpha = L$ and vice versa. The assumption that electrons can only tunnel once is used here, allowing to write $G_{\beta\beta}^{0,\text{eph},\,<}$ and $G_{\beta\beta}^{0,\text{eph},\,>}$ for the fermion propagator lines. Calculation of the retarded self energy is not required. With the implicit energy dependence defined in Table 4.2 and the definitions from Eqs. 4.16, the elastic transmission function can be written as:

$$g^e_\alpha = (n_\alpha - n_\beta) \text{Tr} \left[ \rho_{\alpha\beta}^{0,\text{eph}} t_{\alpha\beta} A_{\beta\beta}^{0,\text{eph}} t_{\beta\alpha} \right].$$

For inelastic tunneling, $\gamma = \text{inel}$

For inelastic tunneling the self energy $\Sigma_{\alpha\alpha}^{\text{inel},\lambda}$ per vibrational mode can be written down with the Feynman diagram shown in Figure 4.7b, resulting in:

$$\Sigma_{\alpha\alpha}^{\text{inel},\,<} = i \int_0^\infty \frac{d\omega}{2\pi} M_{\alpha\beta} D_{\lambda,\,<}^{\lambda,\,\,<} (\omega) G_{\beta\beta}^{0,\text{eph},\,<} (E - \omega) M_{\beta\alpha},$$

$$\Sigma_{\alpha\alpha}^{\text{inel},\,>} = i \int_0^\infty \frac{d\omega}{2\pi} M_{\alpha\beta} D_{\lambda,\,>}^{\lambda,\,>} (\omega) G_{\beta\beta}^{0,\text{eph},\,>} (E - \omega) M_{\beta\alpha}. $$

Here, $D_{\lambda}^{\lambda} (\omega)$ is the phonon Green’s function, as defined in Eq. 4.8. Again, the assumption that electrons can only tunnel once is used here, allowing using the Green’s functions with the superscript 0. Calculation of the retarded self energy is also here not required. The inelastic transmission function per vibrational mode can be written as:

$$g^\text{inel,}\lambda_\alpha (E) = \left( -n_\alpha n_\beta^{-\lambda} n_B^{+\lambda} + n'_\alpha n_\beta^{-\lambda} n_B^{+\lambda} \right) \times \text{Tr} \left[ \rho_{\alpha\beta}^{0,\text{eph}} M_{\alpha\beta} A_{\beta\beta}^{0,\text{eph},-\lambda} M_{\beta\alpha} \right]$$

$$+ \left( -n_\alpha n_\beta^{+\lambda} n_B^{-\lambda} + n'_\alpha n_\beta^{+\lambda} n_B^{-\lambda} \right) \times \text{Tr} \left[ \rho_{\alpha\beta}^{0,\text{eph}} M_{\alpha\beta} A_{\beta\beta}^{0,\text{eph},+\lambda} M_{\beta\alpha} \right].$$

This equation has the same structure as Eq. 4.24, which is not surprising if the simple picture of Fig. 2.3 is adopted. The first term refers to the process in Fig. 2.3b, the second to 2.3c, the third to 2.3a and the last to 2.3d if $\alpha = L$. From comparing Eq. 4.26 with Eq. 4.24, it can be seen that the calculation of the inelastic current takes approximately twice as long per vibrational mode as the calculation of the elastic current.
Interference tunneling, $\gamma = i\hbar$

For interference effects the self energy $\Sigma_{LL}^{\text{if},\lambda}$ per vibrational mode can be written down with the Feynman diagrams shown in Figures 4.7c and 4.7d, resulting in:

$$
\Sigma_{aa}^{\text{if},\lambda,<} = i \int_0^\infty \frac{d\omega}{2\pi} M_{\alpha\beta} D_{\lambda,<}^{\lambda,.} (\omega) G_{\beta\beta}^{0,\text{eph},<} (E - \omega) M_{\beta\beta} G_{\beta\beta}^{0,\text{eph},<} t_{\beta\alpha},
$$

4.27

$$
\Sigma_{aa}^{\text{if},\lambda,>} = i \int_0^\infty \frac{d\omega}{2\pi} M_{\alpha\beta} D_{\lambda,>}^{\lambda,.} (\omega) G_{\beta\beta}^{0,\text{eph},>} (E - \omega) M_{\beta\beta} G_{\beta\beta}^{0,\text{eph},>} t_{\beta\alpha}.
$$

for the first diagram and similar expressions for the second diagram. Since all Green’s functions (including the phonon Green’s function) are purely imaginary, this term is purely real. When this is substituted in Eq. 4.21, the real part (current-carrying part) of the transmission function is zero for this contribution, and therefore these terms can be neglected.

To summarize this Subsection, the elastic and inelastic transmission per vibrational mode are given by the Eqs. 4.24 and 4.26, which are similar in appearance. These are substituted in Eq. 4.17 and hence the current per voltage point is calculated to lowest order in elastic tunneling ($t_{LR}$) and inelastic tunneling ($M_{LR}$).

### 4.3.4 Estimate for inelastic tunneling matrix element

Eq. 4.32 shows that inelastic effects can be expected if $M_{LR} = t_{LR}$. To provide an estimate for $M_{LR}$ with respect to $t_{LR}$, a typical C-H vibration is considered in this Subsection. The matrix element $M_{\alpha\beta}^\lambda$ between state $\alpha$ and $\beta$ due to vibration $\lambda$ is written in terms of the Hamiltonian matrix element $H_{\alpha\beta}$ in Eq. 3.28. In this treatment, the derivative is approximated with:

$$
\langle \alpha | \frac{\partial \hat{H}}{\partial Q_{I,v}} | \beta \rangle \approx \frac{\partial}{\partial Q_{I,v}} \langle \alpha | \hat{H} | \beta \rangle = \frac{\partial H_{\alpha\beta}}{\partial Q_{I,v}}.
$$

4.28

For simplicity, it is assumed that only the hydrogen atom is moving, and only in the vertical direction. The normalized displacement vector $v_{I,v}^\lambda$ is then equal to 1 for $I = H$ and $v = z$ and is equal to 0 for all other combinations of $\{I,v\}$. The states $\alpha$ and $\beta$ are assumed to be $s$ orbitals (spherical symmetric) and the matrix elements $H_{\alpha\beta}$ are given an exponential decay with rate $\kappa$, appropriate to the tunneling regime:

$$
H_{\alpha\beta} (\tilde{R}) = A \cdot e^{-\kappa R}.
$$

4.29
Here $R = |\vec{R}_\alpha - \vec{R}_\beta|$, where $\vec{R}_\alpha$ ($\vec{R}_\beta$) denotes the position of the atom to which atomic orbital $\alpha$ ($\beta$) belongs. With the additional parameters $\kappa = 1$ Å$^{-1}$, $M_I = 1$ a.u. = $1.67 \cdot 10^{-27}$ kg and $\Omega^J = 395$ meV, it is found that $M_{LR} = 0.19 \cdot H_{LR}$. This value would lead to an increase of conductivity of 3.6% in a WBL model. It can be treated as a general estimate for $M_{LR}$. Since in general the atomic displacement is not parallel to the separation vector $\vec{R}_\alpha - \vec{R}_\beta$, and the mass of all other ions is greater than the one for hydrogen, one might expect in general lower couplings. However, most vibrational energies are lower than 395 meV, resulting in a higher coupling.

### 4.4 LOIT vs. SCBA

In this Section, the validity of the LOIT approach is investigated for different regimes by varying the parameters introduced in Subsection 4.1.2 and comparing it with the SCBA approach. In general, it is found that the LOIT approach is valid if the interelectrode electron-vibration coupling ($M_{LR}$) is large and/or the intraelectrode electron-vibration coupling ($M_{LL}/M_{RR}$) is small. They cannot be compared directly however, but need to be compared with $t_{LR}$ and $\Gamma_L$ respectively, as argued in Section 4.3.

![Figure 4.8 IETS intensity curves shown at voltages around the vibrational threshold.](image)

The legend indicates the value of $t_{LR}$ in meV, the value of $M_{LR}$ is 30% of this value. The rest of the used parameters are (all in meV): $\varepsilon_L = 500$, $\varepsilon_R = 500$, $\Gamma_L = 500$, $\Gamma_R = 500$, $\Omega = 130$, $M_{LL} = 30$, $M_{RR} = 0$, $kT = 1$, $E_i = 1$, energy range is 2001 points from -1000 to 1000, voltage range is 501 points from -500 to 500 mV.

Fig. 4.8 shows the IETS intensity spectrum plotted against the bias voltage around the vibrational thresholds of a model system with only one vibration present. Note that the area under any peak in the IETS intensity curve gives the change of conductance at this threshold. The full lines are the results from the SCBA approach, the dashed lines are the results from the LOIT approach. In both cases the curves for various values of $M_{LR}$ and $t_{LR}$, keeping the ratio $M_{LR}/t_{LR}$ fixed, are identical. This result is still valid upon
increasing or decreasing the ratio $M_{LR}/t_{LR}$, $\Gamma_L$ or $M_{LL}$, or when either one or both levels are considered in the WBL. Therefore, it is concluded that the value of $M_{LR}$ is meaningless if not compared with $t_{LR}$ and this ratio should always be compared with the other parameters in this model. This also means that the IETS intensity curves contain as much information as the $d^2I/dV^2$ curves themselves if there are no elastic effects in the $d^2I/dV^2$ curves.

Figure 4.9 Normalized IETS intensity vs. voltage for different values of $M_{LR}$, $M_{LL}$ and $\Gamma_L$. The legend indicates the value for $M_{LR}$ in meV, the headers indicate the values for $\Gamma_L$ and $M_{LL}$ in meV. The rest of the parameters is (all in meV): $\epsilon_L = 500$, $\epsilon_R = 500$, $\Gamma_R = 500$, $t_{LR} = 1$, $\Omega = 130$, $M_{RR} = 0$, $kT = 1$, $E_i = 1$, $E = [-1000, 1000]$, energy range is 2001 points from -1000 to 1000, voltage range is 501 points from -500 to 500 mV.

This ratio of $M_{LR}/t_{LR}$ is compared with the value for $M_{LL}$ for various values of $\Gamma_L$. Fig. 4.9 shows six different plots of the IETS intensity around the negative vibrational threshold in a system where there is only one vibration present. The features at positive voltages look similar but opposite in sign. In each graph, the ratio $M_{LR}/t_{LR}$ is varied.
and shown in the legend. Since the intensity of the peak changes significantly upon changing the ratio $M_{LR}/t_{LR}$, all curves are normalized. In particular, the curves obtained with the SCBA approach are shifted such that the baseline is at 0 and scaled such that the peak intensity is 1. The curves obtained with the LOIT approach are shifted and scaled identically as the corresponding SCBA curve. This makes comparing the relative agreement between the two methods possible. All graphs show that the agreement between the SCBA and LOIT approaches is better for a higher ratio $M_{LR}/t_{LR}$. For high values of $M_{LL}$ (Figs. 4.9c and f), the LOIT approach gives qualitatively different results than the SCBA approach for low values of $M_{LR}/t_{LR}$.

To pinpoint an exact crossover where the LOIT approach is not valid anymore, the value of $\Gamma_L$ should also be taken into account. The influence of $M_{LL}$ is smaller for larger values of $\Gamma_L$, and hence a better agreement is then expected between the two methods. Qualitatively, this can also be seen in this model for intermediate values of $M_{LL}$ (i.e. $-300 \cdot M_{LR}/t_{LR}$): the blue lines in Fig. 4.9b and red lines in Fig. 4.9c show a better agreement between the two methods than the ones in Fig. 4.9e and f. It is difficult to quantify this relationship however. The graphs do not fall on top of each other as in Fig. 4.8 if the ratio $M_{LL}/\Gamma_L$ or the ratio $M_{LL}/\sqrt{\Gamma_L}$ is fixed, where a square root is tried because $\Gamma_L$ is a broadening matrix and scales with the corresponding matrix elements squared. Therefore, a quantitative comparison between the ratio $M_{LR}/t_{LR}$ and $M_{LL}$ in relation with $\Gamma_L$ cannot be made. The same qualitative conclusions can be drawn if either one or both levels are considered in the WBL.

In conclusion, the LOIT approach is a good approximation when compared to the SCBA approach if the ratio $M_{LR}/t_{LR}$ is large compared to a certain ratio between $M_{LL}$ and $\Gamma_L$. A functional form for this ratio and a quantitative limit on $M_{LR}/t_{LR}$ cannot be given, since this depends crucially on other parameters as well. For values of $M_{LL} < 10$ meV, the LOIT approach is hardly distinguishable from the SCBA approach, even for $\Gamma_L$ as low as 100 meV. In realistic STM cases, all values of $M_{LL}$ are found smaller than 10 meV and the contact matrix is also larger than 100 meV. This means that under STM conditions, the LOIT approach is valid.

### 4.5 LOIT implementation in GREEN

Section 4.3 introduced the LOIT approach for a 1D model defined as a two level system (2LS) in order to mimic more realistically the real STM setup. Therefore it is straightforward to generalize it for realistic STM related 3D calculations. Accordingly, it has been implemented in the GREEN program, which is described in Section 3.2, so that the code is now capable of calculating topography maps as well as inelastic $dl/dV$
and \( d^2I/dV^2 \) spectra and maps, all on the same footing. This Section gives the details of this implementation.

### 4.5.1 Spectral decomposition

When the density of scattering states matrices, defined in Eq. 4.16, are diagonalized:

\[
\rho_{\alpha}^{0,eph} = \sum_{m_a} \rho_{\alpha}^{m_a} \langle \rho_{\alpha}^{m_a} \rangle, \\
A_{\alpha}^{0,eph} = \sum_{m_a} a_{\alpha}^{m_a} \langle a_{\alpha}^{m_a} \rangle,
\]

4.30

then the elastic current at electrode \( \alpha \), given by integrating Eq. 4.24 over energy, can be written in the form of Fermi’s golden rule:

\[
I_{\alpha}^{el} = \int_{-\infty}^{\infty} dE \left( n_{\alpha} - n_{\beta} \right) \text{Tr} \left[ \sum_{m_{\alpha},m_{\beta}} \left| a_{\beta}^{m_{\beta}} \right| t_{\beta\alpha} \rho_{\alpha}^{m_{\alpha}} \right]^2, \]

4.31

and the inelastic current at electrode \( \alpha \) per vibrational mode \( \lambda \), given by integrating Eq. 4.26 over energy, is written as:

\[
I_{\alpha}^{\lambda} = \int_{-\infty}^{\infty} dE \left( -n_{\alpha} n_{\beta}^{-\lambda} n_{B}^{\lambda} + n_{\alpha}' n_{\beta}^{\lambda} n_{B}^{-\lambda} \right) \\
\times \text{Tr} \left[ \sum_{m_{\alpha},m_{\beta}} \left| a_{\beta}^{m_{\beta}^{-\lambda}} \right| M_{\beta\alpha}^{\lambda} \rho_{\alpha}^{m_{\alpha}} \right]^2 \]

4.32

This is called the spectral value decomposition.

### 4.5.2 LOIT vs. LOIT+SCBA

As shown in Subsection 4.2.3, inclusion of the vibrations inside the isolated electrodes hardly contribute to the inelastic current as long as \( M_{LL} \ll \Gamma_L \) which is the usual situation for molecules chemisorbed on surfaces. Since this limit is well satisfied for all the systems studied in this thesis, it is decided not to include these corrections in the current work. However, one should recall that they cannot be neglected in the case of physisorbed (or weakly bound) molecules. Nevertheless, the main advantages of neglecting intra-electrode vibrations are:

1. There is no need to calculate the electron-vibration couplings inside the electrodes ( \( M_{LL} \)), resulting in less required DFT calculations and skipping the computationally demanding SCBA procedure.
2. The two density of scattering states matrices defined in Eqs. 4.14 and 4.16 are equal, and the diagonalization of these (Eq. 4.30) and storing to disk is only performed once.

3. The current is symmetrized: \( I_L = -I_R \).

### 4.5.3 Calculation of inelastic tunneling matrix elements

A general expression for the calculation of inelastic matrix elements is given in Eq. 3.28. It is assumed that the Hamiltonian matrix element between state \( |\alpha\rangle \) in the surface and state \( |\beta\rangle \) in the tip is given by a Slater-Koster expression, as discussed in Subsection 3.2.7, implying that this interaction only depends on the states \( |\alpha\rangle \) and \( |\beta\rangle \) themselves and their relative positions. It is furthermore assumed that state \( |\beta\rangle \) is not influenced by any vibration at the surface and state \( |\alpha\rangle \) is not influenced by any vibration at the tip apex, such that Eq. 3.30 can be employed to calculate the derivative of the Hamiltonian with respect to the displacement coordinates. In principle, since the Slater-Koster expression is an analytical expression, the derivative can be calculated analytically and hence an analytical expression for \( M_{\alpha\beta} \) does exist. However, this method has not been implemented in GREEN yet, and the derivatives are calculated using finite displacements.

### 4.5.4 LOIT vs. LOIT+WBL

It is discussed in Section 4.3 that the calculation of the inelastic current takes roughly twice as long per vibrational mode as the calculation of the elastic current, once the DFT calculations are finished. Most vibrational modes however do not contribute to the inelastic current, due to various reasons such as being localized close to the surface thus overlapping hardly with the apex states, a larger emission/adsorption threshold than the bias range to be explored, small electron-vibration coupling elements or other reasons involving symmetry arguments. More about propensity rules for detecting vibrational modes in IETS will be discussed in Subsection 5.2.6.

If the DOS of the sample and tip do not change drastically over several hundreds of meV around the Fermi energy, qualitatively they can be assumed to be in the WBL. This means that wherever the isolated Green's functions are used, only the value at \( E = E_F \) is evaluated. The LOIT approach with the use of Eq. 4.7 instead of Eq. 4.4 is termed LOIT+WBL. In a realistic 3D calculation, this drastically speeds up the calculation by roughly a factor 1,000 (5 minutes vs. 4 days). In most STM experiments, the DOS measured with STS is rather flat around the Fermi energy, and the assumption made here holds. The problem in the simulations however is that for systems with highly dispersive bands, such as noble metals, a good \( k \)-convergence in the DOS is hardly achievable with DFT due to the large number of \( k \)-points required (well over 1,000). For these cases, the DOS turns out spiky, and often
results in extra features in the \(d^2I/dV^2\) curves which are not realistic and conceal any inelastic fingerprints. Therefore the LOIT+WBL approach may even give qualitative better agreement between measured and simulated IETS curves than the LOIT approach. This will be further investigated in Subsection 5.2.4.

### 4.6 Summary

The main conclusion of this Chapter is that inclusion of inelastic tunneling up to first order, as employed in the LOIT method, is both necessary and sufficient to correctly simulate inelastic effects in a tunnel junction. Further key observations of this Chapter are:

- With the LOIT approach, the calculation of the inelastic current per vibrational mode is similar to the calculation of the elastic current, and takes approximately only twice as long per mode.
- The LOIT approach is valid as long as the ratio \(M_{LR}/t_{LR}\) is larger than some ratio between \(M_{LL}\) and \(\Gamma_L\). In general STM conditions, this requirement is met.

In the next Chapters the LOIT approach will be employed in various systems, ranging from simple to complex, to study how well this method can predict inelastic intensities and to study how this could help in understanding STM observations.

### 4.7 Bibliography

Chapter 5 – STM and IETS on CO adsorbed on Ag(110) with clean and modified tips

In Chapter 4, the lowest order in inelastic tunneling (LOIT) method is introduced, and it is shown for a simple 1D model and under standard tunneling conditions that inclusion of the inelastic tunneling term to lowest order is both necessary and sufficient to reproduce the results obtained from an approach in which all interactions are taken into account to full order (SCBA). In this Chapter the LOIT method, implemented in a realistic 3D model as described in Section 4.5, is employed to calculate the inelastic effects in a realistic model system of a single CO molecule adsorbed on a Ag(110) surface. This system has been thoroughly investigated experimentally by Hahn and Ho\textsuperscript{1} in an STM study where the influence of the tip condition on the STM imaging and IETS spectra was addressed.

This Chapter is organized as follows. Section 5.1 gives the necessary details of the experiments and calculations. Section 5.2 is the main Section of this Chapter and shows the results from the STM and IETS simulations with the LOIT approach, and gives a comparison with their experimental counterparts. In the end, the main conclusions are summarized in Section 5.3.

5.1 Details of experiments and calculations

All the theoretical formalisms employed in this Chapter have already been explained in this thesis: the mechanisms of STM and IETS, required to understand the experiments, are described in Chapter 2, the theoretical method used to simulate STM images is described in Chapter 3, while that employed to calculate the IETS curves is described in Chapter 4. This Section presents only specific details of the STM experiments and of the calculations. Parameters not explicitly mentioned in this Section are given in the above mentioned Chapters.

5.1.1 Details of the STM experiments

The STM experiments of Hahn and Ho\textsuperscript{1} were performed in UHV at 13 K. The tips were etched polycrystalline tungsten tips and were cleaned by cycles of Ne\textsuperscript{+} ion sputtering and annealing. The tips were sharpened \textit{in situ} by dipping, as explained in Subsection 2.2.8. Due to the low coverages of CO molecules, dispersed on the surface, it is assumed there are no interactions between them. Controlled transfer of a single molecule between the tip apex and the surface was possible by applying an appropriate tunneling current and sample bias.
5.1.2 Details of the DFT calculations

All DFT calculations have been performed using the SIESTA code under the generalized gradient approximation (GGA). In order to minimize adsorbate-adsorbate interactions, a 4×4 supercell relative to the Ag(110) inplane lattice is employed, with a single CO molecule adsorbed upright at a top site with the C atom attached to the surface. The fcc lattice constant for Ag is determined from a bulk optimization, in which the total energy is calculated as a function of the lattice parameter. The result for the used GGA functional is shown in Fig. 7.8a, where the minimum is found at 4.15 Å, which is slightly larger than the experimental value of 4.09 Å. This overestimation is common if a GGA functional is used.\(^3\) The slab consists of five layers, of which the bottom two layers are fixed at bulk positions. The chosen k-grid sampling is a 5×6 Monkhorst Pack (MP) grid, equivalent to a 20×24 grid of a 1×1 Ag(110) inplane lattice. This grid size is chosen asymmetric, since the Ag-Ag distance in the [001] direction is 4.15 Å, while the Ag-Ag distance in the [-110] direction is 2.93 Å. Van-der-Waals interactions have not been taken into account, since CO is known to strongly chemisorb on the metal and there are no intermolecular interactions.

In order to explore in detail any tip effect, both in the topography and IETS curves, four different tip apex structures have been considered. Since a silver apex is expected after the reported experimental dipping process, all tips considered are based on a Ag(111) oriented surface with a pyramid of 10 Ag atoms forming the apex. First, a clean sharp tip apex is modeled by a single atom terminated pyramid, while a clean blunt tip is obtained by removing the end atom. CO terminated tips are next modeled by adding a CO molecule. For the sharp tip, the adsorption site is the end atom, for the blunt tip, the adsorption site is the threefold hollow site, see Fig. 6.2a and b. These four tips are chosen to make the distinction between sharp and blunt, and between clean and modified tips, while still dealing with a limited selection and relatively easy tips.

For all cases a 4×4 supercell relative to the Ag(111) is defined and the pyramid is stacked below a three layer slab. In the geometry optimizations all apex atoms were allowed to relax while the Ag(111) atoms were fixed to bulk positions. A 4×4 MP grid, equivalent to a 16×16 grid of a 1×1 Ag(111) lattice, is used for the tips. For both the surface and the tips, the resolution of the real space mesh is set to 500 Rydberg. The mesh is sampled over four different origins to improve the convergence with the mesh size. The convergence threshold for the Hamiltonian elements is set to 0.5 meV and all free atoms are fully relaxed until the remaining forces are below 0.01 eV/Å.

Vibrational modes for the surface are calculated by displacing the atoms of the CO molecule and the 9 Ag atoms which are closer than 5 Å to the C atom by 0.01 Å in all directions and calculating the eigenmodes of the corresponding force matrix, as explained in Subsection 3.1.3. A diagonal element correction\(^4\) has been employed here. For the clean tips, the vibrational modes are not determined and not taken into account in subsequent calculations. For the CO terminated tips, the allowed atoms to move are the C and O atoms and the 10 Ag atoms of the pyramid (9 Ag atoms...
for the truncated pyramid). All vibrational modes with an energy lower than 10 meV are disregarded in subsequent calculations.

5.1.3 Details of the Green's functions calculations

All Green's functions based calculations have been performed using the GREEN code. In order to generate the self-consistent Hamiltonian, three more Ag layers are added after ionic optimization to the surface structure, and three more layers of Ag(111) are added on top of the fcc 4×4 slabs of the tips. The self-consistent field procedure in GREEN is checked by comparing the on-site energies of the AOs between the bulk calculation and the atoms in the center of the slab, where a maximum deviation of 16 meV is found for the surface and 11 meV for the tips. The Slater-Koster parameterization has been performed using scheme 3 from Subsection 3.2.7. The used imaginary energy in all STM/IETS simulations, being a measure for the width of the elastic peaks, is 20 meV. The value for $kT$, being a measure for the width of the inelastic peaks, is 5 meV. The used k-grids for the tips are the same as for the DFT calculations. While the DFT calculations are converged in k-grid size, the elastic current can still change strongly with increasing number of k-points. Therefore the k-sampling is varied for the surface and its influence is investigated. In the STM simulations, the energy ranges from 0 to 100 meV with an increment of 10 meV, and the lateral resolution is 0.4 Å. In the IETS simulations, the energy ranges from -300 to 300 meV for the wide band limit (WBL) calculations to cover all vibrational modes, but ranges from -50 to 50 meV for the full Green's functions calculations since all vibrational modes except one are contained in this window, while the computational cost is significantly increased if this would be included. The used increment of 2.5 meV is the maximum increment that should be used with the chosen value of $kT$ for a good resolution of any IETS peak. The height of the tip has been adjusted such that the elastic current is 1 nA at a bias voltage of 60 mV.

5.2 Results and discussion

This Section is the main Section of this Chapter and presents a comparison between simulated STM and IETS results and their experimental counterparts. First, the experimental results are shown in Subsection 5.2.1. The DFT derived optimal geometry and list of vibrational modes is shown in Subsection 5.2.2. These DFT results are used for the simulations with the Green's functions based LOIT method, which are presented in the subsequent Subsections: elastic STM images in Subsection 5.2.3, IETS curves in Subsection 5.2.4 and IETS maps in Subsection 5.2.5. Finally, an ansatz for extracting propensity rules will be discussed in Subsection 5.2.6.

5.2.1 STM and IETS experiments

The relevant STM images and IETS spectra are shown in Fig. 5.1. With a bare metallic tip, the CO molecule is imaged as an inverted sombrero (a round depression with an elevated rim), as shown in Fig. 5.1a.
Figure 5.1  

**a-b)** Topographical images of CO molecules adsorbed on a Ag(110) surface. The images are obtained with **a)** a bare metallic tip and **b)** a CO terminated tip. Both images, 25×25 Å, were taken at $V_b = 70$ mV and $I_{sp} = 1$ nA.  

**c-d)** Single molecule vibrational spectra obtained by STM-IETS for CO with **c)** a bare metallic tip and **d)** a CO terminated tip. The spectra taken over the clean Ag(110) surface (dashed lines) were subtracted from the corresponding spectra taken directly over the center of the molecular images (thin solid lines) to reveal spectra for single molecules adsorbed on the surface (thick solid lines). The tunneling gap is set with $V = 70$ mV and $I_{sp} = 1$ nA. Figure adapted from Ref. 1.

With this tip, the surface atoms could not be resolved. However, with a CO terminated tip, the CO molecule on the surface is imaged as a sharp protrusion at the center with four depressions around it, as shown in Fig. 5.1b. With this tip, atomic resolution of the surface atoms is achieved, allowing determining the adsorption site as atop.

In the IETS spectra, the only vibrational mode found is the hindered rotation mode at -19 meV and 21 meV for both tips. The assignments of the modes in this experiment are taken from Ref 1 as well. For the CO terminated tips, this is convoluted with the vibrational modes found for the tip apex: antisymmetric peaks at -19 meV and 17 meV and -268 meV and 271 meV are measured for the hindered rotation and the C-O stretch respectively for a CO terminated tip positioned over the clean Ag(110) surface. Since the same hindered rotation is measured for tip and sample, it is assumed that the bare metallic tip is terminated with Ag atoms prior to transferring a CO molecule to the tip as a result of the dipping procedure. The C-O stretch for the molecule on the surface
cannot be measured, because the molecule on Ag(110) at 13 K is moved laterally when the bias is increased toward the C-O stretch energy. The difference in vibrational energy between negative and positive bias has been explained by an electric field effect for a C-O stretch mode, but is disregarded in this Chapter.

Spatial IETS maps have been recorded as well, but the authors did not show these in Ref 1. The IETS intensity of the hindered rotation mode exhibits a maximum at the center of the molecules. The IETS maps are found to be more spatially localized than the corresponding topographical images.

5.2.2 DFT calculations

![Figure 5.2](image)

**Figure 5.2** Unit cells of relaxed tip and surface geometries. The large spheres are Ag atoms, the light small spheres are C atoms, and the dark small spheres are O atoms. Figure made with XCRYSDEN.  

a) Side view of a sharp CO terminated Ag tip; b) side view of a blunt CO terminated Ag tip; c) side view and d) top view of a single CO molecule adsorbed on Ag(110).

The relaxed surface and tip structures are shown in Fig. 5.2. The clean tips, not shown in this Figure, are visually identical to their CO terminated counterparts after removing the adsorbed molecule. The C-O and nearest Ag-C distances are given for the surface and the two CO terminated tips in Table 5.1. These values are consistent with calculated values from literature. The optimized C-O distance in the gas phase is 1.15 Å, while the
The experimental value is 1.13 Å. The discrepancy is assigned to the use of the GGA functional, which tends to overestimate bond lengths.6

**Table 5.1** Geometric results of CO chemisorption on Ag(110) and on a sharp and blunt Ag tip. The distance of the C atom to the plane with the three outermost Ag atoms in the blunt CO terminated tip is 1.62 Å.

<table>
<thead>
<tr>
<th>Structure</th>
<th>C-O distance (Å)</th>
<th>Ag-C distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO in gas phase</td>
<td>This work</td>
<td>Ref. 5</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>-</td>
</tr>
<tr>
<td>CO on Ag(110) surface</td>
<td>1.16</td>
<td>1.163</td>
</tr>
<tr>
<td>CO terminated sharp tip</td>
<td>1.16</td>
<td>-</td>
</tr>
<tr>
<td>CO terminated blunt tip</td>
<td>1.19</td>
<td>-</td>
</tr>
<tr>
<td></td>
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<td>2.08</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.34</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 5.2** Energies (in meV) and assignments of vibrational modes for CO on Ag(110) and on a sharp and blunt Ag tip. ν = stretch, R = hindered rotation, T = hindered translation. Atoms in parentheses indicate moving atoms in vibrational mode, subscripts indicate the layer of the corresponding atom. Note that in the blunt tip, the actual first layer is labeled layer 2.

<table>
<thead>
<tr>
<th>Surface, this work</th>
<th>Surface, Ref. 5</th>
<th>Surface, Ref. 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>hω Assignment</td>
<td>hω Assignment</td>
<td>hω Assignment</td>
</tr>
<tr>
<td>251 ν(C-O)</td>
<td>262 ν(C-O)</td>
<td>268 ν(C-O)</td>
</tr>
<tr>
<td>33 ν(Ag1-CO)</td>
<td>33 ν(Ag1-CO)</td>
<td></td>
</tr>
<tr>
<td>14-19 R(C-O)</td>
<td>26-29 R(C-O)</td>
<td></td>
</tr>
<tr>
<td>2-3 T(C-O)</td>
<td>8-9 T(C-O)</td>
<td></td>
</tr>
<tr>
<td>Sharp CO terminated tip, this work</td>
<td>Sharp CO terminated tip, Ref. 2</td>
<td>Blunt CO terminated tip, this work</td>
</tr>
<tr>
<td>hω Assignment</td>
<td>hω Assignment</td>
<td>hω Assignment</td>
</tr>
<tr>
<td>253 ν(C-O)</td>
<td>275 ν(C-O)</td>
<td>220 ν(C-O)</td>
</tr>
<tr>
<td>38 ν(Ag1-CO)</td>
<td>24 ν(Ag2-CO)</td>
<td></td>
</tr>
<tr>
<td>21 ν(Ag2-Ag1CO)</td>
<td>11, 17, 21 R(C-O)</td>
<td></td>
</tr>
</tbody>
</table>

The calculated vibrational modes are displayed in Table 5.2, where they are compared with calculated values from literature.2,5 A more detailed overview of all vibrational modes found is given in Table A.1 in Appendix A. For the gas phase, the energy of the ν(C-O) mode is 261 meV, slightly lower than the experimental value of 266 meV. This discrepancy is again assigned to the use of the GGA functional. The energy of the ν(C-O) mode is 11 and 17 meV lower in this work compared with Refs. 5 and 2 respectively. HREELS measurements7 yield a vibrational energy of 261±4 meV, which is close to the gas phase value of 266 meV.8 Note that the energies reported in Ref. 2 are higher than those for the gas phase CO and might be less accurate. In this work, the ν(C-O) mode is unaltered in the CO terminated sharp tip, but Ref 2 reports a hardening of this vibrational mode with 7 meV. The threefold adsorption of the CO molecule at
the blunt tip results in a significant softening of the ν(C-O) mode down to 220 meV. This can be explained by the larger C-O distance as presented in Table 5.1, indicating a weakening of the C-O bond. A vibrational mode at 268 meV is reported in Ref. 1, suggesting that the used tip is not the blunt CO terminated tip. However, the reported IETS signal is rather weak, while it is surprising that this energy is larger than for the gas phase, making this assignment doubtful.

The energy of the ν(Ag1-CO) mode (metal-molecule stretch mode) at the surface is similar to that found in Ref. 5. The ν(Ag1-CO) mode is hardened (5 meV) for the CO terminated sharp tip and significantly softened (9 meV) for the CO terminated blunt tip. For the CO terminated sharp tip no R(C-O) mode is observed; the only modes around 21 meV are Ag related. A qualitative argument for this is that the CO molecule is very loosely bound to the tip apex, and hence a rotation of the molecule is almost unhindered. The energy associated to this vibrational mode is then lower than 10 meV and therefore disregarded.

5.2.3 Simulated STM images

The simulated STM images and line scans in the horizontal direction for the four different tips are presented in Fig. 5.3. The simulated STM images obtained with the SK parameters from the parameterization scheme 2 in Subsection 3.2.7 are displayed in Fig. A.1 in Appendix A. Overall, the agreement with the experimental images displayed in Fig. 5.1 is quite satisfactory. For the clean tips (Figs. 5.3a and c), the CO molecule is imaged as a depression, as in the experiment shown in Fig. 5.1a. However the elevated rim has not been reproduced. The shape of the molecule in Fig. 5.3c reflects the actual shape of the tip apex. The reported experimental STM images obtained with bare metallic tips are circular symmetric, which indicates that the actual tips employed in the experiments are probably more complex than the simple models used here. For the CO terminated tips (Figs. 5.3b and d), the CO molecule is imaged as a protrusion, as in the experiment shown in Fig. 5.1a. Also the additional protrusion at the center is reproduced for the sharp tip while for the blunt tip it appears slightly less bright than the ring. The CO terminated tips provide an enhanced resolution for the substrate, again in line with the experiments. The calculated corrugation is ~1.5 Å. Finer details, such as the four depressions around the molecule have not been reproduced, probably due to the unknown precise tip apex termination. Instead, an elevated ring is observed at 5 Å from the center of the CO molecule. From these images, it is hard to determine which model tip resembles better the experimental ones, although the clean tips provide a better overall agreement.
5.2.4 Simulated IETS curves

To check whether the LOIT(+WBL) approach reproduces the experimental results from Subsection 5.2.1, IETS curves are simulated with different tips. The results of these simulations under the WBL as explained in Subsection 4.5.4 (LOIT+WBL) are shown in Fig. 5.4, following the same visualization scheme as that used in Ref. 1 to present their experimental data. The legends display the size of the used MP k-grid. In the WBL, the IETS curves are converged in k-grid size for very small k-grids already.
Figure 5.4 IETS curves for different tips, obtained with the LOIT+WBL method. The dashed line is the IETS curve over the bare Ag(110) surface, the thin solid line is the IETS curve over the CO molecule and the thick solid line is the difference between these two. The insets show a sketch of the used tip; the legends display the amount of surface k-points taken into account in the corresponding calculation. The blue, red and black lines are overlapping. Tunneling gap is set with a setpoint current of 1 nA at 60 mV.

With the sharp Ag tip, the main antisymmetric peak around ±15 meV is due to the R(C-O) mode as in the experiment. The $\nu$(Ag-CO) mode is only visible as a shoulder. With a blunt tip or upon CO adsorption however, the peak around ±32.5 meV becomes stronger. With the blunt CO terminated tip these intensities are similar in intensity and results in a plateau, while with the sharp CO terminated tip the intensity from the $\nu$(Ag-CO) mode is higher than that of the R(C-O) mode. This is in contrast with the experiment; the intensity of the $\nu$(Ag-CO) mode is overestimated. Most probably the agreement would improve upon increased peak broadening, since the two peaks will shift towards each other, or a tilted tip geometry, since it would reduce the contribution from the $\nu$(Ag-CO) mode and the peak would shift down towards the R(C-O) mode.

In all graphs in Fig. 5.4, the curves are the result of a convolution of multiple vibrational modes. If they are excited with similar intensity, e.g. Fig. 5.4d, it can be difficult to distinguish between the individual modes. A powerful feature of the LOIT method is that the inelastic current can be studied per vibrational mode individually. This is shown in Fig. 5.5, where the IETS curves for each individual surface and tip apex vibrational mode are plotted for the blunt CO terminated tip. The obtained intensities per vibrational mode that way are summarized for all tips in Tables A.2 and A.3 in Appendix A.
Figure 5.5 IETS curve per vibrational mode, obtained with the LOIT+WBL method, for the CO terminated blunt tip a) over the CO molecule and b) over the bare surface. The dashed lines show the peaks due to the surface vibrational modes, the full lines those due to the apex vibrational modes. The curves have been shifted upward for clarity.

In principle it would be more accurate to not use the WBL, but to use the energy dependent Green's functions to simulate $IV$ curves. In practice however, the details of the $IV$ curves and its derivatives depend crucially on the size of the k-grid used to obtain the curves. This is shown in Fig. 5.6, where simulated $dI/dV$ and $d^2I/dV^2$ curves are shown for different surface k-grid sizes. Inelastic effects are not taken into account in these calculations. The imaginary energy, responsible for broadening of elastic features in $dI/dV$, is set to 20 meV. Although the absolute value of $dI/dV$ is converged, the details of the curves and therefore the features in the $d^2I/dV^2$ curves are not converged for even a 24×32 k-grid, which is equivalent to a 96×128 k-grid of a 1×1 Ag(110) inplane lattice. The reason behind this is the large dispersion of the Ag sp bands.

For each k-grid size, the curves for the two clean tips and the curves for the two CO terminated tips are similar. This can be on the one hand explained by the WBL used for the tip. The $dI/dV$ curve then represents approximately the calculated DOS of the surface, which is of course the same in all cases. Furthermore, the main current carrying orbitals are the same for both clean tips and for both CO terminated tips. It is difficult to discriminate the tip termination by comparing the simulated STS with the experiment, especially since the STS is not converged in k-grid size.

There are in principle two ways to reach convergence in these graphs: increasing the k-grid size even further or increasing the imaginary energy. However, due to memory
issues, it is not desirable to calculate these curves with an even larger k-grid, and increasing the imaginary energy further decreases the current drastically due to the evanescent component in each channel introduced by this. Therefore it is concluded that for this particular system it is not yet tractable to converge the $dI/dV$ curves on this energy scale in k-space by employing DFT and Green's functions calculations with the current resources. Accordingly, no additional simulated $d^2I/dV^2$ curves obtained with full Green's functions are shown in this thesis, since they do not provide additional information.

**Figure 5.6** Simulated elastic $dI/dV$ and $d^2I/dV^2$ curves for different tips over the CO molecule (pictured on the right), and for different surface k-grid sizes, colors, defined in legend in (a). The tip is assumed to be in the WBL. Tunneling gap set with a setpoint current of 1 nA at 60 mV.
5.2.5 Simulated IETS maps

Besides STM imaging and IETS spectroscopy, another way to discriminate between possibly used tips is by comparing theoretical and experimental IETS maps. In general it is very challenging to experimentally obtain a stable $d^2I/dV^2$ map, and therefore this comparison is most of the times not possible. Also in this specific case of CO on Ag(110), no experimental IETS map is available, only a description of the performed experiment. Still a theoretical investigation into the possible appearances is presented here.

The IETS maps for several voltages with the four considered tips are shown in Fig. 5.7. The height of the tip is adjusted at each pixel to obtain the setpoint current at the corresponding voltage. Only the surface vibrational modes are taken into account in these maps: modes 11 through 21 at 15.0 mV, mode 22 at 37.5 mV and mode 23 at 250.0 mV, where the numbering refers to the numbering in Table A.1 in Appendix A.

The $dI/dV$ and $d^2I/dV^2$ maps are too noisy to interpret, therefore only the maps corresponding to the inelastic current are shown in Fig. 5.7, which are referred to as IETS maps in this Subsection. They can be straightforwardly obtained after saving for each pixel the inelastic terms given by Eq. 4.32. Note that the CO molecule is imaged as a dip with a CO terminated tip in Figs. 5.7n and s. It is possible that the tunneling path giving the bright ring has a smaller decay rate than the tunneling path giving the bright center, and hence with larger voltages or smaller setpoint currents (i.e. larger tip-sample distances), the ring becomes more pronounced than the center. Note however that these STM images are obtained using the WBL; it is not investigated if this contrast change is also observed in the simulated STM images beyond the WBL.

In most cases, vibrational modes are only excited when the tip is above the molecule. The IETS maps are more localized in space than the corresponding topographical images, as observed in the experimental $d^2I/dV^2$ maps. Figs. 5.7j and r show IETS maps where the inelastic current is not the highest above the CO molecule, but around it. This is consistent with Ref. 12, where an enhancement of the IETS peak around 35 mV is found for CO on Cu(111) upon lateral displacement of the tip, which consists of a CO molecule adsorbed at a hollow site on a Cu(111) surface, most closely resembling the CO terminated blunt tip in this work. The main factor behind this behavior is the increase in the number of allowed tunneling paths when the symmetry is reduced.
Figure 5.7 $2 \times 2 \text{ nm}^2$ $I^{\text{inel}}$ maps (right image per pair) and the corresponding STM images (left image per pair), obtained with the LOIT+WBL method. The voltages with which the maps are obtained are given in the insets. 

- **a-b)** Clean sharp tip, $I_{sp} = 1 \text{ nA}$; 
- **c-h)** Clean blunt tip, $I_{sp} = 1 \text{ nA}$; 
- **i-n)** CO terminated sharp tip, $I_{sp} = 0.1 \text{ nA}$; 
- **o-t)** CO terminated blunt tip, $I_{sp} = 1 \text{ nA}$.

5.2.6 Propensity rules

When measuring the energies of vibrational modes of molecules in an infrared or Raman spectroscopy experiment, there are clear optical selection rules that determine which vibrational modes will be excited and which not. In IETS experiments, there are not such selection rules, but still some vibrational modes are more likely excited than others. Which vibrational modes will be excited and which not are governed by so-called propensity rules. While selection rules result from exact symmetries or other
properties of the system, propensity rules result from less clearly identified circumstances. The propensity rules for vibrational modes in molecular transport junctions have been addressed before in literature.\textsuperscript{11,12} For the similar system of CO on Cu(001), probed with a single Cu atom on a Cu(111) plane, an intensity of 9.2\% for the T-mode, 12.7\% for the R-mode, 0.2\% for the $\nu$(Cu-CO) mode and 0.7\% for the $\nu$(C-O) mode are found.\textsuperscript{11} These intensities are higher than those found with a clean sharp tip in this Chapter. One possible explanation is that the tip-sample distance in Ref. 11 is significantly smaller. This might lead to an overestimation of derivatives of Hamiltonian elements to normal mode coordinates. Another possible explanation is that their main current carrying tip apex orbitals are s-orbitals, which are necessary to be able to excite a T- or R-mode. In the more realistic tips taken into account in this Chapter, the main current carrying orbitals are not solely apex s-orbitals, which can easily explain a factor 2 in inelastic intensity.

Three main factors are influencing the intensity of an IETS peak: i) the size of the involved electron-vibration coupling elements ($M_{LR}^\lambda$), ii) the contribution of the corresponding AOs to the tunneling current and iii) possible interference effects.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.8.png}
\caption{LOIT+WBL intensity of the inelastic conductance vs. the maximum value of the matrix $M_{LR}^\lambda$. The colors indicate in which system the intensity is calculated, as is shown in the legend. The dots give the data points for the different vibrational modes, the solid lines are quadratic fits per system. For the clean sharp tip on CO (red curve), the indicated modes are excluded from the fit.}
\end{figure}
To investigate the role of the values of the elements of $M_{LR}^\lambda$, the intensity of the peaks per vibrational mode is presented in Tables A.2 and A.3 in Appendix A, together with the maximum element of the matrix $M_{LR}^\lambda$. In general, one can state that the higher $M_{LR}^\lambda$, the higher the IETS intensity. To visualize this, the columns of Tables A.2 and A.3 are plotted in Fig. 5.8. Per system of surface + tip the inelastic signal of any vibrational mode is roughly proportional to its electron-vibration coupling elements squared. The same trend is observed if the intensity is not compared with the maximum element of $M_{LR}^\lambda$, but with the average element of $M_{LR}^\lambda$, because a linear relation is found between these two characteristic numbers of the matrix $M_{LR}^\lambda$.

**Table 5.3** Pairs of atomic orbitals (by index and by type) with the highest value of $M_{LR}^\lambda$, the highest elastic current and the highest inelastic current for vibrational mode 6 (defined in Table A.1 in Appendix A), a $\nu$(Ag) mode. The columns $S$ indicate the surface AO, the columns $A$ indicate the apex AO. A number behind a chemical species indicate the layer in which the atom resides.

<table>
<thead>
<tr>
<th>Highest $M_{LR}^\lambda$</th>
<th>Highest $I^{el}$</th>
<th>Highest $I^\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>A</td>
<td>S</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>C(s)</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>C(s)</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>O(p_z)</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
<td>C(p_z)</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>C(s)</td>
</tr>
<tr>
<td>21</td>
<td>5</td>
<td>C(p_z)</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>O(d)</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>C(s)</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>O(p_z)</td>
</tr>
<tr>
<td>1</td>
<td>61</td>
<td>O(s)</td>
</tr>
</tbody>
</table>

Although in general a higher $M_{LR}^\lambda$ leads to a higher IETS intensity, it might be lower than expected if the involving atomic orbitals are not contributing to the tunneling current. From Eq. 4.32 it can be understood that the inelastic current is only high if the transmission through the channels $\left| \rho_{\beta\alpha}^{m_{\mu},\pm\lambda} \right|$ in the tip and $\left| \rho_{\alpha\alpha}^{m_{\sigma}} \right|$ in the surface are high as well. In the WBL, if these transmissions are high, the elastic current is in general high as well. An inelastic tunneling path involving AOs $\alpha$ and $\beta$ is therefore low if the corresponding elastic tunneling path is also low. An example is one of the $\nu$(Ag) modes in the system with the clean sharp tip, indicated in Fig. 5.8. Table 5.3 shows the pairs of AOs for which $M_{LR}^\lambda$ is high for this particular mode, and also the
pairs of AOs which contribute the most to the elastic current. Since they are not the same, this is an indication that the inelastic tunneling paths involving the AOs for which $M_{LR}^\lambda$ is high contribute hardly to the total tunneling current. Indeed, the most contributing inelastic tunneling paths are the ones also contributing to the elastic tunneling current, shown in the last column of Table 5.3. Since for these AOs, $M_{LR}^\gamma$ is smaller, the total contribution of this vibrational mode is low.

Another reason why a high $M_{LR}^\lambda$ does not automatically lead to a high IETS intensity is the possibility for destructive interference. For instance, Table A.2 in Appendix A shows that the $\nu$(Ag-CO) mode has the highest value of $M_{LR}^\lambda$ for all used tips. However, with the clean sharp tip it does not exhibit the largest intensity. This is due to destructive interference between different pathways exciting this vibration. This is shown in Table 5.4, where the inelastic contribution per pair of AOs is shown after interference with all the inelastic tunneling paths. Negative numbers indicate a net destructive interference of this particular path with the other paths. The total of all the individual intensities add up to the total inelastic intensity of this vibrational mode and is only 1.1%. A similar destructive interference is found for the channels involving the $\nu$(C-O) mode.

**Table 5.4** Inelastic contribution of the $\nu$(Ag-CO) mode to the total tunneling current in % for the 10 most contributing pairs of AOs. The contribution is defined as the inelastic transmission involving the $\nu$(Ag-CO) mode and AOs $\alpha$ and $\beta$ after interference with all inelastic tunneling paths, divided by the total elastic + inelastic transmission.

<table>
<thead>
<tr>
<th>S</th>
<th>A</th>
<th>S</th>
<th>A</th>
<th>Inel. contr.</th>
<th>S</th>
<th>A</th>
<th>S</th>
<th>A</th>
<th>Inel. contr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>O(s)</td>
<td>Ag(s)</td>
<td>1.10</td>
<td>5</td>
<td>1</td>
<td>O(p_z)</td>
<td>Ag(s)</td>
<td>0.57</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>O(s)</td>
<td>Ag(d)</td>
<td>-0.85</td>
<td>5</td>
<td>15</td>
<td>O(p_z)</td>
<td>Ag(d)</td>
<td>-0.47</td>
</tr>
<tr>
<td>1</td>
<td>14</td>
<td>O(s)</td>
<td>Ag(d)</td>
<td>0.79</td>
<td>5</td>
<td>14</td>
<td>O(p_z)</td>
<td>Ag(d)</td>
<td>0.44</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>O(s)</td>
<td>Ag(p_z)</td>
<td>-0.77</td>
<td>5</td>
<td>5</td>
<td>O(p_z)</td>
<td>Ag(p_z)</td>
<td>-0.35</td>
</tr>
<tr>
<td>1</td>
<td>18</td>
<td>O(s)</td>
<td>Ag(z)(p_x)</td>
<td>0.62</td>
<td>1</td>
<td>10</td>
<td>O(s)</td>
<td>Ag(d)</td>
<td>-0.21</td>
</tr>
</tbody>
</table>
5.3 Summary

The main conclusion of this Chapter is that applying the computationally cheap LOIT+WBL approach to the simulation of IETS spectra gives qualitatively correct predictions for which vibrations are excited in a system. The results also demonstrate the relevance of having adsorbed molecules at the tip apex when interpreting the inelastic spectra and, more importantly, the peak intensities show a large sensitivity to the precise apex geometry. Therefore, these simulations may be regarded as an additional tool to characterize the tip employed in an STM experiment, which is the great unknown in this technique. Further key observations of this Chapter are:

- No R(C-O) mode is found for the CO terminated sharp tip. A softening of the R(C-O) mode is found for the CO terminated blunt tip with respect to CO on Ag(110) surface. (Subsection 5.2.2)
- Simulations of STM images reveal a contrast change of a CO molecule imaged with clean tips or CO terminated tips, in good agreement with the experiment. (Subsection 5.2.3)
- In the system of CO on Ag(110), the R(C-O) and, depending on the used tip, the v(Ag-CO) mode are singled out as the mostly excited vibrational modes. An overall good agreement with the experimental IETS spectra has not been attained mainly due to the presence of the v(Ag-CO) peak in the spectra calculated with CO contaminated tips. This is most probably due to the simplified apex structures modeled in this study. Still, the results give good hints on which vibrational modes are active for each tip structure. (Subsection 5.2.4)
- The details of the elastic $dI/dV$ and $d^2I/dV^2$ curves are very tough to converge in k-grid size for this particular system. Therefore, the LOIT+WBL approach seems to provide more accurate results than if the energy dependence of the full Green's functions is fully taken into account. (Subsection 5.2.4)
- IETS maps provide molecular features more localized in space than the STM images, in agreement with the experiment. Sometimes they show the highest intensities around the surface molecule instead of on top of it due to broken symmetry arguments. (Subsection 5.2.5)
- The IETS intensity of a given vibrational mode $\lambda$ is large if i) the matrix elements $M^2_{LR}$ are large, ii) the corresponding AOs contribute to the elastic current and iii) there is no destructive interference. (Subsection 5.2.6)

In the next Chapter the LOIT+WBL approach will be employed on a system which has a richer variety of STM images. It will be investigated if the inclusion of inelastic effects to existing STM simulations can put additional constraints on the used tip apex.
5.4 Bibliography

Chapter 6 – STM and IETS on NO adsorbed on Rh(111) with clean and modified tips

The lowest order in inelastic tunneling (LOIT) method described in Chapter 4 has been applied in Chapter 5 to a realistic system of CO adsorbed on Ag(110). In this Chapter, the LOIT+WBL method is employed to use the observed IETS curves taken over NO adsorbed on Rh(111) to extract the possible tip termination. This system has been chosen since it has, compared with the CO on Ag(110) system, a much richer variety in STM imaging, depending on the details of the tip apex, but it is still a rather simple system to study theoretically. Matching different simulated STM images obtained with different tips to experimental ones have been reported before in literature.¹ There it was found that the STM images could be reproduced if a wide variety of tips is available. The extension of reproducing IETS curves and IETS maps with the same formalism as reproducing the STM images puts extra constraints on the possible tip terminations. This Chapter is similarly organized as Chapter 5. Section 6.1 gives the necessary details of the experiments and calculations. Section 6.2 is the main Section of this Chapter and shows the results from the STM and IETS simulations with the LOIT+WBL approach, and gives a comparison with their experimental counterparts. In the end, the main conclusions are summarized in Section 6.3.

6.1 Details of experiments and calculations

Just as Section 5.1, this Section presents only specific details of the STM experiments and of the calculations. Parameters not explicitly mentioned in this Section are given in the Chapters 3 and 4.

6.1.1 Details of the STM experiments

All experimental results are obtained by Joris Hagelaar in the group Molecular Materials and Nanosystems at the Eindhoven University of Technology, and published in Ref. 2. The STM experiments have been performed in UHV at 77 K. The Rh(111) surface is cleaned by cycles of Ar⁺ ion sputtering at 500 °C for 90 minutes and annealing at 500, 600 and 700 °C for 20 minutes at each temperature, after which the sample was flashed to 1200 °C. Nitric oxide is dosed by keeping the Rh sample at 200 K while exposing it to NO gas. The used tips are etched polycrystalline tungsten tips and heated in UHV to remove the native oxide layer. Care has been taken not to dip the tip into the surface, as explained in Subsection 2.2.8, although substrate atom transfer to the tip can not be excluded. Since the tip is already mounted in the STM during exposure of the sample to the NO gas, it can also be covered by NO molecules.
Controlled transfer of single molecules between the tip apex and the surface was not possible.

### 6.1.2 Details of the DFT calculations

All DFT calculations have been performed using the SIESTA code. Three surface structures of NO on Rh(111), found in the experiments in Ref. 2, are examined in this Chapter. They are illustrated in Fig. 6.1. Two of them, called the 2×2 and the c2×4 surface, are monolayers with a coverage of one NO molecule per two Rh atoms, which both have been found in the experiments. They consist of zigzag chains of alternating NO species adsorbed at hcp and fcc sites. The relative orientation of each chain with respect to its neighbor chain, separated by a $\sqrt{3}a$ distance with $a$ the Rh-Rh distance in the 111-plane, distinguishes one phase from the other. The third structure is called the 4×4 structure, in which one NO is adsorbed in a unit cell of 16 Rh atoms. This represents a single molecule on the surface. In all cases, the NOs are adsorbed upright with the N atom closest to the metal.

![Figure 6.1 Schematic overview of the three investigated structures of NO on Rh(111).](image)

The fcc lattice constant for Rh, determined from a bulk optimization, is 3.848 Å, while the experimental value is 3.80 Å. The slab consists of five layers, of which the bottom two layers are fixed at bulk positions. The calculations are performed in SIESTA under the generalized gradient approximation (GGA). The chosen k-grid sampling is an 8×8 Monkhorst Pack (MP) grid for the 2×2 and c2×4 surfaces and a 4×4 MP grid for the 4×4 surface, both equivalent to a 16×16 grid of a 1×1 Rh(111) inplane lattice. Van-der-Waals interactions have not been taken into account, since NO is known to strongly chemisorb on the metal.

In order to explore in detail any tip effects, both in the topography and IETS curves, eight different tip apex structures have been considered. It is assumed that the apex consists of W atoms. Bulk tungsten has a bcc lattice structure, but in order to obtain sharper tips, W tips in the hypothetical fcc phase have been used as well as W tips in the bcc phase. For both crystal structures, the tips considered are based on a W(111) oriented surface with a pyramid of 10 Ag atoms forming the apex. First, a clean sharp
tip apex is modeled by a single atom terminated pyramid, while a clean blunt tip is obtained by removing the end atom. NO terminated tips are next modeled by adding an NO molecule. For the sharp tip, the adsorption site is the end atom, for the blunt tip, the adsorption site is the threefold hollow site, as in Figs. 5.2a and b. For fcc tips a 4×4 supercell relative to the W(111) is defined and the pyramid is stacked below a 3 layer slab. The fcc lattice constant, determined from a hypothetical fcc bulk optimization, is 4.09 Å, and a 2×2 MP grid is employed, equivalent to a 8×8 grid of a 1×1 fcc W(111) lattice. For bcc tips a 3×3 supercell relative to the W(111) is defined, and the pyramid is stacked below a 12 layer slab. This high amount of layers is necessary to guarantee bulklike behavior for the deepest W atoms, since the interlayer distance in a bcc(111) structure is only 0.29 Å, where a is the lattice constant. The bcc lattice constant of tungsten, obtained from a bulk optimization, is 3.237 Å, while the experimental lattice constant is 3.165 Å. Note that with these lattice constants, the atom density in the bcc and fcc bulk is similar within 1%. A 3×3 MP grid, equivalent to a 9×9 grid of a 1×1 bcc W(111) lattice, is used for the bcc W tips.

For both the surface and the tips, the resolution of the real space mesh is set to 500 Rydberg and a similar mesh sampling is employed as in Chapter 5. The convergence threshold for the Hamiltonian elements is set to 1 meV and all free atoms are fully relaxed until the remaining forces are below 0.02 eV/Å.

Vibrational modes are calculated by displacing the free atoms in all directions and calculating the eigenmodes of the corresponding force matrix, as explained in Subsection 3.1.3. A diagonal element correction has been employed here.3 For the 2×2 and c2×4 surfaces, the free atoms are the NO molecules and the top layer of the Rh(111) surface. For the 4×4 surface, the free atoms are the NO molecule and the 27 Rh atoms which are less than 6.5 Å away from the N atom. For the NO terminated tips, the free atoms are the NO molecule and the 10 W atoms of the pyramid (9 W atoms for the truncated pyramid). Vibrational modes of the clean tips have not been determined.

6.1.3 Details of the Green's functions calculations

All Green's functions based calculations have been performed using the GREEN code. In order to generate the self-consistent Hamiltonian, three more Rh layers are added after ionic optimization to the surface structure, 6 more layers of W(111) are added on top of the fcc 4×4 slab and 5 more layers on top of the bcc 3×3 slab. The self-consistent field procedure in GREEN is checked by comparing the on-site energies of the AOs between the bulk calculation and the atoms in the center of the slab, where a maximum deviation of 16 meV is found for the surfaces and 24 meV for the tips. The Slater-Koster parameterization has been performed using scheme 3 from Subsection 3.2.6. The used imaginary energy in each calculation, being a measure for the width of the elastic peaks, is 20 meV. The value for kT, being a measure for the width of the inelastic peaks, is 5 meV. The used k-grids are the same as for the DFT calculations. While the DFT calculations are converged in k-points, the elastic current can still change strongly with increasing number of k-points. It has been shown in Subsection 5.2.4 that the
LOIT+WBL method provides a clearer picture for the IETS interpretation. Therefore, although the STM images are calculated using the full Green's functions, all IETS curves are calculated using the LOIT+WBL approach. In the STM simulations, the energy ranges from 0 to 100 meV with an increment of 10 meV, and the lateral resolution is 0.4 Å. In the IETS simulations, the energy ranges from -400 to 400 meV to cover all vibrational modes. The used increment of 2.5 meV is the maximum value that should be used for proper resolution of the IETS peaks given the value for $kT$. The height of the tip has been adjusted such that the elastic current is 1 nA at a bias voltage of 100 mV. The calculation of these IETS curves require typically only a few seconds on a 3 GHz Intel processor.

6.2 Results and discussion

This Section is the main Section of this Chapter and presents a comparison between experimental STM and IETS results and their simulated counterparts. First, the experimental results are shown in Subsection 6.2.1. The DFT results, including the energies and assignments of the vibrational modes, are presented in Subsection 6.2.2. These DFT results are used for the simulations with the Green's functions based LOIT+WBL method, which are presented in the subsequent Subsections: elastic STM images in Subsection 6.2.3, IETS curves in Subsection 6.2.4 and IETS maps in Subsection 6.2.5.

6.2.1 STM and IETS experiments

![Figure 6.2 Topographical images of NO molecules adsorbed on a Rh(111) surface. a-c) 2×2 monolayer; d-e) c2×4 monolayer; f) unordered NO molecules. Experimental parameters: a) 3×3 nm², V = -99 mV, I_{sp} = 0.44 nA; b) 2×2 nm², V = -99 mV, I_{sp} = 0.44 nA; c) 3×3 nm², V = -99 mV, I_{sp} = 0.25 nA; d) 1.5×1.5 nm², V = 94 mV, I_{sp} = 0.35 nA; e) 5×5 nm², V = 127 mV, I_{sp} = 0.42 nA; f) 6.5×6.5 nm², V = 221 mV, I_{sp} = 1.07 nA. All images are taken from Ref. 2.](image-url)
A selection from the wide variety of STM images is shown in Fig. 6.2. Since controlled transfer of NO molecules from and to the tip was not possible, it cannot be concluded upfront which images are obtained with which tip. Figs. 6.2a-c show three different images of the 2×2 surface. In Fig. 6.2a, each NO molecule is imaged as a protrusion with an equal intensity, but in Fig. 6.2b the fcc adsorbed NO molecules have a higher corrugation than the hcp adsorbed NO molecules, or vice versa. Fig. 6.2c shows a possible interference effect, wherein a triangle of bright spots is observed around each NO molecule. Figs. 6.2d-e show two different images of the c2×4 surface. In Fig. 6.2d the molecules are imaged individually, while in Fig. 6.2e the molecules are imaged as zigzag lines without resolving individual molecules. Fig. 6.2f shows an example of individual unordered NO molecules, in this Chapter modeled as the 4×4 surface. With this particular tip, they are imaged as rings.

Figure 6.3 a) Topographical STM image showing a mixture of isolated NO molecules and molecules arranged in the c2×4 structure. b) d²I/dV² curves measured on the single molecule (thick solid line, upper black cross in (a)), on the c2×4 structure (thin solid line, lower black cross in (a)) and on the bare Rh(111) surface (dotted line, white cross in (a)). Experimental parameters: a) 4.9×4.9 nm², V = 100 mV, I_{sp} = 2 nA; b) tunneling gap set with same V and I_{sp}; spectrum is an average over 4 curves of 1 minute each; lock in parameters: V_ω = 14 mV RMS, ω = 4.7 kHz. Figure adapted from Ref. 2.

There are several d²I/dV² curves reported in Ref. 2, each accompanied by an STM image which is taken just before measuring the d²I/dV² curve, giving a hint of the used tip. Most STM images resemble the images in Figs. 6.2b and 6.2f, which could not be theoretically reproduced in this study, as will be shown in Subsection 6.2.3. The only STM image which could be reproduced with the used tips is similar to the image in Fig. 6.2d; the corresponding measured d²I/dV² curve is shown in Fig. 6.3. Antisymmetric loss peaks show up at -57 and 56 mV with respective IETS intensities of 1% and 3.5%, and at -18 and 17 mV with unspecified IETS intensities, but in the order of 1%. There is no qualitative difference observed between the loss peaks on the c2×4 and the isolated molecule. Different measurements with the same tip taken consecutively show qualitative similar curves, but slightly varying intensities. There are no experimental IETS maps available.
6.2.2 DFT calculations

Table 6.1 Geometric results of NO chemisorption on Rh(111) and on sharp and blunt bcc and fcc W tips.

<table>
<thead>
<tr>
<th>Structure</th>
<th>N-O distance (Å)</th>
<th>Rh – N distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2×2 surface</td>
<td>1.21</td>
<td>2.09</td>
</tr>
<tr>
<td>c2×4 surface</td>
<td>1.21</td>
<td>2.06-2.10</td>
</tr>
<tr>
<td>4×4 surface</td>
<td>1.22</td>
<td>2.07</td>
</tr>
<tr>
<td>NO terminated sharp bcc tip</td>
<td>1.22</td>
<td>1.86</td>
</tr>
<tr>
<td>NO terminated sharp fcc tip</td>
<td>1.21</td>
<td>1.88</td>
</tr>
<tr>
<td>NO terminated blunt bcc tip</td>
<td>1.41</td>
<td>2.02-2.06</td>
</tr>
<tr>
<td>NO terminated blunt fcc tip</td>
<td>1.28</td>
<td>2.16</td>
</tr>
</tbody>
</table>

The geometric parameters of the relaxed surface and tip structures are given in Table 6.1. The surface NO adsorption is visually similar as that of CO on Ag(110), shown in Figs. 5.2c and d, except that the NO molecules are adsorbed in a hollow site. The geometry of the fcc tips is visually similar as the fcc Ag tips, shown in Figs. 5.2a and b. The geometry of the bcc NO terminated tips is shown in Fig. 6.4, while the clean bcc tips are visually identical to their NO terminated counterparts after removing the adsorbed molecule. The NO molecule adsorbed on the blunt bcc tip has two nearest neighbors and makes a tilt angle of 66° with respect to the tip axis. This geometry is probably a metastable phase, but in any case worth studying. In all other structures the NO tilt angle with respect to the surface normal or tip axis is 0°. The NO molecules adsorbed on the surface or on the blunt fcc tip have three nearest neighbors, the NO molecules adsorbed on the sharp tips have one nearest neighbor.

Figure 6.4 Unit cells of relaxed bcc NO terminated tip geometries. The large spheres are W atoms, the light small spheres are N atoms, and the dark small spheres are O atoms. Figure made with XCrySDen. The insets show the pictograms representing the tips. a) sharp bcc NO terminated tip; b) blunt bcc NO terminated tip.
Table 6.2 Energies (in meV) and assignments of vibrational modes for NO on Rh(111) and on W tips. \( \nu = \) stretch, \( R = \) hindered rotation, \( T = \) hindered translation. Atoms in parentheses indicate moving atoms in vibrational mode.

<table>
<thead>
<tr>
<th></th>
<th>2( \times )2</th>
<th>c( \times )4</th>
<th>4( \times )4</th>
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</thead>
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<tr>
<td>( h \sigma )</td>
<td>Assignment</td>
<td>( h \sigma )</td>
<td>Assignment</td>
</tr>
<tr>
<td>183-198</td>
<td>( \nu )(N-O)</td>
<td>185-197</td>
<td>( \nu )(N-O)</td>
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<tr>
<td>49-59</td>
<td>R(N-O)</td>
<td>51-57</td>
<td>R(N-O)</td>
</tr>
<tr>
<td>46-50</td>
<td>( \nu )(Rh-NO)</td>
<td>45-46</td>
<td>( \nu )(Rh-NO)</td>
</tr>
<tr>
<td>30</td>
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<td>28-29</td>
<td>( \nu )(Rh-NO)</td>
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<tr>
<td>11-26</td>
<td>R(Rh-NO)</td>
<td>10-27</td>
<td>R(Rh-NO)</td>
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<table>
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<th>Sharp bcc tip</th>
<th>Assignment</th>
<th>Sharp fcc tip</th>
<th>Assignment</th>
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<tr>
<td>( h \sigma )</td>
<td>( h \sigma )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>197</td>
<td>( \nu )(N-O)</td>
<td>250</td>
<td>( \nu )(N-O)</td>
</tr>
<tr>
<td>60</td>
<td>( \nu )(W-NO)</td>
<td>73</td>
<td>( \nu )(W-NO)</td>
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<tr>
<td>35-37</td>
<td>R(N-O)</td>
<td>51-52</td>
<td>R(N-O)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blunt bcc tip</th>
<th>Assignment</th>
<th>Blunt fcc tip</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
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<td>( h \sigma )</td>
<td>( h \sigma )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>104</td>
<td>( \nu )(N-O)</td>
<td>204</td>
<td>( \nu )(N-O)</td>
</tr>
<tr>
<td>55</td>
<td>( \nu )(W-NO)</td>
<td>49</td>
<td>( \nu )(W-NO)</td>
</tr>
<tr>
<td>37, 53</td>
<td>R(N-O)</td>
<td>47-50</td>
<td>R(N-O)</td>
</tr>
<tr>
<td>22, 44</td>
<td>T(N-O)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The calculated vibrational modes are summarized in Table 6.2. A more detailed overview of all vibrational modes found is given in Table B.1 in Appendix B. For the two dense surface structures 2\( \times \)2 and c\( \times \)4, the \( \nu \)(N-O) mode is split in an out-of-phase \( \nu \)–mode of the two molecules and an in-phase \( \nu \)–mode, which is 12-15 meV higher than the out-of-phase stretch mode. A similar splitting occurs in the R-mode, but here the out-of-phase R-mode is 6-8 meV higher than the in-phase R-mode. The energies of the \( \nu \)(N-O) mode and \( \nu \)(Rh-NO) have experimentally been determined with electron energy loss spectroscopy (EELS) to be 183-203 meV and 45-50 meV respectively,\(^5,6\) where the higher values are found for higher coverages. This agrees well with the calculated values. No experimental values for the R-modes have been reported so far. For the tips, the same vibrational modes have been found for the three tips with the upright NO adsorbed to it, but the energies of the vibrational modes depends significantly on the details of the tip. Due to its particular geometry, the blunt bcc NO terminated tip presents a set of vibrational modes that differs significantly from the rest, particularly the \( \nu \)(N-O) mode which is found 100 meV lower in energy.
6.2.3 Simulated STM images

The simulated STM images for the three different surfaces are presented in Figs. 6.5 and 6.6 for the clean and NO terminated tips respectively. Qualitatively they match the simulated STM images obtained with different tips\(^1\) and under the extended Hückel approximation, explained in Subsection 3.2.7. The circles in the STM images indicate the positions of the NO molecules on the surface. It follows from Fig. 6.5 that with a clean tip, the NO molecules are in general imaged as dips, with the exception of Figs. 6.5g and h. This can be explained by a reduction of DOS in the metal surface due to the adsorbates combined with a low probability of tunneling through the orbitals of the NO molecule.\(^7\) The experimental image in Fig. 6.2e resembles closely the simulated image in Fig. 6.5e, and thus it might have been acquired with an apex with a structure similar to that of the sharp fcc W tip.

![Figure 6.5 Simulated 2×2 nm² STM images for the three different NO on Rh(111) surfaces with four different clean tips. Simulation parameters: \(V = 100\) mV, \(I_{sp} = 1\) nA.](image)

Figs. 6.6a-f and j-l show that with an NO adsorbed upright on the tip, the surface NO molecules are imaged as protrusions, similar to the CO imaging with CO terminated tips in Chapter 5. This suggests that the interaction between tip states and orbitals of the surface NO molecules is increased and hence the probability for tunneling through the orbitals of the surface NO molecules is increased for an NO terminated tip. Atomic resolution on the Rh(111) surface is achieved with an NO terminated sharp tip, as can
be seen in Figs. 6.6c and f, where the individual Rh atoms are images as dips. The experimental image in Fig. 6.2a resembles the simulated images in Figs. 6.6a, d and j, while the experimental image in Fig. 6.2d resembles the simulated images in Figs. 6.6b, e and k, and thus these images are probably made using a tip with an NO adsorbed upright on the tip. The inequivalent imaging of the fcc and hcp adsorbed NO molecules, seen in Fig. 6.2b, the interference effects between different tunneling paths,1,2 seen in Fig. 6.2c, and the ring-shaped imaging of NO molecules, seen in Fig. 6.2f, have not been reproduced with these tips. The first two images can be reproduced however by tilting an appropriately chosen tip.1 It should be noted that the details of any simulated STM image are sensitive to the parameterization of the interactions between tip and sample. Since no optimal scheme has been developed yet to obtain robust SK parameters, care must be taken to not overinterpret the simulated STM images.

![Simulated STM images for the three different NO on Rh(111) surfaces with four different NO terminated tips. Simulation parameters: V = 100 mV, I_{sp} = 1 nA.](image)

**Figure 6.6** Simulated 2×2 nm² STM images for the three different NO on Rh(111) surfaces with four different NO terminated tips. Simulation parameters: V = 100 mV, I_{sp} = 1 nA.

### 6.2.4 Simulated IETS curves

The results of the simulated IETS curves on top of the center of the NO molecules and on top of the bare Rh(111) substrate are shown in Fig. 6.7. The blue lines present the IETS curves with only the surface vibrational modes taken into account, the red lines those with only the tip apex vibrational modes taken into account and the green lines
those with all vibrational modes taken into account. The legends display the intensity of the peaks, defined here as the integral of the IETS intensity between 0 and 100 mV. The inelastic peaks around ±200 mV due to the surface and tip v(N-O) modes are also observed, but not shown here. They are not observed in the described experiment.

Inelastic effects are mostly observed with tips with an NO molecule adsorbed upright. For the clean tips and the tip with the NO adsorbed flat, the intensity is less than 1%. With an NO adsorbed upright, the peaks are independent of the used tips and not sensitive to the surface structure. In Figs. 6.7b-l the same peaks have been found as in the experiment: one around 20 meV and one around 55 meV, which is a convolution of a peak just below 50 mV at the surface and a peak around 60 mV at the tip. The peak around 60 mV is also observed on the clean Rh(111) surface, Figs. 6.7n and o, although the intensity of this peak is smaller than on the NO molecule. This is in line with the experiment, where no peak has been found at this energy on the bare Rh, but the broad tail of the peak at 20 mV might be interpreted as a shoulder feature around 55 mV.

Figs. 6.7a-m show the spectra obtained with the clean sharp fcc W tip. The curves with the other W tips are similar, but lower in intensity. The peak around 55 mV is seen as a shoulder, not as pronounced as on the positive side of the experimental spectrum, but rather similar to the negative side of the experimental spectrum. Since this experimental curve is ambiguous whether the peak around 55 mV is excited or not, it does not exclude any of the clean or NO terminated tips. If the experimentally used tip is a bare metallic tip, then the NO molecules in the c2×4 surface are imaged as dips, as can be seen in Fig. 6.5e, and the spectra in Fig. 6.3b are taken in between the molecules. Simulated spectra on top of the NO and in between the NO molecules in the c2×4 structure are however similar in appearance and intensity.

Quantitatively, the intensities of the two peaks and the ratio between them vary per tip and surface structure. The calculated intensities with NO terminated tips are higher than the intensity measured in the experiment, while with clean tips they are lower than measured. The intensity obtained with this LOIT+WBL method is however highly sensitive to the SK parameters. Together with the spread in the experimental intensities and the vast plethora of possible tip terminations in mind, a quantitative agreement is not expected.

The intensity and assignment of the most excited vibrational modes is shown in Tables B.2 and B.3 in Appendix B, including the stretch modes around 200 mV. In all cases the most excited vibrational modes are metal-NO stretch modes at the surface (45-50 mV) and tip (60 mV), making up the peak around 55 mV. The peak around 20 meV is assigned to a convolution of the in phase v(Rh-NO) mode and several R(N-O) modes. In some cases, e.g. Figs. 6.7k and l, these combined peaks around 20 mV have a higher total intensity than the peak from the v(Rh-NO) mode around 50 mV. The experimental peak could also include vibrational modes below 10 meV, which are not taken into account in these calculations.
Figure 6.7 a-o) IETS curves for different tips (columns) and surfaces (rows) and with different vibrational modes taken into account (colors, see main text), obtained with the LOIT+WBL method. The insets show a sketch of the used tip and surface, the legends display the intensity of the sum of the peaks for the corresponding curve. In all graphs, the tunneling gap is set with a setpoint current of 1 nA at 100 mV. p) Repetition of the experimental $d^2I/dV^2$ curve, Fig. 6.3b.

The observation that inelastic effects are small in the IETS curves obtained with tips without NO adsorbed upright is consistent with the suggestion put forward in the previous Subsection that with these tips - clean tips or the tip with a flatly adsorbed NO molecule - the probability of tunneling through the surface NO molecules is low. The generalization of Eq. 4.26 to the 3D case indicates that a vibrational mode $\lambda$ is not excited if the corresponding electron states (i.e. states $|\alpha\rangle$ for which the elements $M_{\alpha\beta}^\lambda$ are large) are not involved in the transport. At this point it is not investigated if the electrons indeed traverse a path that does not include the orbitals of the NO molecule.
6.2.5 Simulated IETS maps

As pointed out in Subsection 5.2.5, it is very challenging to obtain experimental IETS maps. Also in this study there is not such a map of NO on Rh(111) available. Still a theoretical investigation into the possible appearances is presented here.

Tables B.2 and B.3 in appendix B show that the contributions from tip apex vibrational modes dominate over the surface vibrational modes. Therefore only the tip apex modes are considered in the IETS maps calculated in this Subsection. The IETS maps for several voltages for the 2×2 and 4×4 surface with the three tips which give the largest inelastic effects are shown in Fig. 6.8. The height of the tip is adjusted at each pixel to obtain the setpoint current of 1 nA at the corresponding voltage. The STM images shown in Fig. 6.8 are only for the lowest voltages, but qualitatively they are similar for all considered voltages. For the NO sharp fcc W tip, the considered vibrational modes are modes 18 and 19 at 42.5 V, mode 20 at 57.5 V and mode 21 at 202.5 V; for the NO blunt fcc W tip, the considered vibrational modes are modes 17, 18 and 19 at 40.0 V, and mode 20 at 165.0 V; for the NO sharp bcc W tip, the considered vibrational modes are mode 12 at 60.0 V, and mode 13 at 197.5 V, where the numbering refers to the numbering in Table B.1 in Appendix B. The $\frac{dI}{dV}$ and $\frac{d^2I}{dV^2}$ maps are too noisy to interpret, therefore only the maps providing the inelastic current are shown in Fig. 6.8, which are referred to as IETS maps in this Subsection.

The most striking result is the large sensitivity of the maps to voltage, or equivalently, to the apex vibrational modes. This reflects that each vibrational mode is probed by different states at the surface, in line with the propensity rules outlined in the previous chapter. The IETS maps show that the inelastic current is in general largest if the tip is positioned over the NO molecules. The apex vibrational modes are then probed by these molecules. There are some cases though where the intensity is highest in a region around the surface NO molecules. In Figs. 6.8b and f, the NO molecules are imaged as bright rings with a dark center. This can in principle be used in experiments to confirm the location of the NO molecules, and when this coincides with the bright spots in the STM image, the conclusion of an NO terminated tip can be drawn. Note however that the surface vibrations are also in this voltage range and are not taken into account in this calculation. They might compensate for the dark centers in the IETS maps. Isolated molecules are also imaged as dark centers at higher voltages (Figs. 6.8h, n and t), but in the 2×2 structure, the IETS intensities are highest above the NO molecules proper. The induced asymmetry between the hcp and fcc adsorbed NO molecules is probably too subtle to be detectable in any real experiment.
Figure 6.8 2×2 nm² IETS maps and the corresponding STM images, indicated in the top left of each image. Images (a-h) are obtained with an NO sharp fcc W tip over the surface indicated on the left with V indicated above the images. Images (i-t) are obtained with the tips indicated above the images over the surface indicated above the images with V indicated left of the images. All images are obtained with $I_{sp} = 1$ nA.
6.3 Summary

The main conclusion of this Chapter is that inclusion of inelastic effects in STM simulations and its comparison against the experimental counterparts can become a highly useful tool for the correct characterization of the tip apex structures. Further key observations of this Chapter are:

- The stretch and hindered rotation mode of the NO molecule are hardened if the NO coverage on a surface is increased. (Subsection 6.2.2)
- In the STM simulations, NO molecules are only imaged as a protrusion if an NO molecule is adsorbed in upright position on the tip. This suggests that without an NO molecule adsorbed upright on the tip, the probability for electrons to tunnel through the orbitals of the surface NO molecules is low. Simulated STM images match corresponding experimental ones for both the 2×2 and the c2×4 structure. (Subsection 6.2.3)
- The LOIT+WBL approach gives qualitatively correct predictions which vibrations are excited. In particular, in this system the measured peaks around ±18 mV are assigned to a convolution of the out-of-phase $\nu$(Rh-NO) and several R(N-O) modes and the peaks around ±55 mV to a convolution of the surface in phase $\nu$(Rh-NO) and tip $\nu$ (W-NO) modes. (Subsection 6.2.4)
- Geometric details of the tip and surface are crucial for the obtained IETS intensities. The low intensity of inelastic effects in the curves obtained with the tips without an NO molecule adsorbed upright is consistent with the low probability of tunneling through the orbitals of the surface NO molecules for these tips. (Subsection 6.2.4)
- While most apex modes are mostly excited with the tip above the surface NO molecules, some of them have a higher intensity just around the surface NO molecules. (Subsection 6.2.5)

In the next two Chapters, the more complex system of thiophenol on Ag(111) is studied, for which it is investigated if the LOIT+WBL approach can be used to explain the much-observed but little-explained zero-bias anomaly.

6.4 Bibliography

Chapter 7 – Structure of a thiophenol monolayer on Ag(111)

Single molecule transistors are widely regarded as the successor of current silicon-based technology.\textsuperscript{1} To investigate the electronic properties of single molecules, they must be connected to the macroscopic world via electrodes. In previous studies, molecules have been sandwiched between Au crosswires,\textsuperscript{2} adsorbed inside Au\textsuperscript{3} or Pt\textsuperscript{4} mechanical break junctions, or they are deposited onto Au,\textsuperscript{5,6} Ag,\textsuperscript{7,8} or Cu\textsuperscript{9} surfaces and contacted by an STM tip. The geometric details of the entire junction are of paramount importance for the electronic transport.\textsuperscript{10,11} The most used linker group to connect the molecule to the metal leads is a thiol group. Upon adsorption, the sulfhydryl hydrogen is dissociated\textsuperscript{12} and the molecule attaches to the surface through the S atom. In break junctions, these details are experimentally impossible to extract, but since thiols often form self-assembled monolayers (SAMs) on metal substrates, these structures can be studied in detail and used for electronic transport modeling, assuming that an STM tip and electric fields do not distort this structure significantly. For a correct description of electrical transport properties, it is important to include inelastic effects as well. Therefore, additional knowledge of the vibrational modes and its influence on electron dynamics is required, for which again the details of the geometry are required.

In this Chapter, low energy electron diffraction (LEED), STM and ab initio calculations are used to determine the adsorption geometry and the vibrational modes of a thiophenol (TP) on Ag(111) SAM, which will later be used in modeling the electronic transport in this system. The geometric structure of this SAM has been reported in literature before, although there seem to be inconsistencies regarding the packing density, ring tilt angle, S-C bond angle and adsorption site.\textsuperscript{12,13,14,15,16,17,18} In this Chapter, not only is DFT used to optimize the geometry of the unit cell, but it is also used in conjunction with the Green's functions formalism to simulate STM results and to calculate the vibrational modes of the monolayer. The results are compared with LEED, STM and high resolution electron energy loss spectroscopy (HREELS) experiments.

This Chapter is organized as follows: Section 7.1 gives a brief overview of the literature about this monolayer. Section 7.2 describes the details of the experimental and theoretical methods. Experimental LEED and STM results are presented and discussed in Section 7.3, followed by the results of the DFT and Green's functions calculations. Furthermore an experimental and theoretical analysis of the vibrational modes is presented. The conclusions of the Chapter are summarized in Section 7.4. The results of this Chapter will be used in the next Chapter to simulate IETS curves on this monolayer.
7.1 TP on Ag(111) in literature

Fig. 7.1a shows the structure formula of TP, and the definitions of the tilt angle \( \theta \), the SC bond angle \( \alpha \) and the azimuthal angle \( \zeta \). The angle \( \xi \) indicating the rotation of the carbon ring over the SC bond is not shown and not considered in this thesis. Upon adsorption on Ag(111), the sulfhydryl hydrogen dissociates and the sulfur atom binds to the silver. It is claimed by Gui et al.,\(^\text{12}\) based on Van-der-Waals radii, that there are 4 TP molecules within a unit cell of 17 Ag atoms. This packing density is subsequently assumed in other works.\(^\text{13}\) In this Chapter it will be argued however that there are 6 TP molecules within this 17 Ag atom unit cell.

**Figure 7.1** a) Structure formula of thiophenol; b-c) side view and d) top view of TP on Ag(111). Blue circles represent Ag atoms, yellow circles S atoms, green circles C atoms and red circles H atoms. Shown are the definitions of b) the ring tilt angle \( \theta \), c) the S-C bond angle \( \alpha \) and d) the azimuthal angle \( \zeta \).

Gui et al.\(^\text{12}\) have used electron energy loss spectroscopy (EELS) to determine the tilt angle \( \theta \) of the molecule, defined in Fig. 7.1b as the angle between the carbon ring and the surface normal, and found a perfectly vertical orientation. Taylor et al.\(^\text{13}\) found with surface enhanced Raman spectroscopy (SERS) experiments that \( \theta \approx 0 \) and Carron et al.\(^\text{14}\) concluded from their SERS experiments \( \theta \approx 9° \pm 4° \). On the other hand, Frey et al.\(^\text{15}\) used angle-resolved X-ray photoemission spectroscopy (ARXPS) to measure \( \theta = 24° \pm 5° \) and from a theoretical point of view, Bilić et al.\(^\text{16}\) used density functional theory (DFT) to find an optimal \( \theta \) of 65° for a packing density of 1 TP molecule per 9 Ag atoms. Mani et al.\(^\text{17}\) used sum frequency generation spectroscopy to determine the angle \( \alpha \), defined in Fig. 7.1c as the angle between the S-C bond and the surface normal, to be 37°±10°. However, Lee et al.\(^\text{18}\) calculated \( \alpha \approx 0 \) with the atom superposition and electron delocalization method. They also calculated with this method the adsorption site of the TP to be the hollow site, while Bilić et al.\(^\text{16}\) concluded from DFT calculations that the adsorption site is the bridge site, slightly shifted towards hollow. However, in the similar system of alkanethiols on Au(111), DFT calculations also suggest the bridge site as adsorption site,\(^\text{19}\) while normal incidence X-ray standing wave experiments suggest the top site,\(^\text{20}\) and even a complete reconstruction of the Au layer has been suggested upon adsorption of alkanethiols.\(^\text{21}\)
7.2 Details of experiments and calculations

Just as Sections 5.1 and 6.1, this Section presents only specific details of the experiments and of the calculations presented in this and the next Chapter. Parameters not explicitly mentioned in this Section are given in Chapters 3 and 4.

7.2.1 Details of the STM experiments

The samples used are Ag(111) single crystal samples (Surface Preparation Laboratory, Zaandam, The Netherlands). The surface is cleaned by repeated 30 minutes cycles of Ar⁺ ion bombardment and annealing to 450-500 °C. Thiophenol (Fluka, >99.5%) is applied to the surface by transferring the sample back to the fast entry chamber and backfilling this chamber through a leak-valve to 3·10⁻⁶ mbar at room temperature for 20 minutes. The structural quality of the monolayer is checked with LEED in the preparation chamber, and recorded by manually taking photographs of the fluorescent screen with a digital camera with an 8 second shutter time. STM images have been obtained at 77 K using a PtIr tip.

7.2.2 Details of the HREELS experiments

In a HREELS experiment, the sample is bombarded with electrons with a known energy and inplane momentum. After reflection at the sample, the intensity of outgoing electrons with a certain inplane momentum loss is measured as a function of their energy loss. The momentum loss is measured by changing the angle under which the electrons are collected. With this technique one can measure which excitations exist in the sample, and which inplane wave vector corresponds to this excitation. Molecular vibrational modes do not carry momentum, and hence their corresponding inplane wave vector is zero.

The experimental HREELS results are obtained by Richard Vanraes in the group Molecular Materials and Nanosystems at the Eindhoven University of Technology. They are performed in UHV at a base pressure of 10⁻¹⁰ mbar. Sample preparation was similar as in the STM experiments. The used electron energy was 6.5 eV, and the FWHM of the specular peak is 3 meV.

7.2.3 Details of the DFT calculations

Tip and surface geometries have mostly been optimized with the SIESTA code under the generalized gradient approximation (GGA). The surface is modeled with two different unit cells: a (√3×√3,60°)R30° supercell with one TP molecule and three Ag atoms per layer and a (√7×√3,92°)R8.9° supercell with six TP molecules and 17 Ag atoms per layer, corresponding to coverages of 0.33 and 0.35 MLs, respectively. In this notation the first angle indicates the angle between the two lattice vectors and the second angle indicates the angle between this unit cell and the underlying Ag lattice. These unit cells are illustrated in Fig. 7.2. The choice for the √7×√3 cell and the number of molecules is motivated in Subsection 7.3.1. The smaller √3×√3 cell
resembles the larger $\sqrt{7} \times \sqrt{31}$ cell and is used to investigate if the vibrational modes can also be calculated with this calculationally cheaper structure.

![Figure 7.2 Schematic overview of a) the ($\sqrt{3} \times \sqrt{3}, 60^\circ$)R30° unit cell, and b) the ($\sqrt{7} \times \sqrt{31}, 92^\circ$)R8.9° unit cell.](image)

Metastable geometries have been obtained starting from several initial configurations. The parameters of these initial structures are summarized in Tables 7.1 and 7.2, where the azimuthal angle $\alpha$ is defined in Fig. 7.1d as the angle between the benzene plane and the y-axis. The structures $f0$ and $h0$ are the results of a pre-optimized geometry with various tilt and azimuthal angles. In the other structures, the distance between the S atoms has been maximized and hence a quasi-hexagonal packing is adopted. The initial lateral position of the six S atoms is:

$$
\begin{align*}
(0, -\frac{1}{3}) & \\
(\frac{1}{2}, -\frac{1}{6}) & \\
(\frac{1}{2}, \frac{1}{6}) & \\
(0, \frac{1}{3}) & \\
(\frac{1}{2}, \frac{1}{3}) & \\
(\frac{1}{2}, \frac{1}{2}) & 
\end{align*}
$$

where the first coordinate is in the $\sqrt{7}$ lattice vector direction and the second coordinate is in the $\sqrt{31}$ lattice vector direction. The three nearest neighbors’ distances are 6.60, 6.81 and 7.70 Å and the three azimuthal angles given in Table 7.2 correspond to the three directions of these nearest neighbors. The choice for $\theta = 16^\circ$ is motivated in Subsection 7.3.2. All initial configurations for the $\sqrt{7} \times \sqrt{31}$ cell are summarized in Fig. 7.3.

**Table 7.1 Initial geometries and naming convention for the $\sqrt{3} \times \sqrt{3}$ unit cell.**

<table>
<thead>
<tr>
<th>Name structure</th>
<th>Ads. site</th>
<th>Ring tilt angle $\theta$</th>
<th>Azimuthal angle $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>f0</td>
<td>fcc</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>f20</td>
<td>fcc</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>f45</td>
<td>fcc</td>
<td>45</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 7.2 Initial geometries and naming convention for the $\sqrt{7} \times \sqrt{31}$ unit cell. The adsorption site refers only to the molecule in the center of the unit cell.

<table>
<thead>
<tr>
<th>Name structure</th>
<th>Ads. site</th>
<th>Ring tilt angle $\theta$</th>
<th>Azimuthal angle $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_0$</td>
<td>fcc</td>
<td>various</td>
<td>various</td>
</tr>
<tr>
<td>$f_{-40}$</td>
<td>fcc</td>
<td>16</td>
<td>-40</td>
</tr>
<tr>
<td>$f_{+15}$</td>
<td>fcc</td>
<td>16</td>
<td>+15</td>
</tr>
<tr>
<td>$f_{+80}$</td>
<td>fcc</td>
<td>16</td>
<td>+80</td>
</tr>
<tr>
<td>$h_0$</td>
<td>hcp</td>
<td>various</td>
<td>various</td>
</tr>
<tr>
<td>$h_{-40}$</td>
<td>hcp</td>
<td>16</td>
<td>-40</td>
</tr>
<tr>
<td>$h_{+15}$</td>
<td>hcp</td>
<td>16</td>
<td>+15</td>
</tr>
<tr>
<td>$h_{+80}$</td>
<td>hcp</td>
<td>16</td>
<td>+80</td>
</tr>
</tbody>
</table>

Figure 7.3 Initial geometries and naming convention for the $\sqrt{7} \times \sqrt{31}$ unit cell. The grey circles indicate the top Ag layer atoms, the white circles indicate the S atoms. The thick black lines indicate the position and orientation of the benzene rings and the thin black line indicates the unit cell.

In all cases, the initial distance from the S atoms to the top Ag layer is 2 Å. The surface unit cell consists of 5 layers, of which the bottom 2 layers are fixed to bulk positions. The fcc lattice constant of Ag is determined from a bulk optimization and is 4.15 Å, which is shown in Fig. 7.8a.

The chosen k-grid sampling is a Monkhorst Pack (MP) equivalent to a 14×14 grid of a 1×1 Ag(111) inplane lattice for the $\sqrt{3} \times \sqrt{3}$ cell and equivalent to a 17×17 grid of a 1×1 Ag(111) inplane lattice for the $\sqrt{7} \times \sqrt{31}$ cell. A smearing of 100 meV is introduced, and the convergence threshold is 1 meV with respect to subsequent Hamiltonian matrix elements. In addition, the optimal geometry of the $\sqrt{3} \times \sqrt{3}$ cell has also been determined using VASP, with a cutoff energy of 400 eV, a smearing energy of 200 meV, a convergence threshold of 0.1 meV with respect to the total energy and a force threshold of 2 meV/Å.
It can be expected that for a close packed molecular system Van-der-Waals forces between the TP molecules are important to obtain the final geometry. Therefore, the surface structure is also relaxed using either the semi-empirical correction or the \textit{ab initio} functional, as explained in Subsection 3.1.6. Since in the experiments, the PtIr tips have been dipped into the Ag surface, it is assumed that the apex of the tip consists of Ag atoms. The same tips which were used in Chapter 5 are used in this Chapter as well.

Vibrational modes are calculated by displacing the atoms of the TP molecules and the top Ag layer by 0.015 Å in all directions and calculating the eigenmodes of the corresponding force matrix. A diagonal element correction has been employed here.\textsuperscript{22}

7.2.4 Details of the Green's functions calculations

All STM simulations have been performed using the GREEN code. In order to generate the self-consistent Hamiltonian, three more Ag layers are added to each structure after ionic optimization. The self-consistent field procedure in GREEN is checked by comparing the on-site energies of the AOs between the bulk calculation and the atoms in the center of the slab, where a maximum deviation of 17 meV is found for the surfaces obtained employing the GGA functionals, and 44 meV for the surface structures obtained employing the vdW functional. The Slater-Koster parameterization has been performed using scheme 3 from Subsection 3.2.7, where the molecular entity used is one TP molecule plus three Ag atoms attached to the S atom. The used imaginary energy in each calculation is 20 meV, while the value for $kT$ is set to 5 meV. The used k-grids are the same as for the DFT calculations. In the STM simulations, the energy ranges from 0 to 100 meV with an increment of 10 meV, and the lateral resolution is 0.5 Å.

7.3 Results and discussion

In this Section, the experimental and theoretical results are presented. In Subsection 7.3.1, experimental STM and LEED images together with simplified LEED simulations are shown to identify the unit cell's coverage and packing arrangement. In Subsection 7.3.2 the details of the geometry is analyzed using the DFT results. These results are used in Subsection 7.3.3 to simulate STM images and finally a vibrational analysis based on HREELS experiments and DFT calculations is given in Subsection 7.3.4.

7.3.1 STM and LEED

Fig. 7.4 shows a 60×60 nm$^2$ STM image of a full monolayer of TP on Ag(111). Three different rotational domains can be identified, indicated by the black lines. Typical domain sizes are 10-50 nm. The 2D Fourier transform (FT) of the image, shown in the inset of Fig. 7.4, shows 6 triangles pointing outward at $k = 1.4$ Å$^{-1}$. The quality of the STM image is however inadequate to resolve the details of the FT within this ring of triangles.
The structure is confirmed by LEED experiments, shown in Fig. 7.5a. The most striking features, the 6 pairs of triangles pointing outward and the inner ring of 6 pairs of spots, 30° rotated with respect to the triangles, shown in Fig. 7.5b, are consistent with previous reports, and indicate a \((\sqrt{7}\times\sqrt{3}\times1,92°)R8.9°\) supercell, which has a c3vm symmetry. This means that the structure does not change upon unit cell rotation over 0°, 120° or 240° or mirroring in any symmetry plane of the underlying Ag surface. The FT in Fig. 7.4 only shows single triangles because no mirror symmetry is observed in this small area. Gui et al. claim, based on Van-der-Waals radii, that there are 4 TP molecules within this unit cell. Figs. 7.5c, d and e show simulated LEED images, obtained by 2D Fourier transforming real space maps, in which each molecule is modeled as a 2D circular Gaussian with the same apparent height for all molecules. The c3vm symmetry has been taken into account when obtaining these LEED images by applying the symmetry operations mentioned above on the FT image. Figs. 7.5c and d show that neither a rectangular nor a quasi-hexagonal packing of 4 equivalent molecules in this unit cell gives rise to triangles pointing outward. On the other hand, a unit cell with 6 equivalent TP molecules in it, quasi-hexagonally packed, does result in these triangles, as shown in Fig. 7.5e. The experimentally observed inner ring is most probably due to inequivalent molecules within the cell, since it can be reproduced in the FT images if the molecules are given different apparent heights, shown in Fig. 7.5f. A unit cell with 6 TP molecules rectangularly packed in it does not result in these triangles.
**Figure 7.5**  

**a)** Experimental LEED image of a TP on Ag(111) monolayer, measured with electron energy of 39 eV.  

**b)** Experimental LEED image of the same monolayer, taken from Ref. 12.  

c-f) Simulated LEED images from simplified STM images, shown in the corresponding insets. The darker the spot, the higher the intensity. The shown k-space is from $-1.8 \text{ Å}^{-1}$ to $1.8 \text{ Å}^{-1}$.

STM images with higher resolution are measured to investigate the structure within the unit cell in more detail. Depending on tip condition, different imaging has been achieved. Fig. 7.6 shows two different STM images, measured under similar conditions, although more types of images have been measured. Fig. 7.6a suggests that there are 6 molecules in the unit cell, which are not all equivalently imaged. This inequivalency is clearer in Fig. 7.6b, where not all 6 TP molecules appear equally bright. The most striking feature is the appearance of dark lines in the $\sqrt{7}$ lattice vector direction. A typical corrugation in these images is 50-70 pm. In Fig. 7.6a the ordering of the molecules appears quasi-hexagonal, while in Fig. 7.6b the ordering appears rectangular.

**Figure 7.6**  

Experimental 5×5 nm$^2$ STM images of the TP on Ag(111) SAM.  

Experimental parameters:  

**a)** $V = -25$ mV, $I_{sp} = 0.2$ nA;  

**b)** $V = -30$ mV, $I_{sp} = 0.2$ nA.
7.3.2 DFT optimized geometry

The total energies of all the relaxed geometries of the $\sqrt{3}\times\sqrt{3}$ cell for all the methods are given in Table 7.3. The bold numbers indicate the most stable structure per method. It can be seen that the differences in stability are small and depend on the inclusion of Van-der-Waals interactions. This suggests that the tilt angle cannot be precisely determined from these DFT calculations. The structures with an initial tilt angle of 20° seem to be slightly favorable. In this final geometry, $\theta = 15° \pm 1°$, $\alpha = 22° \pm 4°$ and the average height of the S atom above the top Ag layer is 1.96 Å ± 0.08 Å, where the error is defined as the standard deviation when only the three SIESTA based calculations are taken into account. The final adsorption site is bridge-toward-hollow for all four methods. The value for $\theta$ in this most favorable structure is the motivation for the initial $\theta = 16°$ in the $\sqrt{7}\times\sqrt{3}$ cell.

**Table 7.3** Relative total energies in eV with respect to the most stable structure of the optimized $\sqrt{3}\times\sqrt{3}$ cell from different initial configurations and with different methods.

<table>
<thead>
<tr>
<th></th>
<th>VASP no vdW</th>
<th>SIESTA no vdW</th>
<th>SIESTA empirical vdW</th>
<th>SIESTA ab initio vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>f0</td>
<td>0.000</td>
<td>0.000</td>
<td>1.025</td>
<td>0.023</td>
</tr>
<tr>
<td>f20</td>
<td>0.003</td>
<td>0.015</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>f45</td>
<td>0.004</td>
<td>0.087</td>
<td>0.014</td>
<td>0.011</td>
</tr>
</tbody>
</table>

The total energies of all the relaxed geometries of the $\sqrt{7}\times\sqrt{3}$ cell for all the methods are given in Table 7.4. The calculations of the f+80 and h+80 structures with vdW forces were not fully relaxed as it was clear that they were much more unfavorable compared with the other structures. Again, the differences in stability are small and depend on the inclusion of Van-der-Waals interactions.

**Table 7.4** Relative total energies in of the optimized $\sqrt{7}\times\sqrt{3}$ cell from different initial configurations and with different methods with respect to the most stable structure.

<table>
<thead>
<tr>
<th></th>
<th>SIESTA no vdW</th>
<th>SIESTA empirical vdW</th>
<th>SIESTA ab initio vdW</th>
</tr>
</thead>
<tbody>
<tr>
<td>f0</td>
<td>0.421</td>
<td>0.000</td>
<td>0.666</td>
</tr>
<tr>
<td>f-40</td>
<td>0.152</td>
<td>0.133</td>
<td>0.000</td>
</tr>
<tr>
<td>f+15</td>
<td>0.598</td>
<td>0.533</td>
<td>0.105</td>
</tr>
<tr>
<td>f+80</td>
<td>0.969</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>h0</td>
<td>0.342</td>
<td>0.244</td>
<td>0.619</td>
</tr>
<tr>
<td>h-40</td>
<td>0.000</td>
<td>0.042</td>
<td>0.068</td>
</tr>
<tr>
<td>h+15</td>
<td>0.019</td>
<td>0.513</td>
<td>0.197</td>
</tr>
<tr>
<td>h+80</td>
<td>0.804</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The adsorption sites differ per molecule and per calculation. An example is shown in Fig. 7.7; all adsorption sites are summarized in Table 7.5 for the calculations without vdW interactions. They do not change drastically when including vdW forces at the semi-empirical or \textit{ab initio} level. No correlation between the adsorption sites and the stability of the structure has been found. The big spread in adsorption sites might explain the difficulty to experimentally determine a single adsorption site.

![Figure 7.7](image)

**Figure 7.7** $25 \times 25 \text{ Å}^2$ top view of the adsorption sites of the optimized geometry from the h-40 initial configuration without vdW interactions taken into account. The dark circles represent the Ag atoms in the top layer, the light circles represent the S atoms. The black line indicates the unit cell. The numbering labels the molecules throughout the remainder of this thesis.

**Table 7.5** Adsorption sites of the six molecules in the $\sqrt{7} \times \sqrt{31}$ cell when no Van-der-Waals interactions are taken into account.

<table>
<thead>
<tr>
<th></th>
<th>TP 1</th>
<th>TP 2</th>
<th>TP 3</th>
<th>TP 4</th>
<th>TP 5</th>
<th>TP 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>f0</td>
<td>bridge</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>hcp-bridge</td>
<td>bridge</td>
</tr>
<tr>
<td>f-40</td>
<td>hcp-bridge</td>
<td>fcc</td>
<td>fcc</td>
<td>bridge</td>
<td>hcp</td>
<td>bridge</td>
</tr>
<tr>
<td>f+15</td>
<td>bridge</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc-bridge</td>
<td>hcp</td>
</tr>
<tr>
<td>f+80</td>
<td>hcp</td>
<td>fcc</td>
<td>fcc</td>
<td>fcc</td>
<td>hcp-bridge</td>
<td>fcc</td>
</tr>
<tr>
<td>h0</td>
<td>fcc</td>
<td>hcp-bridge</td>
<td>hcp</td>
<td>bridge</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>h-40</td>
<td>fcc</td>
<td>hcp</td>
<td>bridge</td>
<td>hcp</td>
<td>fcc</td>
<td>bridge</td>
</tr>
<tr>
<td>h+15</td>
<td>fcc</td>
<td>hcp</td>
<td>fcc</td>
<td>hcp</td>
<td>fcc</td>
<td>bridge</td>
</tr>
<tr>
<td>h+80</td>
<td>fcc</td>
<td>hcp</td>
<td>hcp</td>
<td>hcp-bridge</td>
<td>fcc</td>
<td>fcc</td>
</tr>
</tbody>
</table>
The values for $\theta$ of the various molecules are shown in Table C.1 in Appendix C. The average of all structures with all methods is $\theta=13^\circ\pm6^\circ$, which is in agreement with the one found for the $\sqrt{3}\times\sqrt{3}$ cell. With the error margins taken into account, this average angle is consistent with $\theta$ measured with ARXPS.\textsuperscript{15} There is a big spread in $\theta$ however, which suggests that the energy differences between the tilt angles are small and would explain why it is difficult to measure precisely one value for $\theta$. For the structures without vdW interactions, $\theta$ is on average $3^\circ$ smaller than for the structures with empirical vdW interactions, and on average $1^\circ$ smaller than for the structures with \textit{ab initio} vdW interactions. No correlation between adsorption site and $\theta$ has been found.

The values for $\alpha$ of the various molecules are shown in Table C.2 in Appendix C. The average over all structures and all methods is $\alpha=23^\circ\pm9^\circ$, which is in agreement with the one found for the $\sqrt{3}\times\sqrt{3}$ cell. With the error margins taken into account, this average angle is consistent with $\alpha$ measured with SFG spectroscopy.\textsuperscript{17} There is an even bigger spread in $\alpha$ however, which makes it even more difficult to determine it experimentally. For the structures without vdW interactions, $\alpha$ is on average $2^\circ$ smaller than for the structures with empirical vdW interactions, and on average $4^\circ$ smaller than for the structures with \textit{ab initio} vdW interactions. Again, no correlation between adsorption site and $\alpha$ has been found.

The average height of the S atoms above the top Ag layer is presented in Table C.3 in Appendix C. The distance between the S atom and the top Ag layer is increased by 0.15 Å when the vdW functional is used. However, also the bulk lattice constant increases for this case from 4.16 Å for the PBE GGA functional\textsuperscript{23} to 4.26 Å for the GGA+vdW functional,\textsuperscript{24} which is shown in Fig. 7.8. The increase of lattice constant has not been taken into account in the calculations. It is a known fact\textsuperscript{25} that the GGA+vdW functional tends to overestimate bond lengths, and hence this feature is ignored in the rest of the analysis.

Fig. 7.9 shows the azimuthal orientation $\zeta$ of the benzene rings for the eight structures where vdW interactions have not been taken into account. The numbers under each graph are the minimum distances in Å between any two benzene rings. The energetically least favorable structures, f$^+$80 and h$^+$80, are the most aligned. This results in the smallest minimum distance between the benzene rings, which could explain the energetic disfavor. The most favorable structures, h$^-$40 and h$^+$15, have a large minimum distance between the rings. The structure with the largest minimum distance between the rings, f$^-$40, is however not the energetically most favorable structure, implying that the inter-ring distance is not the only stabilizing mechanism. The same qualitative conclusion holds if not the minimum inter-ring distance in the unit cell, but the average inter-ring distance per molecule is considered instead.
Figure 7.8 Relative total energy with respect to the most stable structure vs. fcc bulk Ag lattice constant for a) the PBE GGA functional\textsuperscript{23} and b) the Van-der-Waals functional.\textsuperscript{24} The dots are calculated energy points, the lines are third order polynomial fits.

Figure 7.9 Azimuthal orientation of the benzene rings in the final geometry for the structures without vdW taken into account. The dotted lines indicate the unit cell. Each image is 3×3 nm$^2$.

To summarize this Subsection, the optimal structure depends critically on the initial configuration and the used method. Energy differences upon varying adsorption sites, ring tilt angles and S-C bond angles are very small and their variations are large. Therefore it is difficult to measure these parameters experimentally. With only these DFT calculations, it is not possible to determine which of these structures, if any, is the real structure. The only correlation found is that the final geometry tends to favor a large minimum distance between the molecules.
7.3.3 STM simulations

Simulated STM images for the three most stable configurations are presented in Fig. 7.10, obtained with a blunt (a-c) and sharp tip (d-f) respectively. An overview of all obtained STM images is shown in Figs C.1-C.3 in Appendix C. In Figs. 7.10a, c, d and f the ordering of the molecules appears rectangular, like in Fig. 7.6b, while in Figs. 7.10b and e it appears quasi-hexagonal, like in Fig. 7.6a. Dark lines in the \( \sqrt{31} \) lattice vector direction can be distinguished in most simulated STM images. As in 7.6b, the protrusion in the rectangularly packed surfaces of three molecules in one row in the \( \sqrt{7} \) lattice vector direction is higher than in the second row. In Fig. 7.10b each molecule is imaged as a three lobe protrusion due to the three atom tip apex termination of the blunt tip. This feature is less resolved in Figs. 7.10a and c.

The simulated STM images are calculated with a higher voltage than the experimental STM images are obtained with. This is done to withdraw the tip to ensure the tunneling regime holds. The details of the STM images depend critically on the used tip, the used SK parameters, and on the precise surface geometry, which in turn depends on the initial configuration and on the implementation of Van-der-Waals interactions. Therefore a one-to-one correspondence between theory and experiment cannot be expected. In general the simulations justify the wide variety of experimental STM images and reproduce the most robust features of inequivalent molecules and dark lines in the \( \sqrt{7} \) lattice vector direction. However they cannot be used to determine which of these structures, if any, is the real structure.

![Simulated STM images](image)

**Figure 7.10** Simulated 4×4 nm² STM images of the TP on Ag(111) SAM for three different surface geometries and two different tips. The black lines indicate the unit cell. Simulation parameters: \( V = 100 \) mV, \( I_{\text{sp}} = 1 \) nA; insets show the initial configuration and approximation for vdW interactions; a-c) blunt Ag tip; d-f) sharp Ag tip.
7.3.4 Vibrational modes

Besides the ground state geometry, knowledge of the vibrational modes of this monolayer is required as well to perform IETS simulations in the next Chapter. The measured and calculated vibrational spectra are displayed in Fig. 7.11. The upper line presents the HREELS spectrum, averaged over 2.5 meV, the middle and lower lines are the results of adding Lorentzian peaks with FWHM of 2.5 meV at each theoretically found vibrational energy in the $\sqrt{3} \times \sqrt{3}$ and $\sqrt{7} \times \sqrt{31}$ cell respectively. These peaks are not corrected for HREELS cross sections. The individual peaks and their assignments are presented in Table C.4 in Appendix C. They are in general consistent with previous reports.\textsuperscript{12,13,14,17} Measured HREELS peaks at 373 meV and 40 meV cannot be accounted for by theory. Both unit cells reproduce all other HREELS peaks within 5 meV.

The vibrational mode frequencies and assignments are almost identical between the two cells, signaling that the vibrations are only weakly coupled between different molecules and that the impact of the precise S adsorption is small. Therefore, almost each vibrational mode in the small cell can be identified with six vibrational modes in the big cell. The $\delta_{oo}(C-C)$ mode at 30 meV found in the small cell, which is an azimuthal twist of the benzene ring, is not found in the big cell. The $\delta_{oo}(C-C)$ mode at 56 meV found in the small cell, is softened by 7-10 meV in the big cell. The rest of the vibrational mode energies and assignments are similar within 3 meV.

![Figure 7.11](image.png)

**Figure 7.11** Vibrational spectra calculated with DFT for the $\sqrt{3} \times \sqrt{3}$ and $\sqrt{7} \times \sqrt{31}$ cells and measured with HREELS. The curves have been shifted upward for clarity.\textsuperscript{12}
7.4 Summary

The main conclusion found in this Chapter is that the packing density is determined to be six molecules per 17 Ag atoms. Further key observations of this Chapter are:

- LEED experiments have revealed the $\sqrt{7} \times \sqrt{31}$ unit cell of the TP on Ag(111) SAM and hinted for 6 molecules within the unit cell. STM imaging confirmed the amount of molecules within the unit cell. (Subsection 7.3.1)

- The optimal structure of TP on Ag(111) obtained by DFT depends critically on the initial configuration and the approximation employed for the vdW interactions. Given the enormous number of possible relative configurations that the molecules may attain within the unit cell and the fact that the three methods are not clearly more accurate from one another, the geometry of the most stable phase cannot be determined precisely from the current DFT study. (Subsection 7.3.2)

- The simulated STM images justify the wide variety of experimental STM images and reproduce the most robust features of inequivalent molecules and dark lines in the $\sqrt{7}$ lattice vector direction. However, no perfect agreement with the experimental images is found for any of the models, suggesting that none of the DFT derived geometries corresponds to the one found in the experiments. (Subsection 7.3.3)

- The vibrational modes calculated with DFT for a big unit cell are nearly identical to those calculated for a small unit cell, and reproduce reasonably well those measured with HREELS. The vibrational modes are not very sensitive to the details of the surface. (Subsection 7.3.4)

In the next Chapter the zero-bias anomaly observed in this system is introduced, and several possible explanations are explored. One of the possible explanations is investigated with the LOIT+WBL approach employed on one of the structures found in this Chapter to study if inelastic effects can be responsible for this anomaly.

7.5 Bibliography


Chapter 8 – Zero-bias anomaly in thiol-bound molecular junctions

Chapter 7 shows many examples of molecular transport junctions made with thiols. For all reported junctions, $IV$ curves are recorded to probe the electronic transport mechanism from one electrode through the molecule to the other electrode. By measuring the $dI/dV$ curve, information about the density of states (DOS) of the molecule is obtained. When using thiols as binding groups for the molecular junction, the sulfhydryl hydrogen dissociates and the sulfur atom binds to the metal electrode, forming thiolates. One feature that is often observed in these systems is a significant reduction in conductance ($\Delta \sigma/\sigma \sim 10-20\%$) in a narrow region around the Fermi energy.\textsuperscript{1,2,3,4,5,6} While most authors choose to ignore this feature, it is in general attributed to excitations of the $\nu$(metal-S) mode or phonon interactions in the metal leads.\textsuperscript{3,6,7}

To explain the origin of this zero-bias anomaly (ZBA), \textit{ab initio} calculations taking into account the exact geometry of the junction are required. The geometric details and ground state electronic structure of this monolayer have been examined in Chapter 7, which makes further modeling possible. While in principle a combination of DFT and NEGF would give predictions for $IV$ curves,\textsuperscript{8,9,10} an accurate description of the shape of $dI/dV$ curves in this energy range has not yet been reported by our knowledge. This is most probably due to the tough k-convergence as explained in Chapter 5. So far, simulated IETS peaks for thiolate molecular wires have not enough intensity to explain the ZBA.\textsuperscript{7}

This Chapter investigates the ZBA observed in a thiophenol (TP) monolayer, adsorbed on a Ag(111) surface and is organized as follows. The observation of the ZBA, together with observations in other similar systems, is presented in Section 8.1. Three possible explanations for the ZBA are explored. The first one, discussed in Section 8.2, is that it is a generic feature of the DOS of the system, but advanced modeling discards this possibility. A second explanation, given in Section 8.3, involves umklapp processes. Fermi contours measured with photoemission spectroscopy (PES) experiments will be shown, showing no nesting and thus discarding this second possibility. The third explanation, discussed in Section 8.4, includes the excitation of low energetic vibrations. The LOIT+WBL approach is employed to investigate if this explanation accounts for such a large change in conductance. Finally, the conclusions of the Chapter are summarized in Section 8.5.
8.1 Experimental observation

Figs. 8.1a and 8.1b show two typical $dI/dV$ curves for TP on Ag(111). The appearance of the curves is similar for PtIr and W tips, probably because the tip is Ag coated due to the dipping procedure as explained in Subsection 2.2.8.

Figure 8.1 STS spectra of a) TP on Ag(111) at 4 K, b) TP on Ag(111) at 77 K, c) clean Ag(111) at 77 K, and d) dimethyl sulfide on Ag(111) at 77 K. All spectra are rescaled to the same current setpoint of 0.2 nA at $V = 100$ mV. These curves are averages over a) 4790 spectra, b) 2638 spectra, c) 456 spectra and d) 320 spectra.

There is a clear reduction of DOS around the Fermi energy with $\Delta \sigma/\sigma \sim 10\text{-}15\%$, which is called a pseudogap due to the similarity in appearance with the STS of cuprate superconductors.\textsuperscript{13} The breakpoints in Fig. 8.1a are at -18 and +18 mV respectively, determined from the peaks of the numerical derivative of the measured $dI/dV$ curve. Raising the temperature from 4 K to 77 K shifts these breakpoints to -28 and +26 mV. The exact position of the breakpoints varies up to ±40 mV however in different measurements, possibly with different tips. STS performed on clean Ag(111) and on physisorbed dimethyl sulfide on Ag(111) does not show this pseudogap, as shown in Figs. 8.1c and d. If the increase in conductivity involves the excitation of a vibration, an additional explanation should be given why the influence is so high in the specific case of thiolates and not in other systems.
This same feature has been reported many times in literature. Fig. 8.2 shows examples of spectroscopy results from thiolates on Au measured with different techniques. Although some authors attribute this feature to electrode phonons, most authors decide to ignore it.

Figure 8.2 Observations reported in literature of the zero-bias anomaly found in thiolate systems. The pseudogap is mostly observed as an antisymmetric peak in the $d^2I/dV^2$ curves. a) STM junction with C$_8$ alkanethiols on Au(111). Figure taken from Ref. 1. b) In-wire junction with dithioacetate oligoalnine dimers between Pd wires. Figure taken from Ref. 5. c) Crosswire junction with fluorinated C$_{16}$ alkanethiol between Au wires. Figure taken from Ref. 4. d) STM junction with C$_{10}$ alkanethiols on Au(111). Figure taken from Ref. 2. e) Electromigrated single molecule junctions with 1,4-benzenedithiols between Au electrodes. Figure taken from Ref. 3. f) Crosswire junction with C$_8$ alkanedithiol between Au wires. Figure taken from Ref. 6.
8.2 Feature of DOS

The easiest explanation possible is that it is a generic feature of a thiolate’s DOS. If this is true, a single-particle DOS calculation using DFT would exhibit the same phenomenon. Fig. 8.3a shows the DOS around the Fermi level of a TP monolayer on Ag(111), calculated with SIESTA, projected onto the different atomic species in the system. The details of the calculation are given in Section 7.2, the DOS over the full energy range is shown in Fig. C.5 in Appendix C. The HOMO of the molecule is found at -0.9 eV, the LUMO is found at 2.5 eV, determined as the flanks of the two levels closest to the Fermi energy. None of the species have a minimum around the Fermi energy; hence the single-particle DOS alone cannot explain the ZBA.

STS however does not measure directly the DOS of the system at one particular position. It is argued in Chapter 3 that STS involves an entire tunneling path of the electron from the tip into the surface or vice versa. Therefore the \( \frac{dI}{dV} \) curves are simulated, employing a sharp Ag tip positioned over the topmost C atoms, while taking no inelastic effects into account. The details of these calculations are given in Section 7.2; the results are shown in Fig. 8.3b. That all curves go through one point at 50 mV is due to the fact that the setpoint was chosen at 100 mV. Only third order effects and higher in the \( IV \) curves cause deviations from this crossing point at 50 mV, which are in general small. Again, no dip can be detected around zero bias. It is concluded from Fig. 8.3 that the ZBA is not a feature of the thiolate’s DOS.

![Graph a) Calculated DOS, projected on the atomic orbitals of the different species. The curves are scaled with the number of atoms in the unit cell. The curves Ag1, Ag2 and Ag3 represent the first, second and third layer Ag atoms respectively. b) Simulated \( \frac{dI}{dV} \) curve of TP on Ag, taken with a sharp Ag tip over the topmost carbon atoms of the TP molecules. Tunneling gap set with setpoint current of 1 nA at 100 mV.](image)

8.3 Many-body physics: umklapp processes

A second explanation is that this pseudogap is induced by many-body physics due to umklapp processes. Since DFT is a mean-field approach, these would not show up in the calculations presented in the previous Section. How these processes might be able to cause a reduction in the DOS is explained in Subsection 8.3.1. The two requirements for
these umklapp processes are a Kohn anomaly in the phonon dispersion relation and nesting of the Fermi surface. This last requirement is explored with PES experiments in Subsection 8.3.2.

**8.3.1 Umklapp processes**

![Figure 8.4 Sketch of a) a normal scattering process and b) an umklapp process.](image)

The physical processes of normal scattering and umklapp scattering are schematically drawn in Fig. 8.4. In both processes an electron with initial wavevector $\vec{k}$ scatters with a phonon with wavevector $\vec{k}_{ph}$. As long as the sum of the wavevectors stays inside the first Brillouin zone, the resulting wavevector is simply this sum: $\vec{k}' = \vec{k} + \vec{k}_{ph}$. If this sum however is no longer inside the first Brillouin zone, the wavevector of the outgoing electron is no longer this sum, but is transformed into an equivalent vector inside the first Brillouin zone: $\vec{k}' = \vec{k} + \vec{k}_{ph} + \vec{G}$. This process is called umklapp scattering and changes the total wavevector of the electron plus phonon. The difference in momentum $\hbar\vec{G}$ is transferred to the sample to maintain momentum conservation. The difference in wavevector between incoming and outgoing electron is denoted by $\vec{q}_c$.

When these scattering processes are present in a system, a gap in the band structure could form, which is illustrated in Fig. 8.5 for a one dimensional example. This hybridization only occurs if an electron scatters from an occupied state to an unoccupied state, and hence a requirement is that the band crossing $E_{cr}$ is at or near the Fermi energy:

$$E_{cr} \in \left[ E_F - \frac{1}{2} \Delta, E_F + \frac{1}{2} \Delta \right]$$

where $\Delta$ is the induced band gap. This requirement is called *nesting* and can be rephrased to the requirement that the difference in momentum of the main band and the umklapp band transformed to the first Brillouin zone is equal to $\vec{q}_c$ at energy $E_F$. For two or three dimensions, nesting is generalized to the requirement that the *Fermi contour* or *surface* consists of parallel lines or planes, separated by momentum $\vec{q}_c$.

The Fermi surface of clean Ag(111) is not known for nesting. If the adsorption of thiols would be able to induce a change in the band structure, nesting could occur. In the next Subsection, PES experiments are presented to search this nesting upon adsorption. If umklapp processes with phonons are present, which is assumed here, the phonon dispersion sharply dips (called phonon softening) at $\vec{k}_{ph}$, which is termed the Kohn
anomaly, which could be visualized with HREELS. A similar analysis with PES and HREELS has been reported in literature to prove that nesting is induced by hydrogen when adsorbed onto Mo(110), but with scattering within the first Brillouin zone, and hence without umklapp processes.

Figure 8.5  
a) Simplified band structure with a band in the first Brillouin zone (main band) and the equivalent band in the second Brillouin zone (umklapp band).  
b) If the crossing of these bands is at or near the Fermi energy, they can hybridize as shown by the thick lines, opening a gap of size $\Delta$.

8.3.2 Photoemission spectroscopy to search for Fermi nesting

Figure 8.6 Fermi surface of a) clean Ag(111) and b) TP on Ag(111), measured with PES with a photon energy of 127 eV. Only the quarter with positive $k_x$ and $k_y$ is shown, the rest of the Fermi surface is assumed mirror symmetric. The hexagonal white line indicates the first Brillouin zone.

The PES experiments presented in this Section are performed at the VUV beamline of Elettra, a synchrotron nearby Trieste, Italy. Sample preparation is similar as explained in Section 2.2. Before adsorption, the quality of the Ag(111) layer is checked with LEED and X-ray photoemission spectroscopy (XPS). No contaminant peaks were found in these spectra. To determine the Fermi surface, a photon energy of 127 eV is used.
which is the energy that is the most surface sensitive. This is also close to the Cooper minimum for the Ag 4d band, which is at 150-160 eV, minimizing contributions from this band.

Fig. 8.6 shows the Fermi contour of clean Ag(111) and of a TP monolayer on Ag(111). The surface state in the center of the Brillouin zone, which can be seen for the clean Ag(111), has disappeared upon TP adsorption. For the rest, no drastic changes can be detected. Therefore it is concluded that TP adsorption does not induce Fermi nesting. The lack of nesting in the PES experiments discards the possibility of umklapp processes as an explanation for the ZBA.

### 8.4 Excitation of low energy vibrational modes

The most common explanation for the ZBA, excitation of low energetic vibrational modes, is investigated in this Section. Fig. 8.7 shows a simulated STS and IETS curve, obtained by positioning the sharp Ag tip over the outermost H atom of molecule 1 in Fig. 7.7. The tunneling gap is set with \( V = 100 \) mV and \( I_{sp} = 0.1 \) nA; the outermost Ag atom of the tip is then 4.6 Å above the outermost H atom of the TP molecule. This indicates that the transport takes place in the tunneling regime and the LOIT approach is valid.

A reduction of conductance is observed in a narrow region around the Fermi energy, in good agreement with the experiment. The antisymmetric peaks in the calculated IETS curve are at ±17.5 mV, ±82.5 mV, ±127.5 mV and at ±385 mV. Table 8.1 shows the assignments of the most contributing vibrational modes. The peak at ±385 mV is solely due to the C-H stretch modes, and is not found in the STM-IETS experiments. The elastic tunneling matrix elements are largest for the AOs of the outermost H atom and hence the contributions of these \( \nu(\text{C-H}) \) modes are large, as explained in Subsection 5.2.6. No robust explanation for the absence of these peaks in the experimental IETS curves can be given, but possible explanations could be a more complex tip geometry, elastic features (not considered in the WBL) which could hide the inelastic peaks or an incorrect SK parameterization for the Ag-H interactions yielding too large interactions.
Further experimental and theoretical work would be necessary to elucidate this issue. A similar reasoning holds for the peak at ±127.5 mV, which is solely due to vibrational modes combining a $\nu$(C-C) and a $\delta_{ip}$(C-H) movement. It is not investigated which of these two contributions dominate, since they make up one single mode. The small peak at ±82.5 mV is due to the $\nu_2$(C-C) and $\nu$(S-C) modes, where the former one is defined in Appendix C.

The ten most contributing vibrational modes presented in Table 8.1 make only up for one third of the total inelastic contribution. There are many vibrational modes which contribute only a small portion each to the total current, but since there are so many of them close in energy, they add up to a considerable IETS peak. Therefore, the peak at ±17.5 cannot be assigned to a single vibrational mode, but is a convolution of many low energetic vibrational modes. Many of these modes involve a tilt of the benzene ring, but most of the modes are difficult to classify.

**Table 8.1 Contribution to the total conductance (columns Int) in % for the ten most contributing vibrational modes in the surface, and associated energies in meV and assignments. The IETS intensities are obtained from Fig. 8.7.**

<table>
<thead>
<tr>
<th>VM</th>
<th>Int.</th>
<th>$\hbar \omega$</th>
<th>Assignment</th>
<th>VM</th>
<th>Int.</th>
<th>$\hbar \omega$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>0.36</td>
<td>385</td>
<td>$\nu$(C-H)</td>
<td>60</td>
<td>0.15</td>
<td>50</td>
<td>$\nu$(S-C), $\nu$(Ag-S)</td>
</tr>
<tr>
<td>194</td>
<td>0.33</td>
<td>382</td>
<td>$\nu$(C-H)</td>
<td>149</td>
<td>0.15</td>
<td>136</td>
<td>$\delta_{ip}$(C-H)</td>
</tr>
<tr>
<td>133</td>
<td>0.24</td>
<td>127</td>
<td>$\nu$(C-C), $\delta_{ip}$(C-H)</td>
<td>85</td>
<td>0.13</td>
<td>82</td>
<td>$\nu_2$(C-C), $\nu$(S-C)</td>
</tr>
<tr>
<td>125</td>
<td>0.20</td>
<td>124</td>
<td>$\nu$(C-C), $\delta_{ip}$(C-H)</td>
<td>155</td>
<td>0.12</td>
<td>151</td>
<td>$\delta_x$(Ag-S-C), $\delta_{ip}$(C-H)</td>
</tr>
<tr>
<td>193</td>
<td>0.15</td>
<td>382</td>
<td>$\nu$(C-H)</td>
<td>84</td>
<td>0.12</td>
<td>82</td>
<td>$\nu_2$(C-C), $\nu$(S-C)</td>
</tr>
</tbody>
</table>

In contrast to the experiment, the position of the tip over the surface is crucial for the obtained IETS intensities. Table 8.2 presents the sum of the IETS intensities, obtained by positioning the tip over the outermost H atoms and over the S atoms of the six molecules, and varying the distance to the surface. The tunneling gaps are all set with $I_{sp} = 0.1$ nA, but the used voltages are 500 mV (far), 100 mV (medium) and 20 mV (close) respectively. At each lateral tip position it is found that the IETS intensities increase upon decreasing the tip-molecule distance, indicating a stronger dependence of the Hamiltonian matrix elements on the atomic coordinates when the tip is closer. This cannot be explained by the exponential decay of the Hamiltonian, since this would influence both the elastic and inelastic terms in a similar manner. In some cases, the tip comes closer than 4 Å, and the cumulative IETS intensity goes up drastically. This is shown in Fig. 8.8, where the IETS intensities obtained above the H atoms are plotted against the distance between the tip and the H atom. It is doubtful if the transport still occurs in the tunneling regime, which is necessary for the LOIT approach to be employed. Extending the approach to a regime in which it is not valid leads to unphysical IETS intensities of over 100%.
Figure 8.8 Cumulative IETS intensity of all vibrational modes vs. tip-molecule distance. The fitted lines are exponentially decaying fits, taking into account all data points (full line) or the points where the tip-molecule distance is larger than 4 Å (dashed line).

Table 8.2 Cumulative IETS intensity of all vibrational modes for different tip locations. The tip is positioned over either the S atom or the outermost H atom of each of the six TP molecules. The columns Int indicate the IETS intensity in %. The indicated distances are projected onto the surface normal axis and are in Å. The given angles per molecule are the ring tilt angles of the corresponding molecules, defined in Fig. 7.1.

<table>
<thead>
<tr>
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<th>TP 1</th>
<th></th>
<th>TP 2</th>
<th></th>
<th>TP 3</th>
</tr>
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<td></td>
<td>0°</td>
<td></td>
<td>16°</td>
<td></td>
<td>22°</td>
</tr>
<tr>
<td>Above S</td>
<td>Distance to</td>
<td>Int.</td>
<td>H</td>
<td>S</td>
<td>Distance to</td>
</tr>
<tr>
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<td>5.86</td>
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<td>7.2</td>
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</tr>
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<td></td>
<td>Int.</td>
<td>H</td>
<td>S</td>
<td></td>
</tr>
<tr>
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<td>5.54</td>
<td>11.18</td>
<td>3.6</td>
<td>6.02</td>
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<td>4.56</td>
<td>10.20</td>
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<td>5.23</td>
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<tr>
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<td>9.21</td>
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<table>
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<th>TP 6</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>6°</td>
<td></td>
<td>10°</td>
<td></td>
<td>14°</td>
<td></td>
</tr>
<tr>
<td>Above S</td>
<td>Distance to</td>
<td>Int.</td>
<td>H</td>
<td>S</td>
<td>Distance to</td>
<td>Int.</td>
</tr>
<tr>
<td>far</td>
<td>6.4</td>
<td>5.55</td>
<td>10.99</td>
<td>2.6</td>
<td>5.79</td>
<td>11.40</td>
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<td>4.77</td>
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<td>10.67</td>
</tr>
<tr>
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<td>3.90</td>
<td>9.34</td>
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<td>9.85</td>
</tr>
<tr>
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<td>Int.</td>
<td>H</td>
<td>S</td>
<td></td>
<td>Int.</td>
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<tr>
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<td>3.8</td>
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<td>9.7</td>
<td>4.69</td>
<td>10.29</td>
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<tr>
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<td>114.5</td>
<td>3.62</td>
<td>9.06</td>
<td>70.9</td>
<td>3.78</td>
<td>9.39</td>
</tr>
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</table>
In conclusion, the zero-bias anomaly can indeed be caused by the excitation of low energetic vibrational modes. The simulated intensities depend however crucially on the tip position. With a realistic tip-sample distance, the obtained intensities are smaller than observed in experiments.

8.5 Summary

The main conclusion of this Chapter is that excitation of low energetic vibrational modes can cause the zero-bias anomaly found in the system of TP on Ag(111). Further key observations of this Chapter are:

- The zero-bias anomaly is not a feature of the single-particle DOS of the surface. (Section 8.2)
- Umklapp processes are not responsible for the zero-bias anomaly. (Section 8.3)
- Several vibrational modes are excited in the simulated IETS spectra which are not seen in the experiment. The reason is not yet known. (Section 8.4)
- The IETS intensities of the peaks depend crucially on the relative tip position along and above the surface. The closer the tip is to the surface, the larger the IETS peaks. (Section 8.4)

8.6 Bibliography

Summary

This thesis has been dedicated to modeling the electron transport in tunnel junctions in order to efficiently describe and predict inelastic effects that occur when electrons pass a tunnel junction. These inelastic effects can be considered at several levels of sophistication, from very simple to very complex. The main innovation in this thesis is the development of the lowest order in inelastic tunneling (LOIT) approach. This approach has been employed to predict inelastic electron tunneling spectroscopy (IETS) intensities of vibrational modes in three different systems of increasing complexity.

The thesis can be divided into three parts. The first part, which contains Chapters 1 and 2, serves as an introduction to STM imaging and inelastic effects in tunnel junctions. Chapter 1 introduces the reader to a debate in biology in which IETS could be the key tool to determine the physical mechanism of smell. The possible link between smell and IETS is explained and a roadmap for future research is outlined which might help answer the question whether our nose detects odors by measuring vibrations of molecules with tunneling electrons. Since all IETS experiments and modeling are performed using a scanning tunneling microscope (STM), Chapter 2 describes the processes of STM, scanning tunneling spectroscopy (STS) and IETS in simple terms and presents the details of the STM experiments.

The second part, Chapters 3 and 4, presents in full detail the modeling of the electron transport in a realistic STM experiment, where Chapter 3 is devoted to the description of elastic transport and Chapter 4 to including inelastic effects. The \textit{ab initio} method described here requires density functional theory (DFT) and Green's functions calculations, which are both introduced in Chapter 3. The crucial interactions between tip and sample are described by Slater-Koster (SK) functions fitted to DFT calculations. Three parameterization schemes are presented in Chapter 3.

In Chapter 4 a two-level system within a one-dimensional model is introduced to describe in more detail the STM setup and to investigate which ingredients are necessary to correctly describe IETS intensities. To obtain correct IETS signals it is crucial to take the inelastic tunneling terms – i.e. the interactions between tip and sample under excitation of a vibrational mode – into account. These inelastic tunneling terms are included up to lowest order in the introduced LOIT approach, which is described in detail. Within the tunneling regime, inclusion of these terms up to lowest order represents an accurate approximation and reduces drastically the computational cost for this type of calculations.

The third and last part of the thesis, which contains Chapters 5-8, concerns the results obtained by employing the LOIT approach to realistic systems for which experimental data is available. Chapter 5 describes IETS on a CO molecule adsorbed onto Ag(110). The simulated STM images reproduce the experimental fact that a tip which is
terminated with a CO molecule leads to a protrusion in the imaging of a CO molecule on the surface, and a clean tip leads to a dip in the imaging of a CO molecule. Next, inelastic spectra are simulated by combining the LOIT method with the wide band limit (WBL). In agreement with the experiment, the hindered rotation modes contribute the most, and, depending on the used tip, also the metal-CO stretch mode. Using full Green's functions leads to problems in convergence in k-grid size and hence the wide band limit must be assumed. Furthermore, propensity rules are explored, which can be used to simply predict IETS intensities. The IETS intensity of a given vibrational mode is large if i) the inelastic tunneling matrix elements are large, ii) the corresponding AOs contribute to the elastic current and iii) there is no destructive interference.

Chapter 6 describes IETS on a monolayer of NO on Rh(111). It is found that NO molecules are imaged as a protrusion if an NO molecule is adsorbed in upright position on the tip. The simulated STM images suggest that without such a tip NO molecule, the probability is low for the tunneling electrons to traverse the surface NO molecules. The LOIT+WBL approach gives qualitatively correct predictions for which vibrations are excited. In this system the measured peaks around ±18 mV are assigned to a convolution of the out-of-phase $\nu$(Rh-NO) and several $R$(N-O) modes and the peaks around ±55 mV to a convolution of the surface in phase $\nu$(Rh-NO) and tip $\nu$(W-NO) modes. Both in Chapter 5 and in Chapter 6 the IETS intensities depend crucially on the used tip. The low intensity of inelastic effects in the curves obtained with the tips without an NO molecule adsorbed upright is consistent with the low probability of tunneling through the orbitals of the surface NO molecules for these tips.

Chapters 7 and 8 deal with the more complex system of a self assembled thiophenol monolayer on Ag(111). Because the full details of a junction are important to describe the IETS signals, the structure of the monolayer is first studied in Chapter 7. From the results of STM and low energy electron diffraction (LEED) experiments and simple LEED modeling, an adsorption model is proposed with six molecules and 17 Ag atoms per layer in the unit cell. It is shown that the optimal structure of the monolayer obtained by DFT depends critically on the initial configuration and the used approximation to incorporate Van-der-Waals interactions. DFT could therefore not be used to determine accurately geometric parameters such as the adsorption site, ring tilt angle or S-C bond angle. Also the STM simulations could not be used to determine which surface geometry corresponds to the experiments, although they justify the wide variety of experimental STM images and reproduce the most robust features. The vibrational modes calculated with DFT for the large unit cell are nearly identical to those calculated for a small model unit cell and reproduce reasonably well those measured with high resolution electron energy loss spectroscopy (HREELS). This suggests that the vibrational modes are not very sensitive to the details of the adsorption geometry of the molecules.

Chapter 8 describes a well-reported narrow reduction in the density of states (DOS) around the Fermi energy, termed zero-bias anomaly (ZBA), in thiol-bound molecular junctions. A few possible explanations are reviewed in Chapter 8. First, the suggestion that the ZBA is part of the single-particle DOS is discarded by means of DFT
calculations, and next a many-body explanation which includes umklapp processes is also discarded by means of experimental photoemission spectroscopy. The excitation of low energetic vibrations, as calculated with the LOIT+WBL approach, does lead to a pseudogap in the conductance at low voltages, although the found intensity is too low for realistic tip-sample distances. By moving the tip closer, the IETS intensity increases, although it is questionable if the transport still takes place in the tunneling regime then.

In conclusion, for junctions in which the transport takes place in the tunneling regime, the LOIT+WBL approach is an efficient method to calculate IETS intensities. The efficiency of the method allows for treating highly complex systems such as the STM setup. The limiting factor in an \textit{ab initio} implementation of the method is the time required to accurately perform the DFT calculations to obtain the ground state geometry, electronic structure and vibrational modes. The relative IETS intensities calculated with this method are correct and the absolute values have the correct order of magnitude.

**Outlook**

Details of simulated STM images as well as accurate values for IETS intensities depend critically on two so far unknown factors: the SK parameters and the details of the tip. The amount of atoms taken into account in the DFT calculations to which the SK parameters are fitted represent a tradeoff between accuracy (many atoms) on the one hand and efficiency and transferability (few atoms) on the other hand. It is thus necessary to develop a more robust yet accurate parameterization scheme, allowing the correct description of both STM images and IETS curves.

The tips used in experiments can differ significantly from one experiment to another. This can be modeled by varying the metal termination, the adsorbates and/or their adsorption sites in the DFT calculations and by rotating the tip axes in the Green's functions calculations. However, in order to prevent from drowning in a sea of possibilities, it is important to i) experimentally make stable tips, including controlled atom transfer, and ii) identify the most important characteristics of tip terminations that determine the transport in an STM junction and model only a limited number of them.

The implementation of the LOIT approach in the STM simulations helps in determining this robust yet accurate SK parameterization scheme and in selecting characteristic tips and brings as a result modeling of molecular transport junctions a step forward. Furthermore, since the LOIT approach is a relatively cheap method to detect which vibrations are excited in molecules, IETS spectra of more complex molecules can be better understood. This can be helpful to better choose systems to test the vibrational odor recognition theory and to predict odor intensities.
Samenvatting

Dit proefschrift beschrijft het modelleren van het transport van elektronen door een realistische tunneljunctie om op een efficiënte manier de inelastische effecten te voorspellen die optreden wanneer elektronen een tunneljunctie passeren. Deze inelastische effecten kunnen op verschillende manieren worden meegenomen, variërend van zeer simpel tot zeer complex. De meest innovatieve bijdrage van dit proefschrift is de ontwikkeling van de laagste orde in inelastisch tunnelen (LOIT) methode. Deze methode is toegepast om van verschillende vibratietoestanden de bijdrage aan het inelastisch elektronentunnelspectroscopie (IETS) signaal te voorspellen in drie verschillende systemen die toenemen in complexiteit.

Het proefschrift kan onderverdeeld worden in drie gedeelten. Het eerste gedeelte, dat de hoofdstukken 1 en 2 omvat, dient als inleiding in de rastertunnelmicroscoop (scanning tunneling microscope, STM) en het meten van inelastische effecten in een tunneljunctie. Hoofdstuk 1 introduceert de lezer in een controverse binnen de biologie waarin IETS een sleutelrol zou kunnen vervullen om het fysische mechanisme waarmee wij ruiken te ontrafelen. De mogelijke relatie tussen geur en IETS wordt uitgelegd en een stappenplan voor toekomstig onderzoek wordt besproken. Het beantwoorden van de vraag of onze neus trillingen van moleculen zou kunnen bepalen met behulp van tunnelende elektronen speelt hierbij een belangrijke rol. Omdat alle IETS experimenten en modelleringen verkregen zijn met een STM worden in hoofdstuk 2 de technieken STM, rastertunnelspectroscopie (scanning tunneling spectroscopy, STS) en IETS in eenvoudige termen uitgelegd en worden de details van de STM experimenten besproken.

Het tweede gedeelte, de hoofdstukken 3 en 4, beschrijft uitvoerig de modellering van het transport van elektronen in een realistisch STM experiment. Hoofdstuk 3 is gewijd aan de beschrijving van elastisch transport en hoofdstuk 4 aan de toevoeging van inelastische effecten. De ab initio methode die hier beschreven wordt, maakt gebruik van dichtheidsfunctionaliteit (DFT) en van berekeningen met Greense functies. Beide raamwerken worden geïntroduceerd in hoofdstuk 3. De cruciale interactie tussen tip en oppervlak worden beschreven met Slater-Koster (SK) functies die gefit worden aan DFT berekeningen. In hoofdstuk 3 worden drie van zulke parametrisatieschema's besproken.

In hoofdstuk 4 wordt binnen een eendimensionaal model een twee-toestanden-systeem geïntroduceerd om in meer detail de STM opstelling te beschrijven en om te onderzoeken welke ingrediënten van het standaard één-toestand-systeem noodzakelijk zijn voor de correcte beschrijving van IETS intensiteiten. Om correcte IETS signalen te verkrijgen blijkt het cruciaal te zijn de inelastische tunneltermen mee te nemen, d.w.z. de interactietermen tussen tip en oppervlak waarbij een vibratietoestand wordt aangeslagen. Deze inelastische tunneltermen worden binnen de LOIT methode tot de
laagste orde meegenomen, een procedure die uitvoerig behandeld wordt. Het meenemen van deze termen tot de laagste orde geeft binnen het tunnelregime een zeer nauwkeurige benadering van het volledige probleem, terwijl benodigde berekeningstijden drastisch omlaag gaan.

Het derde en laatste deel van dit proefschrift, de hoofdstukken 5 tot en met 8, beschrijven de resultaten die behaald zijn door de LOIT methode toe te passen op realistische systemen waarvoor experimentele data voorhanden is. In hoofdstuk 5 wordt IETS aan een CO molecuul, geadsorbeerd op een Ag(110) oppervlak beschreven. Zowel de experimentele als de gesimuleerde STM plaatjes tonen aan dat een tip met een CO molecuul aan het uiteinde een CO molecuul op het oppervlak als een verhoging weergeeft, terwijl een schone tip dit CO molecuul weergeeft als een dal. Vervolgens zijn de IETS spectra gesimuleerd door de LOIT methode te combineren met een vlakke bandbenadering (wide band limit, WBL). In overeenstemming met het experiment dragen de hindered rotation toestanden van het CO molecuul het meest bij en, afhankelijk van de gebruikte tip, ook de metaal-CO stretch vibratie. Het gebruik van de volledige Greense functies leidt tot problemen in convergentie in het aantal k-punten en daarom wordt de vlakke bandbenadering aangenomen. Tevens worden de propensity rules of neigingregels verkend, waarmee op eenvoudige wijze voorspellingen gedaan kunnen worden, maar die minder eenduidig zijn dan selectieregels. Het blijkt dat de IETS intensiteit van een gegeven vibratietoestand groot is indien i) de inelastische tunnelmatrixelementen groot zijn, ii) de bijbehorende atomaire orbitalen bijdragen aan de elastische stroom en iii) er geen sprake is van destructieve interferentie.

Hoofdstuk 6 beschrijft IETS van een monolaag van NO op Rh(111). Het blijkt dat NO moleculen als een verhoging weergegeven worden in een STM plaatje wanneer aan het uiteinde van de tip een NO molecuul verticaal gebonden is. De gesimuleerde STM plaatjes suggereren dat zonder een NO molecuul aan de tip de waarschijnlijkheid klein is dat elektronen naar de orbitalen van de NO moleculen op het oppervlak tunnelen. De LOIT+WBL methode geeft kwalitatief correcte voorspellingen welke vibraties worden aangeslagen. In dit systeem worden de gemeten pieken rond ±18 mV toegeschreven aan een convolutie van de uit-fase $\nu$(Rh-NO) en verscheidene R(N-O) toestanden en de pieken rond ±55 mV aan een convolutie van een in-fase $\nu$(Rh-NO) toestand aan het oppervlak en een $\nu$(W-NO) toestand aan de tip. Zowel in hoofdstuk 5 als in hoofdstuk 6 blijkt dat de IETS intensiteiten essentieel afhangen van de gebruikte tip. De lage intensiteit van inelastische signalen die berekend zijn met tips zonder NO molecuul rechtop aan de tip is consistent met de kleine waarschijnlijkheid dat elektronen de orbitalen van de NO moleculen in tunnelen.

Hoofdstukken 7 en 8 behandelen het complexere systeem van een zelfgeassembleerde monolaag van thiofenol op Ag(111). Omdat de volledige details van de junction van belang zijn om de IETS signalen te beschrijven, wordt in hoofdstuk 7 eerst de structuur van de monolaag bestudeerd. Aan de hand van STM en lage-energie elektronendiffractie (LEED) experimenten en eenvoudige LEED modellering is een adsorptiemodel voorgesteld met zes moleculen in een eenheidscel van 17 zilveratomen per laag. De
optimale structuur van de monolaag, bepaald met DFT, hangt sterk af van de gebruikte beginconfiguratie en de benadering om Van-der-Waals interacties mee te nemen. DFT kon daarom niet gebruikt worden om nauwkeurig enkele structuurparameters te bepalen, zoals de adsorptielocatie, de ringkantelhoek en de S-C bindingshoek. Ook de STM simulaties konden niet gebruikt worden om te bepalen welke oppervlakstructuur overeenkomt met de experimenten, hoewel het wel de grote variëteit aan STM plaatjes rechtvaardigde en de meest robuuste kenmerken reproduceerde. De vibratietoestanden die berekend zijn met DFT met een grote eenheidscel zijn bijna identiek aan de toestanden berekend met een kleine eenheidscel en reproduceerden redelijk goed de toestanden gemeten met hoge resolutie elektronenergieverliesspectroscopie (high resolution electron energy loss spectroscopy, HREELS). Dit suggereert dat de vibratietoestanden niet erg gevoelig zijn voor de details van de adsorptie van de moleculen.

Hoofdstuk 8 beschrijft de veelbesproken nauwe afname in de toestandsdichtheid rond het Fermi-niveau van moleculaire juncties die gebonden zijn met thiolen. Deze afname wordt de nulspanningsanomalie (zero-bias anomaly, ZBA) genoemd. Verschillende verklaringen voor de ZBA worden besproken in hoofdstuk 8. Eerst wordt de suggestie dat de ZBA een onderdeel is van de één-deeltjes-toestandsdichtheid verworpen aan de hand van DFT berekeningen, en vervolgens wordt een veel-deeltjes-verklaring waarbij umklapp-processen meespelen eveneens verworpen aan de hand van experimentele fotoemissiespectroscopie. Het aanslaan van laag-energetische vibratietoestanden, zoals berekend met de LOIT+WBL methode, leidt wel tot een afname in de geleiding bij kleine voltages, hoewel de gevonden intensiteit te laag is voor realistische afstanden tussen tip en oppervlak. Door de tip dichterbij te bewegen, neemt de IETS intensiteit toe, hoewel het twijfelachtig is of het transport dan nog steeds plaatsvindt in het tunnelregime.

In conclusie is voor juncties waarin transport plaatsvindt in het tunnelregime de LOIT+WBL methode een efficiënte methode om IETS intensiteiten te berekenen. De efficiëntie van de methode staat toe dat zeer complexe systemen zoals de STM opstelling tot in detail meegenomen kunnen worden in de berekeningen. De beperkende factor in een ab initio implementatie van de methode is de tijd die nodig is om nauwkeurig de DFT berekeningen uit te voeren om de oppervlakstructuur, de elektronenstructuur en de vibratietoestanden in de grondtoestand te verkrijgen. De relatieve IETS intensiteiten berekend met deze methode zijn correct en de absolute waarden hebben de juiste orde-grootte.

Vooruitzicht

Details van gesimuleerde STM plaatjes en nauwkeurige waarden voor IETS intensiteiten hangen essentieel af van twee tot dusverre onbekende factoren: de SK parameters en de details van de tip. De hoeveelheid atomen die meegenomen wordt in de DFT berekeningen waaraan de SK parameters gefit worden, geven de afweging aan
tussen nauwkeurigheid (veel atomen) aan de ene kant en efficiëntie en overdraagbaarheid (weinig atomen) aan de andere kant. Het is dus noodzakelijk om een robuust, doch nauwkeurig parametrisatieschema te ontwikkelen, dat correcte beschrijvingen geeft voor zowel STM plaatjes als IETS spectra.

De tips die gebruikt worden verschillen significant per experiment. Dit kan gemodelleerd worden door het metalen uiteinde, de adsorbuten en/of hun adsorptielocaties van de tips te variëren in de DFT berekeningen en de tip-assen te roteren in de berekeningen met de Greense functies. Om echter niet te verdrinken in de vele mogelijkheden is het belangrijk om i) experimenteel stabiele tips te vervaardigen, inclusief het gecontroleerd overplaatsen van een atoom, en ii) de belangrijkste eigenschappen van tipuiteinden te identificeren die het transport in een STM opstelling bepalen. Slechts een beperkt aantal van deze karakteristieke uiteinden dienen gemodelleerd te worden.

De implementatie van de LOIT methode in de STM simulaties helpt bij het bepalen van dit robuuste doch nauwkeurige SK parametrisatieschema en bij het selecteren van karakteristieke tips. Hiermee brengt het de modellering van moleculaire juncties een stap dichterbij. Bovendien kunnen IETS spectra van complexere moleculen beter begrepen worden, omdat de LOIT methode een relatief goedkope manier is om te bepalen welke vibraties aangeslagen worden door elektronen in een molecuul. Dit kan bijdragen tot het kiezen van systemen waaruit zou moeten blijken of de neus geuren kan herkennen door het meten van moleculaire vibraties of niet, en indien dit het geval is, het voorspellen van geurintensiteiten.
Appendix A: Details of calculations CO on Ag(110)

This Appendix presents the details of the calculations performed in Chapter 5. Table A.1 lists all vibrational modes found with DFT for the surface and the CO terminated Ag tips. Table A.2 lists the intensities found with the wide band limit (WBL) for each peak corresponding to vibrational modes $\lambda$ in the surface, along with the corresponding maximum elements of the matrix $M_{LR}^\lambda$, and Table A.3 the intensities and maximum matrix elements for the vibrational modes in the tip apex.

**Table A.1** Detailed overview of energies (in meV) and assignments of vibrational modes for CO on Ag(110) and on a sharp and blunt Ag tip. $\nu$ = stretch, $\delta_{ip}$ = inplane bending, $\delta_{oop}$ = out-of-plane bending, $R$ = hindered rotation, $T$ = hindered translation. Atoms in parentheses indicate moving atoms in the vibrational mode, subscripts $x$ and $y$ indicate the direction of the moving atoms, where $x$ indicates perpendicular to the [-110] rows and $y$ indicates along the [-110] rows, and subscripts 1, 2 and 3 indicate the layer of the moving atoms. Note that in the blunt tip, the actual first layer is labeled layer 2.

<table>
<thead>
<tr>
<th>CO on Ag(110)</th>
<th>VM</th>
<th>$h\omega$</th>
<th>Assignment</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23</td>
<td>251</td>
<td>$\nu$(C-O)</td>
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</tr>
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<td>33</td>
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<td></td>
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<td>19</td>
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<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>$R_y$(C-O)</td>
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</tr>
<tr>
<td></td>
<td>19</td>
<td>15</td>
<td>$\nu$(Ag)</td>
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</tr>
<tr>
<td></td>
<td>18</td>
<td>15</td>
<td>$R_x$(C-O)</td>
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</tr>
<tr>
<td></td>
<td>17</td>
<td>14</td>
<td>$R_y$(C-O)</td>
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<tr>
<td></td>
<td>16</td>
<td>12</td>
<td>$\nu$(Ag)</td>
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<td>12</td>
<td>$\nu$(Ag)</td>
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<td>14</td>
<td>12</td>
<td>$R_x$(C-O)</td>
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<tr>
<td></td>
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<td>11</td>
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Figure A.1 Simulated STM images and line scans of a single CO molecule on Ag(110), obtained with the used tips as depicted in the insets and the SK parameterization scheme 2 of Subsection 3.2.7. The line scans e) and f) are taken in the horizontal direction through the center of the CO molecule.
Table A.2 Contribution to the total current in % and maximum element of matrix $M_{LR}$ in meV for each surface vibrational mode $\lambda$ (rows) and for each of the four used tips (columns) over the center of the CO molecule. The assignments of the surface vibrational modes can be found in Table A.1. The intensity is determined from WBL calculations with the $3 \times 4$ k-grid.

<table>
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<th>VM</th>
<th>Clean sharp</th>
<th>Int.</th>
<th>$M_{LR}$</th>
<th>Clean blunt</th>
<th>Int.</th>
<th>$M_{LR}$</th>
<th>CO sharp</th>
<th>Int.</th>
<th>$M_{LR}$</th>
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Table A.3 Contribution to the total current in % and maximum element of matrix $M_{LR}$ in meV for each vibrational mode $\lambda$ in the tip apex for both used CO terminated tips over the center of the CO molecule. The assignments of the apex vibrational modes can be found in Table A.1. The intensity is determined from WBL calculations with the 3×4 k-grid.

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Appendix B: Details of calculations NO on Rh(111)

This Appendix presents the details of the calculations performed in Chapter 6. Table B.1 lists all vibrational modes found with DFT for the surfaces and the NO terminated W tips. Table B.2 lists the intensities found with the wide band limit (WBL) for each peak corresponding to vibrational modes $\lambda$ in the $2\times2$ and $c2\times4$ surfaces and the tip apex, along with the corresponding assignments. Table B.3 lists the intensities for the $4\times4$ surface over the NO molecule and over bare Rh.

Table B.1 Detailed overview of energies (in meV) and assignments of vibrational modes for NO on Rh(111) and on a sharp and blunt fcc and bcc W tip. $v =$ stretch, $R =$ hindered rotation, $T =$ hindered translation, $iph =$ in phase, $ooph =$ out of phase. Atoms in parentheses indicate moving atoms in the vibrational mode, subscripts indicate the layer of the corresponding atom. Note that in the blunt tip, the actual first layer is labeled layer 2.

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Table B.2 Contribution to the total current (columns Int) in % for each vibrational mode in the surface and apex, and energy and assignment of associated vibrational mode. The columns indicate which monolayer structure is used, the rows indicate which tip is used, where A = NO terminated sharp bcc W tip, B = NO terminated sharp fcc W tip, C = NO terminated blunt fcc W tip and D = clean sharp fcc W tip. The upper vibrational modes are surface vibrational modes; the lower vibrational modes are apex vibrational modes, which are not defined in D.

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Table B.3 *Contribution to the total current (columns Int) in % for each vibrational mode in the surface and apex, and energy and assignment of associated vibrational mode.* The columns indicate which surface is used, the rows indicate which tip is used, where $A = NO$ terminated sharp bcc W tip, $B = NO$ terminated sharp fcc W tip and $C = NO$ terminated blunt fcc W tip. The upper vibrational modes are surface vibrational modes; the lower vibrational modes are apex vibrational modes. The contributions of vibrational modes for the clean tips and these surfaces are all 0.01% or lower and hence not shown.

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<td>R(N-O)</td>
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<td>0.18</td>
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| B  | 74   | 2.12            | 45               | ν(Rh-NO) | 20   | 0.82            | 59               | ν(W-NO)         |
|    | 77   | 0.72            | 187              | ν(N-O)   | 21   | 0.53            | 201              | ν(N-O)         |
|    | 63   | 0.24            | 26               | ν(Rh-NO), weak | 2   | 0.31            | 12               | W              |
|    |      |                 |                  |          | 7    | 0.25            | 14               | ν(W-NO)         |
|    |      |                 |                  |          | 18   | 0.16            | 41               | R(N-O)         |
|    |      |                 |                  |          | 19   | 0.15            | 42               | R(N-O)         |

| C  | 74   | 0.25            | 45               | ν(Rh-NO) | 18   | 0.20            | 40               | ν(W-NO)         |
|    | 77   | 0.09            | 187              | ν(N-O)   | 20   | 0.09            | 165              | ν(N-O)         |
|    |      |                 |                  |          | 2    | 0.07            | 12               | W              |
|    |      |                 |                  |          | 19   | 0.06            | 40               | R(N-O)         |
Appendix C: Details of calculations thiophenol on Ag(111)

This appendix gives the details of the final configurations for the various initial configurations and various methods to include Van-der-Waals interactions, as described in Chapter 7. It furthermore shows the species projected density of states of one of the systems.

**Table C.1** Ring tilt angles in ° of the six molecules in the $\sqrt{7} \times \sqrt{31}$ cell for the three different methods. The error in the mean ring tilt angle is defined as the standard deviation.

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Table C.2 S-C bond angles in ° of the six molecules in the √7×√31 cell for the three different methods. The error in the mean S-C bond angle is defined as the standard deviation.

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<td>31</td>
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</table>
Table C.3  *Average height of the six S atoms above the top Ag layer in the $\sqrt{7} \times \sqrt{31}$ cell for the three different methods. The error in the mean distance is defined as the standard deviation.*

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Figure C.1 Simulated 4×4 nm² STM images for a blunt and sharp silver tip of the structures obtained without taking Van-der-Waals interactions taken into account. Simulation parameters: \( V = 100 \text{ mV}, I_{sp} = 1 \text{ nA}. \)
Figure C.2 Simulated 4×4 nm² STM images for a blunt and sharp silver tip of the structures obtained by taking semi-empirical Van-der-Waals interactions into account. Simulation parameters: $V = 100$ mV, $I_{sp} = 1$ nA.
Figure C.3 Simulated $4 \times 4 \text{ nm}^2$ STM images for a blunt and sharp silver tip of the structures obtained by employing the Van-der-Waals functional. Simulation parameters: $V = 100 \text{ mV}, I_{sp} = 1 \text{ nA}$. 
Table C.4 Detailed overview of energies (in meV), degeneracies (numbers in parentheses) and assignments of vibrational modes for TP on Ag(111) in the $\sqrt{3} \times \sqrt{3}$ and the $\sqrt{7} \times \sqrt{31}$ cell. Atoms in parentheses indicate moving atoms in the vibrational mode. $\nu = \text{stretch}$, $\delta = \text{bending}$, $\nu_1$ and $\nu_2$ are defined in Fig. C.4, the subscript in $\delta_{ip}$ and $\delta_{oop}$ indicates the direction of the moving atoms (in-plane or out-of-plane respectively), and the subscript in $\delta_x$, $\delta_y$ and $\delta_z$ indicates the direction of the movement of the S atom, where $z$ is perpendicular to the surface, $y$ is perpendicular to the benzene plane and $x$ is parallel to the benzene plane.

<table>
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<tr>
<td>198-200 (2) $\nu$(C-C)</td>
<td>196-199 (12) $\nu$(C-C)</td>
</tr>
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<td>179 $\nu$(C-C), $\delta_{ip}$(C-H)</td>
<td>175-177 (7) $\nu$(C-C), $\nu$(S-C), $\delta_{ip}$(C-H)</td>
</tr>
<tr>
<td>176 $\nu$(C-C), $\delta_{ip}$(C-H)</td>
<td>174-175 (5) $\nu$(C-C), $\delta_{ip}$(C-H)</td>
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<td>170-171 (6) $\delta_1$(Ag-S-C)</td>
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<td>151-153 (6) $\delta_x$(Ag-S-C), $\delta_{ip}$(C-H)</td>
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<td>136-140 (2) $\delta_{ip}$(C-H)</td>
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<td>132 $\nu$(C-C), $\nu$(C-S)</td>
<td>130-131 (6) $\nu$(C-C), $\nu$(C-S)</td>
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<td>127-129 (2) $\nu$(C-C), $\delta_{ip}$(C-H)</td>
<td>124-131 (12) $\nu$(C-C), $\delta_{ip}$(C-H)</td>
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<td>116-118 (6) $\nu_1$(C-C), $\nu$(S-C), $\nu$(C-H)</td>
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<td>86 $\delta_4$(Ag-S-C)</td>
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<td>19 $\delta_{oop}$(C-C)</td>
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<td>10-18 (6) Ring tilt</td>
<td>10-18 (6) Ring tilt</td>
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</table>

Figure C.4 Moving C atoms in a particular benzene ring in the modes $\nu_1$ and $\nu_2$. 
Figure C.5 Calculated density of states of thiophenol on Ag(111), broadened by 50 meV. The DOS is projected onto the chemical species and scaled by the amount of atoms of the corresponding species in the unit cell. The number behind Ag denotes the layer in which the atoms reside.
Curriculum vitae

Erwin Rossen was born on January 30, 1982 in Nuth, The Netherlands. He obtained his pre-university secondary education at the "Sintermeertencollege" in Heerlen in 2000, and in that year he started to study Applied Physics and Applied Mathematics at the Eindhoven University of Technology (TU/e). He obtained both bachelor's degrees in 2006 and obtained his master's degree in Applied Physics in 2007, with nanotechnology as specialization. His master's thesis describes the influence of STM tips on inelastic spectra. In 2007 he started his PhD research on the experiments and the modelling of inelastic electron tunneling spectroscopy in an STM setup. The work was carried out under the supervision of dr. ir. C.F.J. Flipse in the group Molecular Materials and Nanosystems (M2N) of prof. dr. ir. R.A.J. Janssen and under the supervision of dr. J.I. Cerdá at the Instituto de Ciencia de Materiales de Madrid (ICMM). The outcomes of this research are described in this thesis.
Dankwoord / acknowledgements

Zo, de thesis is af; dat zit erop! Nu alleen nog een dankwoord schrijven, een stuk tekst dat enerzijds niet als het belangrijkste van een thesis ervaren wordt, maar dat paradoxaal genoeg wel het meest gelezen wordt. Natuurlijk wil iedereen die ook maar zijdelings betrokken is geweest bij het werk van de promovendus nagaan of de betrokken persoon vermeld wordt en wat de promovendus hierover te melden heeft. Ik zal jullie dan ook niet teleurstellen door eveneens een dergelijk stuk proza te vervaardigen.

Want hoewel het cliché klinkt, een proefschrift zoals deze komt inderdaad niet tot stand zonder de bijdragen van verschillende mensen om mij heen. Als eerste wil ik mijn co-promotor en dagelijks begeleider van harte bedanken. Kees, ik ben blij dat je altijd tijd voor me vrij wist te maken, waardoor ik praktisch op elk ogenblik van de dag bij je binnen kon vallen om mijn resultaten en ideeën te delen, om inspiratie op te doen voor interpretaties van data, om adviezen te vragen, of om te discussiëren over spannende fysica. Ook buiten de natuurkunde om heb ik je ervaren als een aangenaam persoon, waarmee je altijd zowel een stevige discussie kan voeren als een terloops praatje kan maken, onder het genot van een kop koffie of een glas Italiaanse wijn. Bedankt voor de afgelopen vijf en een half jaar!

During my PhD project, I had the luck to not have only one, but two co-promotors! Almost the entire contents of this thesis are the result of a fruitful collaboration with my daily supervisor, mentor, teacher and colleague during my seven months which I spent in Madrid. Jorge, muchas gracias for your never-ending guidance and enthusiasm! I have learned so much from you about DFT and NEGF in particular, about how to perform gigantic calculations in general, and about how to critically write a thesis. And to all the people who have the luck to work together with Jorge once in their life: try to have him invite you to come over for dinner: he is a great cook and his kids are amazing company.

Behalve twee co-promotoren is een promotor natuurlijk onontbeerlijk: iemand die het overzicht behoudt op je voortgang, iemand die je werk kritisch kan beoordelen vanaf een zeker afstand. René, hartelijk bedankt dat je mij deze mogelijkheid tot het behalen van mijn PhD geboden hebt en voor je opgewekte persoonlijkheid tijdens groepsbijeenkomsten en de spaarzame momenten dat je de tijd vond om koffie te drinken op Spectrum.

Bij deze wil ik ook graag mijn twee paranimfen bedanken. Kevin, je wetenschappelijke kunde, je sterke gevoel voor humor en je nimmer aflatende goedhartigheid zorgen ervoor dat ik al meer dan tien jaar graag met je samenwerk op professioneel vlak, maar nog meer dat ik al die tijd blij ben met jou als vriend. Marian, dankzij onze promoties hebben we elkaar leren kennen, en dat klikte meteen. Ik ben blij dat we elkaar zo goed aanvoelen en altijd een gezellige tijd samen hebben.

Ik heb met vele collega's mogen samenwerken de afgelopen vijf en een half jaar. Bij deze wil ik iedereen bedanken voor zijn of haar bijdrage aan mijn werk. Joris, ik wil jou bedanken dat je mij hebt begeleid tijdens mijn afstuderen en mij wegwijs gemaakt hebt.
met de STM. Gerard, bedankt dat je de STM in topconditie gehouden hebt, door hem binnen no time gerepareerd te hebben wanneer er weer eens iets stuk was of door uitbreidingen te helpen verzinnen en bouwen. Wijnand, bedankt voor het delen van je kunde op het vlak van elektronica en computers; zonder jou had ik al die berekeningen niet kunnen uitvoeren vanuit Eindhoven. Richard, bedankt voor het verrichten van HREELS experimenten voor mij en voor de gezellige spelletjesavonden. Jos en Nando, bedankt voor de samenwerking om de experimenten bij lage temperaturen te kunnen verrichten. Juanma, thanks a lot for keeping the computers in Madrid up and running. Without you, both Jorge and I would be helpless. Take it easy! Erik, bedankt voor het mij introduceren in het fenomeen Adobe; nu kan ik tenminste mooie figuren maken, foto's bewerken en, niet geheel onbelangrijk, belachelijke filmpjes maken! Furthermore, I would like to thank all colleagues of M2N for a pleasant time: Reinder, Martijn, Marta, Cristina, Alex, Friso, Rein, Yingxin, Rik, Nick, Jiří, Ron, J(u)an, Ondra, Zdenek, Stephan, Sjors, Dimitri, Klara, Simon, Wijnand, Christian, Augusta, Marije, Peter, Stan, Michael, Zuhal, Andrzej, Salomon, Siebe, Rein, Marco, Marco, Jos, Pavel, Arpan, Igor, Seva, Willem, and everybody of M2N at the chemistry side.

A sincere thanks to the reading committee, for your critical reading and plentiful comments. Jan, Harald, Henk and Thomas: thanks in advance for the tough defense!

Naast mijn collega's wil ik natuurlijk ook al mijn vrienden bedanken, die ervoor gezorgd hebben dat ik de afgelopen jaren een leuke tijd gehad heb en dat ik Eindhoven echt als mijn 'thuisstad' ben gaan ervaren. Gelukkig zijn het er teveel om allemaal bij naam te noemen hier. Armanda, ik vond het fijn om al die jaren met jou in huis te wonen. Behalve mijn vrienden wil ik hierbij ook mijn vader en moeder, Albert en Annelies, en mijn zus en haar familie, Jolanda, Richard, Isa en Milan, bedanken. Monica, it were this PhD project and faith that brought us together. Since then you know how to get the best out of me. I hope we never stop completing each other.
"Can you tell us who probed you, Ma'am?"

"Howdy fellas! My name is Mr. Slater and this is Mr. Koster, interaction profilers."

"Good afternoon, gents. My name is Mr. Taylor, mathematician"