Local Probe Investigation of the Electronic Structure of Molecule–Based and Transition–Metal–Based Low Dimensional Systems Using Cryogenic Scanning Tunneling Microscopy and Spectroscopy

by

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A dissertation submitted in partial satisfaction of the requirements for the degree of

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Committee in charge:

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Professor Steven G. Louie
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Local Probe Investigation of the Electronic Structure of Molecule–Based and Transition–Metal–Based Low Dimensional Systems Using Cryogenic Scanning Tunneling Microscopy and Spectroscopy

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Abstract

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Of the many fascinating topics in condensed matter physics, this dissertation aims to cover three subtopics in some detail: 1) Functionalization of surfaces – using single molecules and/or atoms to change the behavior of a surface. 2) Low dimensional systems – 0D, 1D, or 2D materials whose behavior is often drastically different from the 3D world. 3) 3D to 2D crossover – studying what happens to materials as they are thinned down from a bulk 3D morphology to a single 2D layer. In addition to these areas of research, there will also be a focus on the modifications I made to the Toucan STM, and the rationale behind those changes. This portion, in combination with Niv Levy’s dissertation, should serve as a user’s manual for that microscope.
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<td>AES</td>
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<td>MBE</td>
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<td>OFHC</td>
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<td>PDOS</td>
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As is customary in dissertations, I would like to extend my gratitude to those who helped me through the Ph.D. process, as well as to those who got me to the point of deciding to spend six years learning more and more about less and less.

I suppose we should start at the beginning. I would like to thank my parents, Robert and Susan Bradley, for creating me. Without that life-changing event, none of this would have been possible. I would also like to thank them for always letting me do my thing. They never tried to push me in one direction or the other, and were always supportive of my decisions, even when they were terrible decisions. This allowed me to choose an academic path in a subject that I truly loved. I would also like to thank them for not getting upset with me when the frequency of my visits dropped off drastically, in connection with the beginning of the Ph.D.

Next I’ll mention the friends that helped me along the way. You can probably skip this section unless you think you’re in it. Chris Smith, a good friend from undergrad, who listened to me complain and helped me see at least some of the positive things in life. He also hates California, so perhaps I should revoke at least some of my profuse gratitude. Soenke Moeller, Joshua Howe, Chuck Sleasman, and Cory Simon for living with me and paying a portion of the insane Berkeley rent. Also thanks Soenke for dirtying (and occasionally cleaning) the bathroom. Nathan Roth, Itamar Kimchi, and Steve Weber for having lives outside of academia and demonstrating that it is actually possible (albeit difficult) to be a well-adjusted Ph.D. student. Victoria Martin for showing me how to take my Ph.D. by the reins and get shit done. Thanks to the friends who listened to me complain and one-upped my stories at beer hour. Without you, I would have been drinking alone (more). IGenSpectrum folks, for bringing visibility to LGBTQIA folks in the hard sciences. You reminded me that I’m not alone. Derek Vigil for bouncing ideas and being an overall awesome friend. At this point I’m rambling, so I’d like to thank any friends that I haven’t thanked up to this point. I’m sure you did something to help me during my graduate school
process and I’m sure it was appreciated. Or should have been.

I’d like to thank my fellow lab-mates as well, for discussing research topics, formulating ideas, writing papers, complaining, and drinking in New York City. I can honestly say that without you, my Ph.D. would not have been possible. If you’re going to do something, make sure to surround yourself with the best people in the world at it. I did that with my coworkers, and it couldn’t have turned out any better. I’d like to also thank Niv Levy, whom I did not overlap with. He built Tucan (more correctly spelled as Toucan) and left it in my care.

Thank you to my postdoc, Miguel Ugeda. You showed me how to perform research and get results. Before you arrived, I had spent my entire graduate school career modifying and fixing Toucan. With your expertise and knowledge, we got Toucan up and flying and never looked back down (until Toucan crash landed again and again and again). Also thank you for showing me how to make nice FFT vibration analysis plots. It seems insignificant (and probably is in the grand scheme of things), but it was somehow a turning point in my academic career.

One of the most important people in my grad school career was my advisor, Mike Crommie. While it is customary to heap undo praise on your advisor in these acknowledgments, I will not be doing that. All praise I give him is actually deserved. As a mentor, Mike was fantastic. He helped me choose research projects, plan them out, and execute at the highest possible level. As an advisor, he always understood which steps to take next, how to get there, and what fat could be chopped away. I would also like to thank Mike for allowing me to take time to pursue my interests in data science. Many advisors would not allow that, but Mike was very supportive. As is customary in Crommie theses, I would also like to thank Mike for giving me just enough rope to hang myself. He understands that researchers need space, and we need to be able to make our own mistakes so that we learn from them. We do. We make a lot of mistakes. Sometimes we learn. Sometimes we repeat these mistakes two or three or four or five times.

I would like to express my extreme gratitude to the staff of the physics department. Donna Sakima was always helpful with teaching assignments and keeping me on track with GSI appointments. The machine shop staff is the most dedicated, professional, and patient group of machinists I’ve ever worked with. Anne Takizawa, who is the most amazing, talented person I have ever had the pleasure to work with. How do you do everything that you do? I honestly don’t understand. I would also like to thank everyone else in the department who helped me during my time at Cal.

Finally, I’d like to express my gratitude to those whom I have yet to mention, but who had an impact on my progress. Apparently your influence wasn’t enough to be called out by name, but I’d still like for you to get an endorphin rush the first time you read this. There are many small acts that get little recognition, but add up to make the overall Ph.D. experience tolerable, and sometimes even enjoyable.
Part I
Background
My research has focused primarily on experimental surface science, with three main themes. The first theme involved the functionalization of semiconductor surfaces. During my PhD I studied the functionalization of GaP(110) using ethylene – a simple alkene [126], as well as iodobenzene and perfluorophenyl azide (PFPA) – molecules based on substituted phenyl rings [124]. The motivation for this work was to help create better catalysts for splitting water. The second theme was the study of low dimensional systems. 2D systems are ideal for surface scientists since they have no bulk – they’re all surface. 2D materials can support even lower dimensional states such as excitons (which can be thought of as being 0D states) as well as edge-states and grain boundaries (which can be thought of as 1D structures). I have explored these lower dimensional systems in single layers of the transition metal dichalcogenide (TMD) semiconductor MoSe$_2$. The third theme of my research has been to understand how the properties of materials change as they undergo a transition from 3D down to 2D. In this area I have studied how TMD materials can be thinned down to 2D, and what happens to their physical, optical, and electronic properties as they make this transition.

1.1 Functionalization of Surfaces

Functionalizing surfaces is one of the standard techniques for surface modification available to materials scientists. Often, a material with the desired properties isn’t readily available or doesn’t exist in nature. In these cases we have to make it. When we can make a material with the desired properties by bonding atoms and/or molecules to a surface, we call it functionalization. This can be done to passivate a surface [10, 110, 53] to make it less reactive, to activate a surface [75, 142] to make it more reactive, or to change the reactivity of a surface in some other desirable way [7, 126]. Each of these comes with its own inherent difficulties and idiosyncracies.

When passivating a surface, the goal is to make it less reactive (and ideally completely
1.2. LOW DIMENSIONAL SYSTEMS

Low dimensional systems are a fascinating playground for exploring fundamental physics. Atomic arrangements and surface energies change with dimensionality [39, 46], optical prop-
1.2. LOW DIMENSIONAL SYSTEMS

Figure 1.1: Schematic representation for reducing hydrogen using a light-absorbing semiconductor coupled to a reduction catalyst. Light is absorbed by the semiconductor, creating an exciton. The electron in this weakly bound pair is funneled to the catalyst through a linker molecule. This causes a conformational change in the catalyst, enabling reduction of the hydrogen.

Properties are closely tied to it \cite{58}, and electronic structure is acutely dependent on the spatial extent of a material \cite{101}. Take, for example, carbon. In 0D, carbon can form C\textsubscript{60} Buckeyballs \cite{82}; in 1D it forms carbon nanotubes \cite{90} and graphene nanoribbons \cite{120}; 2D gives rise to graphene \cite{40}; and 3D produces graphite and diamond. In terms of electronic structure, each of these has its own unique properties. Due to the unique geometry of buckeyballs, the electrons can behave in novel ways. For example, by intercalating it with K, C\textsubscript{60} becomes superconducting with a transition temperature of 18K. Due to the confinement of the electrons, C\textsubscript{60} also displays molecular HOMO and LUMO levels, even when formed into a solid. The electrons in the 1D carbon nanotubes and graphene nanoribbons feel confinement effects too. Depending on the exact arrangement of the carbon atoms, these systems can be either semiconducting or metallic \cite{129} \cite{128}. In the 2D graphene case, electron confinement leads to even more exotic physics. In this case, the electrons behave as though they were relativistic, massless, spin-1/2 particles \cite{40}. This leads to a semimetallic behavior for graphene. It also makes graphene an unexpected benchtop playground for quantum electrodynamics experiments. For example, the electrons have been observed to undergo Klein tunneling \cite{117} and exhibit novel Quantum Hall characteristics \cite{6}. 
1.3 3D to 2D

Many other classes of materials can be found in low dimensional forms. One of the most interesting of these classes includes those materials which can be thinned down from their stable 3D form into 2D layers. This includes 2D graphene from graphite and single layers of Transition Metal Dichalcogenides from their bulk. These can both be obtained through many means, including mechanical exfoliation (e.g. the scotch tape method [40, 74]) of the bulk crystal and chemical exfoliation. There are other 2D materials, such as phosphorene [77] and germanene [94], which are unstable in air, but can be prepared in vacuum for STM and other studies.

One of the reasons that the 3D to 2D transition is so interesting is that one can track the change in optical and electronic structure as a material is thinned down. This is especially apparent in the semiconducting TMDs. We have studied this process in MoSe$_2$ [14]. In its bulk form, MoSe$_2$ is a semiconductor with a bandgap of 1.10 eV [12]. When it is thinned down to three layers, the bandgap increases to 1.32 ± 0.04 eV, at two layers it is 1.56 ± 0.04 eV, and at one layer, the 2D limit, the bandgap is at its maximum value of 2.18 ± 0.04 eV. Similar trends are expected in many other materials as well [130]. In MoSe$_2$, this is due to two competing effects. On the one hand, as the number of layers is decreased, the coupling between layers changes. In the single-layer limit, there is no coupling between layers (because there’s only one layer). On the other hand, changing the number of layers changes the dielectric environment. An electron in a single layer of MoSe$_2$ sees a very different screening cloud than one in the middle of a bulk slab of MoSe$_2$. 

![Figure 1.2: a) Fullerene (0D), b) single-walled carbon nanotubes (1D), c) graphene (2D), d) graphite (3D). Reproduced from [141].](image)
2.1 The Surface Scientist’s Toolkit

As the name implies, surface scientists are interested in what is happening at the surfaces of materials. Interests range from fundamental inquiries, such as structural and electronic composition [125], to technological applications, such as building molecular catalysts on light-active surfaces [126]. There are many tools at the disposal of the modern experimental surface scientist, each with its own strengths and weaknesses. By using a combination of these tools, it is possible to gain great insights into the properties of surfaces and thin films, opening up new avenues of research and supporting the ever-present push to miniaturize devices.

LEED (Low Energy Electron Diffraction) and RHEED (Reflection High Energy Electron Diffraction) are electron diffraction techniques useful in the monitoring of thin film growth and the determination of crystallinity. RHEED especially allows for sub-monolayer thickness monitoring of MBE (Molecular Beam Epitaxy) grown thin films.

AES (Auger Electron Spectroscopy) is an excellent probe for determining the species of atoms on a surface. An incident electron is used to knock out a core electron, leaving behind a core hole. With this being an unstable configuration, an outer shell electron can fall into this hole. If that outer shell electron’s transition energy is sufficiently coupled to another outer shell electron, then the second electron can be ejected if the transition energy imparted is greater than its binding energy. Because this is a fairly complex process involving core states, each atom tends to have a distinct AES fingerprint. Additionally, since the energy of the ejected electrons is generally in the range of eV to a few keV, their mean free path in the material is short and thus the majority of the electrons which escape the materials and are detected originate from the surface [98].

In determining the nature of occupied states at the surface of a material, photoemission spectroscopies are excellent tools. In each of these techniques, an incident photon is used to eject one or more electrons from the surface of a material. The information that can be gained from doing this depends not only on the angle and energy of the incident photon,
but also on the method of analysis. Non angle-resolved techniques such as XPS (X-ray Photoemission Spectroscopy) and UPS (Ultraviolet Photoemission Spectroscopy) collect the ejected electrons in an integrated way, without keeping track of which direction they arrive from. This provides information on the energy of the occupied states. By using a detector which can differentiate electrons coming from different angles, such as in ARPES (Angle Resolved Photoemission Spectroscopy), reciprocal space information about the occupied states can also be obtained. This makes ARPES a very powerful technique for studying the valence band structure of materials. However, regular photoemission cannot, in general, give information on the unoccupied states of materials, and so is not a great tool to study the conduction bands of materials.

Figure 2.1: Electronic structure of monolayer MoSe$_2$ obtained with ARPES. Both the MoSe$_2$ and the underlying bilayer graphene substrate bands are visible [125].

For real space imaging at the nanoscale, there are various microscopy techniques such as TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy), and their variants (Scanning TEM for instance). The most advanced TEMs are capable of imaging atomic lattices and other structures at the atomic scale. In addition, when combined with spectroscopic techniques like EELS (Electron Energy Loss Spectroscopy), they can determine the species of individual atoms. There are two main drawbacks to TEMs however: first, they use relatively high energy electrons (up to 100s of keV) [133] which can be damaging to some materials; second, they require thin samples, because the electrons must be transmitted through the material. [133] SEM, on the other hand, can be used with significantly lower electron energy and, since the electrons need not penetrate through the sample, can image thick samples. Currently, the best resolution obtained with a state-of-
the-art commercial SEM is about 1 nm.

Local probe techniques such as STM (Scanning Tunneling Microscopy) and AFM (Atomic Force Microscopy) provide information where many other probes fail. STM is sensitive to the local electronic structure of surfaces and, when combined with spectroscopic techniques such as STS (Scanning Tunneling Spectroscopy), can provide a wealth of information on both the occupied and the unoccupied electronic states of a material. Similarly, AFM provides details on the chemical and mechanical properties (e.g. the stiffness of bonds) of surfaces on a local scale. These probes are, in general, real space probes which provide little in the form of reciprocal space information. That being said, there are some ways to obtain reciprocal space structure from STM for some systems [115, 44]. In general, these probes are sensitive to what is happening right near the apex of an extremely sharp tip. In the case of STM, the tunnel current that is measured decays exponentially with increasing distance from the tip apex.

As we dive deeper into the world of the nanoscale and continue our incessant march toward miniaturizing electronic devices, it becomes increasingly important to understand the properties of materials at the atomic scale. This is where STM and other local probe techniques fit into the bigger picture.

### 2.2 STM - Working Principles

A scanning tunneling microscope operates by moving a sharp, metal tip close to a conducting or semiconducting surface. If the tip is close enough (usually on the order of a few Å), electrons can quantum mechanically tunnel between the tip and the surface. The rate of tunneling of these electrons is exponentially dependent on the distance between the tip and the surface, and also depends on the electronic structure of both.

To harness the power of the STM, a raster scanning mechanism is used. This allows the tip to be moved back and forth across the surface. All the while a computer system measures the tunnel current. This information is used to create an STM image, where the pixel color map encodes the tunnel current and the pixel location encodes the physical (x,y) location on the surface. If the height of the tip isn’t changing during acquisition of the image, we call this a constant-height image. The more common acquisition method is constant-current. In this scheme, we use a feedback loop to maintain a constant tunnel current as we scan the tip back and forth. We produce images in exactly the same way, except that the color map now encodes how much the tip had to move vertically (i.e. perpendicular to the surface) to maintain the desired tunnel current.

There are trade-offs to operating a microscope in constant-height vs constant-current mode. Constant-height images are often simpler to interpret, as the tip isn’t moving up and down. Changes in the tunnel current can be attributed to either corrugations of the surface or local changes in the surface electronic structure. This mode is, however, quite difficult to perform experimentally. Since the tunnel current is exponentially dependent on the tip-sample separation, this distance must be maintained to high precision (better than 1 part in
Figure 2.2: Schematic diagram of the STM technique. Electrons are shown flowing from the tip to the sample, which would be the case with positive sample bias. As the tip is moved laterally along the surface at constant height, the measured current oscillates with the atomic position, reflecting the empty electronic states distribution on the atoms. The scan consists of a series of such lines at different positions in the orthogonal direction, to produce a contour map of the surface. Reproduced from [13].

100 over the course of several minutes). External vibrations and thermal drift, in particular, make this a difficult task. On top of this, the surface must be very flat. If there is a large protrusion, the tip will run into it. If there is something like a downward step edge, the tip will be substantially further from the lower terrace than the upper one, severely limiting resolution. Constant-current mode helps with all of these issues. By having a feedback loop maintaining the tunnel current, the system is less sensitive to thermal drift perpendicular to the surface (it’s still a problem, but can often be treated in image processing), less sensitive to vibrations, and able to dynamically change the tip height when going over large protrusions or step edges. However, constant-current images are often more difficult to interpret. Instead of just having surface corrugations and electronic structure changes to worry about, the tip is also moving up and down. One thing to be careful of when working in constant-current mode is to ensure that you are scanning slowly enough that the feedback loop can respond to perturbations. If you scan quickly with a slow feedback loop, the interpretation gets even more dicey (not to mention you might run your tip into something).

2.3 Theory

To interpret STM data, we need a theoretical framework. There are two common approaches for this: the Bardeen formalism, and the Tersoff-Hamman approximation. We will start with the Bardeen formalism.
2.3.1 Bardeen Tunneling

Published in 1961, Bardeen’s tunneling formalism \[4\] forms the basis for many of the modern theories of tunneling in STM. The predictions from Bardeen’s theory are generally applicable when the tip-sample distance is sufficiently large, and the bias voltage applied between them is sufficiently small.

One of the best discussions of Bardeen’s tunneling theory as applied to STM is given by Alex Goettlieb and Lisa Wesoloski \[43\]. The following is based on their work. Bardeen’s approach was to separate the tip and sample into separate systems, with a mathematical separation surface in between. With knowledge of the electronic states, one can solve the Schrödinger equation in each separate region and then apply first order time dependent perturbation theory to estimate the rate of electron transfer (i.e. the tunnel current) between the two regions. There are five main assumptions which go into the theory:

1. Electron-electron interactions can be ignored
2. The occupations of tip and sample states are independent of one another and do not change, even though there may be a tunnel current
3. Tip and sample are both in electrochemical equilibrium
4. The tunneling process is weak enough to justify first order perturbation theory
5. Tip and sample states are essentially orthogonal

Using assumption 1, we can write down the single-particle Hamiltonian that the electrons must obey:

\[
H \psi (r) = -\frac{\hbar^2}{2m} \nabla^2 \psi (r) + V(r) \psi (r) \tag{2.1}
\]

Even if we treat each electron as independent with this single particle Hamiltonian, the eigenfunctions and eigenvalues of the associated Schrödinger’s Equation can still be difficult to determine \[21\]. For this reason, Bardeen separated the system into two distinct regions - the tip and the sample - with two distinct Hamiltonians:

\[
H_{\text{tip}} \psi (r) = -\frac{\hbar^2}{2m} \nabla^2 \psi (r) + V_{\text{tip}}(r) \psi (r) \tag{2.2}
\]

\[
H_{\text{sample}} \psi (r) = -\frac{\hbar^2}{2m} \nabla^2 \psi (r) + V_{\text{sample}}(r) \psi (r) \tag{2.3}
\]

where the subscripts \textit{tip} and \textit{sample} refer, as expected, to the tip and sample regions, respectively. The potential \( V_{\text{tip}}(r) \) is defined as

\[
V_{\text{tip}}(r) = \begin{cases} 
V(r) & \text{if } r \text{ is inside the tip region} \\
0 & \text{otheriwse} 
\end{cases} \tag{2.4}
\]
and similarly for $V_{\text{sample}}(\mathbf{r})$:

$$V_{\text{sample}}(\mathbf{r}) = \begin{cases} V(\mathbf{r}) & \text{if } \mathbf{r} \text{ is inside the sample region} \\ 0 & \text{otherwise} \end{cases}$$ (2.5)

In this setup, the tunnel current that we are interested in is the transfer of electrons from the states in the tip region to or from those in the sample region. We assume that the density of states (DOS) in the tip is given by $\rho_{\text{tip}}(E_n)$ and the DOS of the sample by $\rho_{\text{sample}}(E_n)$. The occupation of both the tip and the sample are dictated by Fermi Dirac statistics. Namely:

$$F_{\mu,T}(E) = \frac{1}{e^{E-\mu/k_BT} + 1}$$ (2.6)

where $\mu$ is the chemical potential, $T$ is the temperature, and $E$ is the energy. Using Fermi’s Golden Rule, it can be shown \[43\] that the rate of tunneling from an occupied sample state into a tip state is

$$\frac{2\pi}{\hbar} (1 - F_{\mu_{\text{tip}},T}(E)) \rho_{\text{tip}}(E) M^2(\psi_{\text{sample}})$$ (2.7)

where

$$M^2(\psi) = \frac{1}{N_E} \sum_{k:|E_k - E| < 2\hbar/t} |\langle \phi_k | H - H_{\text{sample}} | \psi \rangle|^2$$ (2.8)

is the square amplitude of a scattering matrix element connecting the sample and tip states, $N_E$ is the number of tip states in the energy range $E - 2\hbar/t$ to $E + 2\hbar/t$. The Fermi function dependence in the scattering rate makes intuitive sense: in order for an electron to scatter into a tip state, the tip state must be unoccupied. If $F_{\mu_{\text{tip}},T}(E)\rho_{\text{tip}}(E)$ gives the occupation of tip states, then $(1 - F_{\mu_{\text{tip}},T}(E))\rho_{\text{tip}}(E)$ gives the empty states. Equation \[2.7\] also gives the rate of electrons tunneling out of occupied tip states and into unoccupied sample states. Assuming that electrons can tunnel out of occupied tip states into unoccupied sample states and out of occupied sample states into unoccupied tip states, the tunnel current can be written as a sum over all of these possible processes:

$$I = \frac{2\pi e}{\hbar} \sum_{n} \left( F_{\mu_{\text{tip}},T}(E_n) (1 - F_{\mu_{\text{sample}},T}(E_n)) - (1 - F_{\mu_{\text{tip}},T}(E_n)) F_{\mu_{\text{sample}},T}(E_n) \right) \rho_{\text{tip}}(E_n) M^2(\psi_n)$$ (2.9)

At zero temperature, the Fermi Dirac function becomes a Heaviside step function. If we approximate the sum in equation \[2.9\] with an integral, the zero temperature tunnel current reduces to

$$I = \pm \frac{2\pi e}{\hbar} \int_{\mu_{\text{tip}}}^{\mu_{\text{sample}}} \rho_{\text{tip}}(E)T(E)\rho_{\text{sample}}(E)dE$$ (2.10)
where $T(E)$ is the mean of $M^2(\psi_n)$ over all sample states whose energy lies in a small interval centered on $E$. The sign of the tunnel current depends on whether $\mu_{\text{tip}} > \mu_{\text{sample}}$ or $\mu_{\text{tip}} < \mu_{\text{sample}}$.

If we are at low bias and low temperature, we can simplify the previous equation because $\rho_{\text{tip}}(E)$ and $\rho_{\text{sample}}(E)$ are both nearly constant for $\mu_{\text{tip}} < E < \mu_{\text{sample}}$ (or $\mu_{\text{sample}} < E < \mu_{\text{tip}}$ if the tip has higher chemical potential). We can also use the fact that $\rho_{\text{sample}}(E)$ is nearly constant to reduce $T(E)$ to

$$T(E) = \frac{1}{(\mu_{\text{tip}} - \mu_{\text{sample}})\rho_{\text{sample}}(E)} \sum_{\psi_n: \mu_{\text{tip}} < E_n < \mu_{\text{sample}}} M^2(\psi_n)$$

(2.11)

which allows us to write the tunnel current as

$$I = \pm \frac{2\pi e}{\hbar} \rho_{\text{tip}}(E) \sum_{\psi_n: \mu_{\text{tip}} < E_n < \mu_{\text{sample}}} M^2(\psi_n)$$

(2.12)

The main challenge now is to approximate the tunneling matrix elements $M(\psi_n)$. Noting that the operator $H - H_{\text{tip}}$ is the zero operator on the tip side of the separation surface:

$$0 = \langle \phi_j | H - H_{\text{tip}} | \psi_n \rangle$$

$$= \int_T \psi_n(\mathbf{r})(H - H_{\text{tip}})\phi_j^\dagger(\mathbf{r})d\mathbf{r}$$

$$= \int_T \psi_n(\mathbf{r})H\phi_j^\dagger(\mathbf{r})d\mathbf{r} - E_j \int_T \psi_n(\mathbf{r})\phi_j^\dagger(\mathbf{r})$$

$$= -\frac{\hbar^2}{2m} \int_T \psi_n(\mathbf{r})\nabla^2 \phi_j^\dagger(\mathbf{r})d\mathbf{r} + \int_T \psi_n(\mathbf{r})V(\mathbf{r})\phi_j^\dagger(\mathbf{r})d\mathbf{r} - E_j \int_T \psi_n(\mathbf{r})\phi_j^\dagger(\mathbf{r})d\mathbf{r}$$

(2.13)

where the integrals are all volume integrals over the tip region. We have used the notation $\phi_k$ to denote the kth component of the tip wavefunction which satisfies the time independent Schrödinger equation

$$H_{\text{tip}}\phi_k = E_k \phi_k$$

(2.14)

Evaluating $H - H_{\text{sample}}$ in the tip region gives

$$\langle \phi_j | H - H_{\text{sample}} | \psi_n \rangle = \int_T \phi_j^\dagger(\mathbf{r})(H - H_{\text{sample}})\psi_n(\mathbf{r})d\mathbf{r}$$

$$= \int_T \phi_j^\dagger(\mathbf{r})H\psi_n(\mathbf{r})d\mathbf{r} - E_n \int_T \phi_j^\dagger(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r}$$

$$= -\frac{\hbar^2}{2m} \int_T \phi_j^\dagger(\mathbf{r})\nabla^2 \psi_n(\mathbf{r})d\mathbf{r} + \int_T \phi_j^\dagger(\mathbf{r})V(\mathbf{r})\psi_n(\mathbf{r})d\mathbf{r} - E_n \int_T \phi_j^\dagger\psi_n(\mathbf{r})d\mathbf{r}$$

(2.15)
Subtracting 2.13 from 2.15:

\[
\langle \phi_j | H - H_{\text{sample}} | \psi_n \rangle = \int \phi_j^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \psi_n(r) - E_n \psi_n(r) \right) dr \\
- \int \psi_n(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \phi_j^* - E_j \phi_j^* \right) dr
\]

(2.16)

By considering only matrix elements where \(E_n\) and \(E_j\) are approximately equal (the so-called elastic tunneling regime) and applying the divergence theorem we find

\[
\langle \phi_j | H - H_{\text{sample}} | \psi_n \rangle \approx -\frac{\hbar^2}{2m} \int_{dT} \left[ \psi_n^*(r) \nabla \psi_j(r) - \phi_j(r) \nabla \psi_n^*(r) \right] \cdot d\mathbf{n}
\]

(2.17)

where \(dT\) is a surface element of the separation surface and \(\mathbf{n}\) is the normal vector to that surface.

### 2.3.2 Tersoff-Hamman Approximation

In 1983, J. Tersoff and D.R. Hamman applied Bardeen’s result (eq. 2.17) to the STM \[121\]. One assumption they made was that they assumed the tip wavefunctions to be radially symmetric (see Fig. 2.3). Using this approximation leads to an important idea (one that we still use today when explaining LDOS): the tunnel current is directly proportional to the sample electron density at the center of the tip. This means that the tip wavefunctions must be of the form

\[
\Phi_j(r) = A_j e^{-\kappa_j r / r}
\]

(2.18)

where

\[
\kappa_j = \sqrt{2m |E_j|} / \hbar
\]

(2.19)

so that \(\Phi_j(r)\) satisfies the time independent Schrödinger’s equation for \(r > R\) (ie points outside of the tip itself). C.J. Chen showed \[20\] that \(\Phi_j(r)\) must also satisfy

\[
-\frac{\hbar^2}{2m} \nabla^2 \Phi_j(r) - E_j \Phi_j(r) = \frac{\hbar^2}{2m} 4\pi \delta_0(r)
\]

(2.20)

We can use 2.16 to compute \(\langle \phi_j | H - H_{\text{sample}} | \psi_n \rangle\) in the tip region, finding that

\[
\langle \phi_j | H - H_{\text{sample}} | \psi_n \rangle = -\frac{\hbar^2}{m} A_j \psi_n(0)
\]

(2.21)

where \(\phi_j\) is approximated by \(A_j \Phi_j(r)\) in the sample region. This results in the squared matrix element

\[
M^2(\psi_n) = \left( \frac{\hbar^2}{m} \right)^2 A_j^2 |\psi_n(0)|^2
\]

(2.22)
where $A^2$ is the average of $|A_j|^2$ over all $j$ such that $\phi_j$ is a state with energy in a small window around $E_n$. Taking the low bias limit (it’s important to note that this is a low bias limit):

$$I = \pm \frac{2\pi e}{\hbar} \rho_{\text{tip}}(\mu) \left( \frac{\hbar^2}{m} \right)^2 A^2 \sum_{\psi_n: \mu_a < E_n < \mu_b} |\psi_n(0)|^2$$

$$= (\mu_t - \mu_s) \frac{e \hbar^3}{m^2} A^2 \rho_{\text{tip}}(\mu) \rho_s(0, \mu)$$

where

$$\rho_s(\mathbf{r}, \mu) = \frac{1}{|\mu_s - \mu_t|} \sum_{\psi_n: \mu_a < E_n < \mu_b} |\psi_n(\mathbf{r})|^2$$

is the Local Density of (sample) States - LDOS - per unit volume per unit energy at the point $\mathbf{r}$ and chemical potential $\mu$. This is where the idea that the tunnel current is proportional to the sample electron density at the center of the tip comes from.
2.4 Scanning Tunneling Spectroscopy

Armed with the Bardeen formalism and the Tersoff-Hamman approximation, we can move beyond the fuzzy realm of topography and into the quantitative world of spectroscopy. There are different types of spectroscopy which allow for exploration of different features. \(dI/dV\) spectroscopy, for instance, helps us probe the LDOS of a sample, while \(dI/dZ\) spectroscopy can help in the determination of image states. These spectroscopic techniques provide local, energy-resolved information which can be difficult or impossible to achieve otherwise. We will discuss \(dI/dV\) spectroscopy in detail.

2.4.1 What is \(dI/dV\)?

The most common spectroscopic technique used by scanning tunneling microscopists is \(dI/dV\) spectroscopy, often referred to as scanning tunneling spectroscopy (STS). In STS, the tip is held a fixed distance from the surface (initially set by holding a constant tunnel current at a predetermined bias voltage, then turning off the feedback) and the bias voltage \(V\) is slowly changed. The current can be measured as a function of \(V\), and then numerically differentiated to give the scanning tunneling conductance, \(dI/dV\). This quantity is related to the LDOS through the theories discussed previously.

While this is the conceptually simplest way to obtain the \(dI/dV\) signal, it is generally not the one used. Instead of measuring \(I\) vs \(V\), and then numerically differentiating to get \(dI/dV\), we usually use a lockin amplifier. This has many advantages, including:

1. Reduced 1/f noise
2. Does not require complete spectral purity (i.e. can be used in the presence of noise)
3. Does not require numerical differentiation

For these reasons, we usually use the lockin technique to perform our spectroscopic measurements. There have been times, however, when we have opted to perform STS measurements using the numerically differentiated \(I - V\) curve. This usually happens when the system is in a low-noise state and we need to obtain data quickly (like when the tip is drifting). We can record \(I - V\) curves in milliseconds, while using the lockin to obtain a \(dI/dV\) curve takes upwards of 1 minute or more.

One method of signal recovery employed by lockin amplifiers is to apply a sine wave \(\sin(\omega_0 t)\) on top of a signal, integrate this signal over one period, and recover the signal at \(\omega_0\). To illuminate this mathematically, let \(f(t)\) be the signal we are interested in. By Fourier decomposition:

\[
f(t) = \frac{B_0}{2} + \sum_{n=1}^{\infty} A_n \sin(n\omega_0 t) + B_n \cos(n\omega_0 t)
\]

(2.25)
where \( \omega_0 = \frac{2\pi}{T} \). Multiplying this by \( \sin(m\omega_0 t) \) or \( \cos(m\omega_0 t) \) and integrating over one period \( (t_0 \rightarrow t_0 + \frac{2\pi}{\omega_0}) \) gives

\[
A_n = \frac{\omega_0}{\pi} \int_{t_0}^{t_0 + \frac{2\pi}{\omega_0}} f(t)\sin(m\omega_0 t)dt \tag{2.26}
\]

\[
B_n = \frac{\omega_0}{\pi} \int_{t_0}^{t_0 + \frac{2\pi}{\omega_0}} f(t)\cos(m\omega_0 t)dt \tag{2.27}
\]

where \( m \) is an integer. Instead of multiplying by \( \sin(\omega_0 t) \), a lockin multiplies the signal by \( \sin(n\omega_{\text{ref}} t + \phi) \), integrates over one period, and multiplies the result by \( \omega_0 \sqrt{2\pi} \):

\[
V_{\text{lockin}} = \frac{\omega_0}{\sqrt{2\pi}} \int_{t_0}^{t_0 + \frac{2\pi}{\omega_0}} f(t)\sin(n\omega_{\text{ref}} t + \phi)dt \tag{2.28}
\]

If we set \( \omega_{\text{ref}} = \omega_0 \) and \( \phi_0 = 0 \), then

\[
V_{\text{lockin}} = \frac{A_n}{\sqrt{2}} \tag{2.29}
\]

In other words, the lockin measures the Fourier component of the signal, at the frequency of the lockin’s “wiggle voltage”. In STS, we are not interested in the entire I(V) signal, but rather just the resistive part. There is a large capacitive component to the signal that occurs just because we have a metal tip near a conducting surface. This capacitive signal is 90° out of phase with the resistive signal. To capture this, we tune \( \phi \) so that, with the tip out of tunneling (usually pulled back 1 nm), all of the signal is in one of the two lockin channels, either X or Y. We then know that the resistive signal is in the other channel. This gives us

\[
V_X = \frac{\omega_0}{2\pi} \int_{t_0}^{t_0 + \frac{2\pi}{\omega_0}} f(t)\sin(n\omega_{\text{ref}} t + \phi_n)dt \tag{2.30}
\]

\[
V_Y = \frac{\omega_0}{2\pi} \int_{t_0}^{t_0 + \frac{2\pi}{\omega_0}} f(t)\cos(n\omega_{\text{ref}} t + \phi_n)dt \tag{2.31}
\]

where \( \phi = \phi_n \) for \( V_X \) and \( \phi = \phi_n + \pi/2 \) for \( V_Y \). Putting together \( \ref{2.30} \), \( \ref{2.31} \) and \( \ref{2.25} \):

\[
V_X = \frac{1}{\sqrt{2}} (B_n\sin(\phi_n) + A_n\cos(\phi_n)) \tag{2.32}
\]

\[
V_Y = \frac{1}{\sqrt{2}} (B_n\cos(\phi_n) - A_n\sin(\phi_n)) \tag{2.33}
\]
If $\phi_n = 0$ (as it usually is for the Toucan STM):

$$V_X = \frac{A_n}{\sqrt{2}} \quad (2.34)$$

$$V_Y = \frac{B_n}{\sqrt{2}} \quad (2.35)$$

If $\phi_n = \pi/2$ (as it usually is for the Beast STM):

$$V_X = \frac{B_n}{\sqrt{2}} \quad (2.36)$$

$$V_Y = -\frac{A_n}{\sqrt{2}} \quad (2.37)$$

A real lockin doesn’t work exactly as described above. Instead of performing a one period integration, a real lockin passes the signal through a low pass filter, which serves as a good approximation to the integration. This can be seen by writing the combined signal in a Fourier series, with the summation index running from $-\infty$ to $+\infty$:

$$f(t)\sin(n\omega_0 t + \phi_n) = \frac{1}{2} \sum_{m=-\infty}^{\infty} B_{n-m}\sin(m\omega_0 t + \phi_n) + A_{n-m}\cos(m\omega_0 t + \phi_n) \quad (2.38)$$

where $A_{-m} = -A_m$ and $B_{-m} = B_m$. Then

$$f(t)\sin(n\omega_0 t + \phi_n) = \frac{1}{2} [B_n\sin(\phi_n) + A_n\cos(\phi_n)]$$

$$+ \frac{1}{2} \sum_{m=-\infty, m \neq 0}^{\infty} B_{n-m}\sin(m\omega_0 t + \phi_n) + A_{n-m}\cos(m\omega_0 t + \phi_n) \quad (2.39)$$

The first term, in square brackets, is the DC component of the signal. This is what makes it through the low pass filter, along with a few non-idealities. The actual output looks like

$$\frac{1}{2} [B_n\sin(\phi_n) + A_n\cos(\phi_n)]$$

$$+ \frac{1}{2} \sum_{m=-\infty, m \neq 0}^{\infty} G(|\omega_0 m|, \omega_c) [B_{n-m}\sin(m\omega_0 t + \phi_n) + A_{n-m}\cos(m\omega_0 t + \phi_n)] \quad (2.40)$$

where $G$ is the transmission function of the low pass filter. The lockin multiplies this output
by $2/\sqrt{2}$ so that

$$V_X = \frac{1}{\sqrt{2}} [B_n \sin(\phi_n) + A_n \cos(\phi_n)]$$

$$+ \frac{1}{\sqrt{2}} \sum_{m=-\infty, m \neq 0}^{\infty} G(|\omega_0 m|, \omega_c) [B_{n-m} \sin(m \omega_0 t + \phi_n) + A_{n-m} \cos(m \omega_0 t + \phi_n)]$$

(2.41)

As is often used in Toucan’s lockin, a second-order butterworth filter has a 12 dB/octave slope with

$$G(\omega, \omega_c) = \frac{1}{\sqrt{1 + (\frac{\omega}{\omega_c})^4}}$$

(2.42)

where $\omega_c$ is the cutoff frequency of the filter. We typically set

$$\omega_c = \frac{\omega_0}{10}$$

(2.43)

which is usually a nice balance between signal and noise. Every term in eq. 2.41 with $m \geq 1$ falls off by at least $10^2$, so to a good approximation

$$V_X \approx \frac{1}{\sqrt{2}} (B_n \sin(\phi_n) + A_n \cos(\phi_n))$$

$$V_Y \approx \frac{1}{\sqrt{2}} (B_n \cos(\phi_n) - A_n \sin(\phi_n))$$

(2.44)

At this point it is also good to note that the lockin technique is very useful in noisy environments, but you must be careful with the spectral distribution of the noise. If there is noise present at frequency $\gamma$, then this noise will **not** be filtered if

$$|\omega_0 - \gamma| \leq \omega_c$$

(2.45)

This means that, when choosing the frequency of your oscillation, look at the frequency distribution of your noise first. Use an oscilloscope with FFT or, better yet, a low frequency spectrum analyzer and choose a frequency that does not overlap with significant sources of noise. You should also be careful to keep the frequency of the wiggle voltage well below the cutoff frequency of the preamplifier. At a gain of $10^9$, the femto preamp has a bandwidth of 1 kHz. To ensure that your signal is not being clipped by the preamp, try to keep the wiggle voltage below 800 Hz, and certainly below 900 Hz. These values will be different at different preamp gain settings.

The final piece left in the lockin puzzle is to write out the equations specifically for STS using the Ametek lockin that is connected to Toucan. The wiggle voltage that we apply is

$$\Delta V = \delta V \sin(\omega_0 t)$$

(2.46)
Let $G$ be the gain of the preamp (usually $G = 10^{-9} \text{ A/V}$). Then, after applying the wiggle voltage to the tip-sample junction, the voltage output of the preamp is

$$f(t) = \frac{I(V + \Delta V)}{G} \quad (2.47)$$

The lockin measures the Fourier components of this signal. We expand $I(V + \Delta V)$ in a Fourier Series:

$$I(V + \Delta V) \approx I(V) + \frac{dI}{dV} \Delta V$$

$$= I(V) + \frac{dI}{dV} \delta V \sin(\omega_0 t) \quad (2.48)$$

If the lockin is phased correctly (you did remember to autophase the lockin with the tip withdrawn, right?):

$$\frac{dI}{dV} \delta V = A_n \approx \sqrt{2} V_X \quad (2.49)$$

Which gives us

$$V_X = \frac{dI}{dV} \delta V \frac{\sqrt{2}}{\sqrt{2}} \quad (2.50)$$

To get this into physical units, we need to scale it by $G$:

$$V_X = \frac{\delta V_{RMS}}{G} \frac{dI}{dV} \quad (2.51)$$

The analog output of the lockin is then scaled by the sensitivity and a factor which is specific to each lockin (look this up before you blindly use the following equation):

$$\frac{dI}{dV} = \frac{G}{\delta V_{RMS}} \frac{\text{sens}}{2.5V} \cdot V_{out,1}[\Omega^{-1}] \quad (2.52)$$

where $V_{out,1}$ is the actual voltage signal reported by the Nanonis software.
Part II

Toucan
When I first started working with Toucan, this homemade STM had recently been used to study nanobubbles in graphene on Pt(111). Unfortunately, the system was on the verge of collapse. To complicate matters, when Sarah Burke and Niv Levy departed, they had minimal overlap with their successor graduate student, Chuck Sleasman. I, coming in some months later in Fall of 2010, had about one year of overlap with Chuck before he left. Needless to say, there was a lack of knowledge transfer from the system designer to me. Working often times alone during the first couple of years, and then with Miguel Ugeda during the last few years, we managed to revive Toucan and turn it into one of the lowest-noise instruments in the world. This chapter is a reflection on what we did (and often what we didn’t do) to bring the system up to code and cement its position as a world-class STM.

Niv Levy’s original design for Toucan was based on three primary principles: (1) create an extremely low-noise STM which (2) has independent x, y, and z coarse motion, and (3) has the capability of shining light into, or collecting light from, the tip-sample junction. In most of the modifications that we made, we attempted to maintain this philosophy. The one glaring exception to that is the optical access - at the time of this writing, Toucan’s optical access has been covered to enhance the stability and performance of the system. Other than that, we have tried to keep the system as low noise as possible, both in terms of electrical and mechanical noise, and to maintain independent x, y, and z coarse motion.

One note that I would like to make here is that many, if not most, of the modifications we made were due to a poorly built cryostat from Cryovac. The nitrogen cryostat is not circular in cross section, and the helium cryostat must hang at an angle so as to avoid touching the nitrogen cryo around it. If it weren’t for these absurd issues, the STM very likely would have been operating well when I joined the group. Thus most of what I will write in this chapter should not be taken as a critique of the original design, but rather a series of hacks to work around the abysmal cryostat which adorns the chamber.
3.1 Radiation Shields

3.1.1 LN\textsubscript{2} Shield

One of the first things to be redesigned on Toucan was the liquid nitrogen (LN\textsubscript{2}) shield assembly. In the original design, the 4K-plate wire anchors were quite close to the inner surface of the LN\textsubscript{2} cryostat. By requiring that the two cryostats didn’t touch up near the neck, we couldn’t find a reproducible position for the He cryostat to hang at so as to avoid having the 4K wire anchors touching the LN\textsubscript{2} cryostat walls. To address this concern, we redesigned the LN\textsubscript{2} shield assembly so that it bulged out around the 4K plate, giving ample space to the wire anchors.

There were advantages and disadvantages to this design. The advantages included having more space for the wire anchors and making it safer to lift the cryostat assembly from the chamber. The disadvantages included having less of a feel when the cryostats were touching (it was fairly easy to tell before when the wire anchors were touching the LN\textsubscript{2} shield), having an excessively overweight LN\textsubscript{2} shield, and making it difficult to fully remove the LN\textsubscript{2} shield assembly. The last of these problems can be solved by the judicious use of patience and a long phillips head screwdriver.
3.1. RADIATION SHIELDS

Figure 3.2: New LN$_2$ radiation shield assembly. The 4K wire anchors go into the bulge in the shield, allowing them significantly more lateral freedom.

3.1.2 Kapton Tape Under Doors

Another simple but important modification made to both the LN$_2$ and the LHe shields was to put a strip of Kapton tape under the sliding doors. We also put a strip of tape on the back side of some of the doors themselves. This allows the doors to move more smoothly. Previously, we had been moving the sliding doors directly against the shield surfaces. This worked well for a time, but the gold plating eventually ran through and the surfaces became quite rough. After finding that Kapton tape sticks to the shields even at 4K, we decided to give it a go. This was one of the more successful changes to the system.
3.2 Wiring

3.2.1 Cryostat Wires

Originally, Toucan was outfitted with coaxial cables to bring signals down from the top of the cryostat to the 4K stage. These coaxial cables had an outer shield of teflon, making them difficult to heat sink. In fact, we could never lower the temperature of the head below \( \sim 7 \text{K} \) with them. As part of our efforts to reduce the heat load at the cold plate, we replaced these wires with stainless steel twisted pairs, with an uninsulated stainless steel outer mesh (Cooner wire AS 631-2SS). These are 40AWG stranded inner conductors with an overall outer diameter of 0.028” (see fig. 3.3). There are 18 of them. We started with an initial length of 2.5m each, then shortened them as needed after running them down the cryostat.

The outer stainless steel shield of the wires is heat-sunk to the outside of the LHe cryostat using thin strips of tantalum foil - a trick learned from the Omicron technician while he was rewiring the Beast - as shown in fig. 3.4. The foil is spot welded to the cryostat using a modified spot welding attachment, which allows for clipping one electrode to a piece of metal on the system (anything electrically connected to the surface of the cryostat will do) with an alligator clip and the other electrode is used to make the spot weld. Since the outer shield on these wires is exposed stainless steel, this significantly reduces the heat load carried to the cold plate.

![Cross-section sketch of cryostat wires. The outer stainless steel sheath is 0.028” in diameter, the inner conductor with its teflon insulation is \( \sim 0.03” \) in diameter, and the inner conductors themselves are 0.011” in diameter.](image)

Figure 3.3: Cross-section sketch of cryostat wires. The outer stainless steel sheath is 0.028” in diameter, the inner conductor with its teflon insulation is \( \sim 0.03” \) in diameter, and the inner conductors themselves are 0.011” in diameter.
You can estimate the heat load that these wires place on the cold plate using the dimensions given in figure 3.3 and the following assumptions:

1. Wire sheaths are thermalized after 50cm of contact with the LHe cryostat
2. Inner conductors are thermalized after the full 2.5m length
3. The teflon thickness on the wires is $\sim$0.010" thick

The heat load on the cold plate through conduction is found by:

$$\dot{q}_c = \frac{A}{L} \int_{T_1}^{T_2} \lambda(T) dT$$

where $A$ is the area of the conducting object, $L$ is its length, $\lambda(T)$ is the temperature-dependent thermal conductivity, and $T_1$ and $T_2$ are the temperatures of the ends of the
3.2. WIRING

We can rewrite this as:

\[ \dot{q}_c = \frac{A}{L} \bar{\lambda} \Delta T \]  

(3.2)

where

\[ \bar{\lambda} = \Delta T^{-1} \int_{T_1}^{T_2} \lambda(T) dT \]  

(3.3)

is the mean thermal conductivity. The reason to define it this way is that we can find the mean thermal conductivity for steel between 4K and 300K, \( \bar{\lambda}_{ss} = 3.06 \text{ kW/m} \cdot \text{K} \) [34]. Armed with this information, we can calculate the heat load on the cold plate for each wire sheath as

\[ \dot{q}_c = \frac{2.23 \times 10^{-5} m^2}{0.050 m} \cdot 3.06 \times 10^3 \text{ W/m} \cdot \frac{1}{300K - 4K} = 4.62 \times 10^{-4} \text{ W} \]  

(3.4)

and for each inner conductor as

\[ \dot{q}_c = \frac{2.41 \times 10^{-6} m^2}{2.5 m} \cdot 3.06 \times 10^3 \text{ W/m} \cdot \frac{1}{300K - 4K} = 9.98 \times 10^{-6} \text{ W} \]  

(3.5)

With 18 total twisted pairs, that’s a heat load of 8.7mW

At the cold plate, the inner conductors of the twisted pairs are soldered to gold pins using UHV solder, which is a 96%/4% Sn/Ag eutectic mixture. These gold pins mate with corresponding partners which are mounted to alumina plates on the cold plate, as shown in figure 3.5. The pins on the cryostat wires and those mounted to the alumina plates are designed to be held together by friction. To make sure that these did not become disconnected, a small amount of Epotek H20E conducting epoxy was applied. The pins mounted on the alumina plates are glued in using Epotek H74f nonconducting epoxy. This epoxy was chosen because of its good thermal properties at low temperature. The wire anchors are intended to not only hold the cryostat wires in place, but also to thermalize the inner conductors at 4K.

As can be seen in figure 3.5, the solder did not always form perfect joints with the wires. This is because the wires are stainless steel (a notoriously difficult metal to solder) and the flux is UHV compatible, so it doesn’t contain acids which will corrode the wires in the future. Due to the presence of possible cold solder joints, this should be a point of scrutiny in the future if any wires appear to be disconnected somewhere in the system. Wherever possible, the solder was augmented with Epotek H20E conductive epoxy.

3.2.2 Wiring Diagrams and Pinouts

Details on the feedthroughs can be found in Niv Levy’s thesis, ref. [71]. The pinouts of the feedthroughs is shown in fig. 3.6. Fig. 3.7 shows the wire connections on the 4K cold plate. The wires are electrically isolated from the cryostat / cold plate using alumina blocks, but they are thermally connected through the same alumina. This is important to be able to achieve a low temperature at the STM head. The word “Front” denotes the front of the STM (i.e. where the sample is inserted). This should be fairly obvious when looking at the
3.2. WIRING

Figure 3.5: The new wire anchors at the cold plate. The wires from the cryostat are soldered into gold pins which mate with pins glued into the white alumina piece using Epotek H74f nonconducting epoxy.

system in air. The numbers correspond to the wires coming from the cryostat feedthroughs. The labels describe what on the STM head the wires connect to. The following list should help you decode the figure:

- Diode: Lakeshore temperature diode
- NC: No connection
- SC: Sample connection
- X-,X+,Y-,Y+: Scan tube quadrants
- Z1-Z6: Z coarse piezos
- X-FL, Y+FR, ...: X and Y coarse piezo

The nomenclature for the X and Y coarse piezos is as follows:

- +,-: Arbitrary direction of motion of stack upon positive voltage application
- B: Back. The stacks at the rear of the STM
3.3 RF Filters

While trying to lower the noise floor of Toucan, we installed radio frequency (RF) filters. In general, RF noise is not important in 4K STM setups. It becomes important when you are trying to measure small spectral features in STS. It is also non-negligible when you have a dilution refrigerator or other mK system. The RF broadening, for instance, can drastically affect the measurement of Kondo temperature [49].

In order to effectively filter RF noise in an STM, you need to make sure to filter every single wire going into the chamber. If you miss one, it tends to radiate inside the chamber, defeating your RF defenses. After discussions with Joe Stroscio (NIST) and Chris Lutz (IBM), we decided on pi-RF filters. The filters are from Spectrum Controls Inc, model 1204-050. They were chosen for a number of reasons:

1. Max current of 25A
2. Minimum capacitance of 3000pF
3. Minimum insertion loss of 8dB at 1 MHz
4. Solder-able

The transmission of the bare filters is shown in fig. 3.11. The transmission is relatively flat until near the $\sim$2MHz resonance frequency. This resonance peak is undesirable, and the -3dB point is too high for our application. For this reason, we added a series resistance of 500Ω. This drops the -3dB point to around 63 kHz (fig. 3.12) and kills the 2MHz resonance. We added this additional 500Ω resistor to every filter except those connected to the coarse walkers. For those wires, we cannot tolerate a 63 kHz low pass filter, as we require the
Figure 3.6: Pinouts for the cryostat feedthroughs. The letters on the diagrams correspond to the letters printed on the non-vacuum side of the feedthrough. The numbers correspond to the wires going to the 4K plate. Pins without numbers are not connected. The black rectangle on each feedthrough represents the alignment notch.
3.3. RF FILTERS

Figure 3.7: Wiring connections on the 4K cold plate. The word “Front” denotes the front of the STM (where the sample is inserted). Each wire block has up to 4 wires connected to it. The numbers correspond to the wires coming from the cryostat. The text labels denote what the wires are connected to on the STM head. Diode: temperature diode; NC: no connection; X-,X+,Y-,Y+,Z: scan tube; X-FL,Y-B,Z1,etc: coarse piezos.
Figure 3.8: Wiring diagram for the 2 ceramic pin blocks on the top of the STM. “Front” denotes the front of the STM. The color of the wires is not meaningful.
Figure 3.9: Wiring diagram for the 3 ceramic pin blocks on the sides of the STM. “Front” denotes the front of the STM. The color of the wires is not meaningful.
3.3. RF FILTERS

Figure 3.10: Wiring diagram for the 4 ceramic pin blocks on the bottom of the STM. “Front” denotes the front of the STM. The color of the wires is not meaningful.
“slip” portion of the stick-slip motion to be as fast as possible. Without the RF filters, we can slew from 0 to 350V in under 1µs. We wanted to be able to still achieve that slew rate. Thus we decided to use bare RF filters for the coarse walkers.

![Graph of RF Filter Transmission](image1)

**Figure 3.11**: Transmission measured for a single, bare Spectrum Controls 1204-050 pi RF filter (bare means no additional series resistor). Note the resonance peak at 1986 kHz.

![Graph of Filter with Series Resistance](image2)

**Figure 3.12**: Transmission measured for a single Spectrum Controls 1204-050 pi RF filter with an added 500Ω series resistance. The -3dB point is around 63 kHz and the 2MHz resonance peak is gone.
3.3. RF FILTERS

Figure 3.13: Completed RF filter for the bias coaxial connection. The pi filter (black) is soldered into a copper-clad board. There is a resistor in series to decrease the corner frequency. The aluminum foil serves to isolate the “clean” side of the box (the left half) from the “dirty” right side. Note that the labels IN and OUT on the lid are incorrect.

To effectively filter RF noise, it is important to make a filter box which separates the “dirty” side of the filter from the “clean”, filtered side. This is accomplished by embedding the filter in a copper board, and putting it in a metal box in such a way that no stray signals can get from one side of the copper board to the other (see fig. 3.13). In our design, the filters are soldered into a copper-clad board which is cut to fit into the middle of a metal box (fig. 3.14). Additional metal foil is glued into the box around the copper-clad board at an attempt to increase the isolation between the two sides of the board. This is probably not going to work very well. To be effective, the copper board and the foil must be extremely well-grounded to the box, and should not let any stray signals through. Our foil is super-glued in place (the glue is non-conductive).

A finished version of one of the filter boxes, without the lid, can be seen in fig. 3.15. When connecting the lid, it is still important to make sure that no signal can get from the clean side to the dirty side. The way we handled this was to add a piece of foil to the lid which glues to the dirty side of the filter box, isolating the two sides. See fig. 3.13 for an example.

We did not put a pi RF filter on the tunnel current. Putting a large capacitance on the tunnel current wire before the preamp would completely destroy the signal. We could have put a pi filter after the preamp, but we instead chose to add a commercial 1.9 GHz RF filter from Mini Circuits.

The performance of the RF filters has not yet been tested. We had intended to test them when we installed them, but the microscope was working so well and we were getting data, so we decided to postpone. In order to test them, you can grow a film of Pb on a Si wafer and measure the superconducting gap. You can then model the gap using BCS theory and adding in an additional broadening due to RF noise [59]. This will allow you to determine
3.4 Coarse Walkers

A Pan-style walker uses piezo stacks in a slip-stick motion to move an object over their top surfaces. Toucan uses this design for the coarse x, y, and z motion. In keeping with the original design of the Pan style walker [99], we modified the electronics for the coarse motion to operate each piezo stack independently of the others during the “slip” portion of the motion. This is in contrast to the Omicron design, which connects all piezo stacks on an axis in parallel and often has trouble walking at 4K. Since the piezo stacks have a capacitance of upwards of 5 nF at room temperature and 2 nF at 4K, it’s not a simple task

Figure 3.14: Partially completed filter assembly. RF filters (black) are soldered into a custom-sized copper-clad board. The green resistors drop the corner frequency of the filters down to around 63 kHz.

the amount of RF broadening present in the system.

There are a few things that you should be aware of and should be carefully checked. The first is the Amphenol connectors on the filter boxes. These connectors are notorious for leaking RF noise. We tried to compensate for this by foiling over the connectors. The second is the efficacy of the copper-clad board. The filters and the board must be very well grounded to the chamber. Third is the foil. The ideal solution would be a custom box with a custom-cut copper board that fits perfectly into the box. We tried to mimick this with the foil, but this should be checked.
3.4. COARSE WALKERS

Figure 3.15: A completed RF filter box (without lid). The smaller top compartment is the “clean” side which connects to the cryostat feedthrough.

to slew from 0V to 350V quickly without a high current power supply. Aside from this issue, it is also not a trivial task to find a high voltage switch which will operate in the required sub-µs regime.

The electronics we built are based on a design from Joe Stroscio at NIST. For the switching, they use a triac, which is essentially two gateable diodes connected in reverse parallel. This allows for high voltage switching on the timescales that we need. By adding in a reservoir capacitor, we can achieve slews from 0V to 350V in around 500ns – 1000ns. The basic idea is to slew each piezo individually during the fast portion of the walk cycle (the
Figure 3.16: Timing of the voltages for each of the six z-piezo stacks during tip approach. The blue line depicts the output of the Trek high voltage amplifier (polarity of the blue HV line has been reversed in this figure to aid in visualization). The other lines are the voltages across each of the six piezo stacks. They are switched sequentially using hardware timing and triac switches (the slip portion of the cycle). After all six stacks have a voltage across them, the HV power supply is slewed slowly back down to 0V (the stick portion of the cycle), where the process starts again.
Figure 3.17: Timing of the voltages for each of the six z-piezo stacks during tip withdrawal. The blue line depicts the output of the Trek high voltage amplifier (polarity is not important in this qualitative figure). The other lines are the voltages across each of the six piezo stacks. With the triacs’ gates conducting, the HV amplifier is slewed to high voltage (the stick portion of the cycle). At this point, the triacs’ gates are disconnected from the HV source and the HV amplifier is slewed to 0V. The gates are then grounded to initiate the slip portion of the cycle.
3.4. COARSE WALKERS

slip part), and then slowly ramp all of the piezos back down together (the stick part). With this configuration, we only need one 2-channel Trek bipolar amplifier. You could design this to only need one 1-channel bipolar amplifier if all piezo stacks for a given direction (i.e. ±x or ±y or ±z) needed the same polarity to walk, as is the case in the Homebuilt VT in B271.

Tip approach follows the scheme outlined above (and in fig. 3.16). Since all of the z piezo stacks require the same voltage polarity for approach, the scheme is somewhat simplified. We still use both channels of the Trek HV amplifier for this motion, however, because we built identical electronics for each of the 3 directions.

For tip withdraw, we initially used the same scheme, with the slip portion of the walking cycle happening first, followed by the stick portion, pulling the tip away from the sample surface. This, however, created problems. If there are any problems with your slip motion (and there were), then the tip is slammed into the sample once, briefly, before being pulled away. To remedy this, we implemented the stick portion of the cycle first, followed by the slip portion. This may seem simple, but with triacs, nothing is ever as simple as you want. The main problem is that triacs are great at turning on (i.e. becoming conductive) quickly, but you can’t turn them off (close the conduction channel) until there is a zero crossing (no voltage). This means that you can’t just slew the piezo stacks to high voltage, and then turn the triacs off and get a fast slip motion. Our solution (fig. 3.17) is to connect the gates of the triacs to the HV and slew the HV amplifier from 0V up to the max (350V for size 10 steps). At this point, the triac gates are disconnected from the HV and the Trek HV amplifier is slewed back down to 0V. During this time, the triacs remain conducting. The trick is to slew the HV down fast enough that the storage capacitors don’t have time to discharge significantly. Then, while there is still high voltage across the piezo stacks, the gates are reconnected to the HV amplifier (which is now at 0V), pushing the triacs (and thus the piezo stacks) to effectively short to ground, thereby quickly slewing the voltage across the piezo stack back to 0V, accomplishing the slip portion of the walking cycle. I should point out that my above recollection of the theory of the tip withdrawal might be incorrect/incomplete in some ways. The waveforms and the timing, however, can easily be verified with a high voltage capacitive probe and an oscilloscope.

One other quick note: if you want to measure the slew rate (i.e. slip time) for a piezo or piezo stack, make sure to measure it with the piezo still connected, and your measurement device in parallel to it. The slew rate is largely determined by the capacitance of the piezo, so measuring the slew rate with it disconnected defeats the purpose and is a waste of time.

All of the timing for the coarse walkers is done in the Labview software program which runs them. This significantly limits the step rate. That being said, it was not worth the added effort to offload the timing to external hardware. To do that would require either preloading the entire waveform for the desired set of steps into the memory of a device, or using hardware timers to trigger individual steps. We are currently able to walk 10,000 steps in about 80s. This is sufficient for the current purposes at the time of this writing.
3.5 Magnetic Damping

As we've discovered, magnetic damping is tricky to get right. The conductivity of oxygen free high conductivity (OFHC) copper increases dramatically between 300K and 4K. This means that tuning a magnetic damping system at 300K is essentially a crapshoot. Even worse, magnetic damping changes drastically from 77K to 4K, so if you test your system at 77K, you still don’t know how it will behave at 4K. When first installing the new magnetic damping on the STM head, we tuned it at 300K to get approximately three full oscillations before being damped out. This was following what we observed on the Omicron LT systems. When we cooled to 77K, the damping was perfect - one oscillation plus a little. It was just under critical damping. When the system was at 4K, the head acted like it was in molasses. When pulled down with the wobble stick, it took multiple seconds to return to its equilibrium position. Needless to say, this was too much magnetic damping. After many trials and even more errors, we managed to tune the damping to work well at 4K. I included this anecdote to relay one important point: **if you want to change the strength of the magnetic damping, do it in small steps and check the system at 4K.**

3.5.1 STM Head

The magnetic damping on the STM is arguably one of the most critical parts of the overall vibration isolation. On Toucan’s head, there are four magnetic damping blocks which hang below it, as seen in fig. 3.18. One thing to be aware of with the STM head damping blocks is to not let them touch the plate on which the xy piezo stacks are glued. As the system cools, this contact is believed to loosen up the xy plate through differential thermal contraction. Make sure there is space, as in fig. 3.19.

On the frame attached to the LHe cold plate, there are four corresponding magnet assemblies, one for each damping block (fig. 3.20). Currently, there are only two magnets in each assembly. My original design was for four magnets per assembly (bottom, rear, right, left of damping block), but that proved too much even for this massive head. The magnets themselves are samarium cobalt, acquired from McMaster Carr.

3.5.2 Cryostat

Due to the general poor quality of the cryostat, we found it necessary to magnetically damp the LHe cryostat with respect to the LN$_2$ cryostat (which is mounted rigidly to the chamber). Since the bottom of the LHe frame is made of OFHC copper, all we needed to do was mount magnets on the inside of the LN$_2$ shield. The magnets are the same ones used for damping the STM head. Just as with other magnetic damping systems, the amount of damping achieved is strongly dependent on the distance between the magnets and the copper damping block (in this case the bottom of the LHe frame). With the adjustable legs at the top of the LHe cryostat, this is much easier to tune than the damping of the STM head. In practice, we lower the LHe cryostat until the vibrational resonances from
3.6. HE RETURN LINE

When connected directly to the He return line, Toucan exhibits low frequency oscillations, on the order of 1/20 Hz. This is believed to be due to pressure fluctuations within the return system itself, either from other labs or from within our own lab. Professor John Clarke, who
Figure 3.19: Make sure to keep a small space between the magnetic damping blocks and the plate on which the xy stacks are glued.

has a great deal of experience with He return systems, suggested that we insert a regulator between Toucan and the return line. This turned out to be an excellent suggestion, and is now the de-facto operating condition for Toucan when measuring. In order to still be able to fill the LHe cryostat, we built a manifold (fig. 3.21) with valves, allowing one to bypass the regulator during filling. The regulator should be adjusted to create a slight overpressure in the LHe cryostat during normal operation. This will serve as a buffer to keep unwanted oscillations in the He return line from affecting the vibrational performance of the STM. On the regulator, there are two valves. The yellow one is the bypass valve, which should be opened during filling. The red on, near the regulator, should always be open unless the cryostat is disconnected from the return line (e.g. during a vent).

3.7 Rebuilding the Head

At one point, when the vibrational noises in Toucan became too much to deal with, we decided to rebuild the scanner assembly, thinking that something in there might have been
3.7. REBUILDING THE HEAD

Figure 3.20: The samarium cobalt magnets used to damp vibrations in the STM head.

loose. We replaced the scan tube, sacrificial macor cup, and all wires going to both the scan tube and the tip [7]. After performing this open-STM surgery and making a number of other modifications (like changing the shielding on the tip wire), we wound up with a much lower-noise STM. The road to get there, however, was windy and we were never quite sure what was the magic change. It is entirely possible that rebuilding the scanner wasn’t necessary, but at least we knew that it wasn’t the source of the noise afterwards.

In order to remove the Z sapphire prism, it is easiest to pull the head out of the frame and put it on the table. This is not strictly necessary, and it does involve removing every wire connected to the head. We did this mainly because we were planning on re-routing all of the wires anyway. After putting the head on the table, you have to remove the Z prism from its confines. Surrounding the prism are six piezo stacks, so pull very gently while removing it. Also keep in mind that two of the stacks are mounted on a separate spring plate, so they will be free after the prism is removed. It is best to pull the prism with this spring plate facing the table so as to not break the wires going to those two stacks. Once you get the prism out of the head, DO NOT TOUCH OR SCRATCH THE POLISHED SURFACES. This is extremely important if you want your STM to be able to walk in Z again. In addition, keep track of the orientation of the prism when you remove it. Make sure that the front face of the prism is again the front face when you reinstall it. The piezo stacks are custom-fit to the prism, so minor changes can make the system unable to walk at low temperatures.

The sacrificial macor piece was designed to allow one to salvage the sapphire prism if the scan tube ever needed to be replaced. What we found is the sacrificial piece is not strictly necessary. In fact, it was extremely difficult to remove the scan tube. I thought it would be fragile and would come out with a little force, but that turned out to be wildly
incorrect. We tried pulling, twisting, and even crushing the scan tube with a pair of pliers (that was immensely cathartic). The nonconductive epoxy which holds everything together in the scanner assembly sets up like concrete. It’s nearly impossible to remove unless you heat it above its degradation temperature. We placed the prism carefully into a quartz tube and heated it in a CVD furnace at 700°C for 30 minutes. Afterwards, the epoxy was in an ashen state, and the sapphire prism was liberated.

A new scan tube was fitted with wires on the outer four electrodes using 96%/4% Sn/Ag solder. The inner electrode was connected with Epotek H20E conductive epoxy to the shield of the tip wire, forming a common ground between the scan tube and the tip. This connection could not be easily verified for robustness, as you can’t see it once the epoxy is applied. If there is ever a problem with strange grounds coming undone that can’t be traced, this would be a place to look. After reassembling the scan tube, sacrificial macor
piece, tip cup, and tip electrode, the assembly was glued into the prism using Epotek H74f non-conductive epoxy. When inserting the scan tube assembly into the prism, make sure that the electrode wires go through the correct holes and come out the bottom. It is no fun to fish the wires through after having applied epoxy. The completed scanner assembly is shown in fig. 3.26.

![Figure 3.22: Finished scanner assembly. This is actually the original scanner, but the new one looks the same, except for the reddish-brown color of the new H74f epoxy.](image)

One thing that we noticed after replacing the scanner is that it seemed to be stable at higher scanning frequencies than it was before. We attributed this to it being more rigid and validating our decision to rebuild it. The rebuild also improved the hysteresis in forward vs backward scan lines. However, after a few months, these issues devolved back to their original state.

Before the rebuild, we had been gluing the tip holder into the tip cup using a small dab of H20E conductive epoxy. After the rebuild, we continued this practice. There is a BeCu spring in the tip cup, but with the epoxy we are sure that the tip holder is rigid. The epoxy is applied between the bottom lip of the tip holder and the copper block which serves as the tunnel current electrode.

### 3.8 Active + Passive Damping Table

In 2012, Toucan’s air legs were swapped out for a combined active + passive damping system from Technical Manufacturing Corp - the Stacis iX. The legs are 4 inches taller than the original ones, making Toucan a bit formidable for the vertically challenged among us. The air legs have a resonance frequency of around 15 Hz, significantly higher than the 1-2 Hz normally found with air legs. To achieve this, there are small bladders on the sides of the legs filled with viscous oil. One major benefit of this high resonance frequency is that it does not overlap with any other prominent resonances in the system. The active portion consists of the four individual legs, each with two accelerometers (one vertical and one horizontal) and a piezoelectric actuator. When the accelerometers pick up a vibration from the floor, they produce a signal out of phase with it and send that signal to the actuators. The net result (in a theoretical world) is an exact cancellation of the vibration. In practice, this system works quite well up to around 100 Hz.
An experimental transmission curve is plotted in fig. 3.23 on top of the curves provided by TMC for the active + passive damping legs. As one can see, there is a resonance at around 3 Hz which is likely caused by the LHe cryostat. Additionally, the transmission does not fall off as quickly as the data provided by TMC. Nevertheless, the combination of active and passive damping improved the performance of the system dramatically. I should also note that these data were taken before careful tuning of the active damping feedback. The transmission function is likely improved in the 1-100Hz range now.

After a careful vibration analysis, we determined that the triangle damping stage at the top of the LHe cryostat was not working adequately. In fact, we found that noise at certain frequencies was even being amplified by up to 10x (see fig. 3.24). For this reason, we stopped using the triangle as a damping stage and now only use it to assist with aligning the cryostat for sample transfer. The LHe cryostat must be carefully aligned to prevent the 20K radiation shield from touching the inside of the LN$_2$ cryostat. After modifying many parts inside the STM frame and shield area, it is relatively easy to tell when the LHe cryostat is free. Open up the front LN$_2$ door and push the LHe door backwards with the wobble stick (gently). If the LHe cryostat gently oscillates for a few periods, then it is free (it is just a big pendulum after all). If the LHe cryostat is touching anywhere, it will damp these oscillations immediately. Adjust the nuts on the posts at the top of the cryostat very slowly, as a little change goes a long way.

The above modifications made a considerable impact on the stability of the tip-sample junction. During good conditions with a good tip, peak-to-peak noises are less than 1pm in z with the feedback on, and less than $\sim$1% in current with the feedback off. You can
3.8. ACTIVE + PASSIVE DAMPING TABLE

Figure 3.24: Transmission of vibrational noise from the floor to the table top (red line) and to the top of the triangle on the LHe cryostat (black line) with all legs engaged and filled with air. The blue line is at a transmission of 1, meaning no damping or amplification of noises.

Figure 3.25: Representative images of the surface of Au(111) without (left) and with (right) active and passive vibration isolation from the Stacis system. System at LHe temperature.

see an example of the effect of the damping system in fig. 3.25. On the left is an image of the Au(111) surface taken with the active and passive table damping legs off. The scan direction is top to bottom. The low frequency noise is extremely apparent. After turning on the active and passive systems in the legs (right), the low frequency noise is significantly reduced.
3.9 Springs

The springs from which the STM head currently hangs are made from stainless steel. We initially tried to use BeCu springs, which are supposed to keep their springiness at 4K. We found that reasonably sized springs required large, plastic deformations in order to support the weight of the head. In fact, the BeCu springs that we used initially had only \( \sim 10 \) turns of wire. This made them quite stiff, with a high resonance frequency. The current stainless steel springs have a combined resonance frequency of around 2 Hz. The first thing you’ll notice about them is that the rear spring is significantly more stretched out than the front two. This is because the weight distribution in the head is not isotropic (or even a close approximation thereof). Theoretically, this should cause a degradation in vibration damping, and is something that should be carefully scrutinized in the future. Perhaps something can be done to even out the weight of the head. It should be noted that the head is already \( \sim 0.6 \) Kg, and so additional mass should be added with care.

Figure 3.26: The spring attached to the rear of the STM head is decisively more stretched than the two front springs, owing to the anisotropic weight distribution in the head. Notice the brown vespel mounting blocks at the termination of the springs.
Part III
Research
4.1 Introduction

Chemical functionalization provides a potentially useful route for tuning the electronic properties of semiconductor surfaces for a variety of energy-related applications. Controlled covalent attachment of molecular elements on semiconducting surfaces, however, requires a detailed understanding of the structure, bonding, and reactivity of the surface. For III–V semiconductors, the chemistry of the (100) and (111) surfaces has been well studied, but the (110) surface is less well understood. For GaP(110) and other III–V semiconductors, the surface undergoes a 1 x 1 surface reconstruction that results in a buckled surface where anions move slightly outward and cations move slightly inward relative to the unreconstructed surface plane. The resulting polar GaP(110) surface is comprised of sp$^3$-like anions ($P^-$) with lone pairs of electrons and sp$^2$-like cations ($Ga^+$) with vacant p$_{rmz}$ orbitals. The chemical reactivity of the (110) surface is influenced by the nucleophilicity of the P atoms and the electrophilicity of the Ga atoms. Most investigations on the chemistry of the (110) surface have focused on the adsorption of metallic ad-layers as well as sulfur and halide compounds. Studies addressing the chemical reactivity of the (110) surface at the atomic scale, including the selectivity of surface reactions and anchoring to these surfaces, remain scarce. The overall high quality of the III–V(110) surfaces as compared to other semiconductor surfaces, which typically require chemical or ultrahigh vacuum (UHV) cleaning treatments, makes them particularly appropriate for surface chemical functionalization.

4.2 Ethylene / GaP(110)

We performed a detailed study of the adsorption and stability of ethylene ($C_2H_4$) on GaP(110), a model system for assessing the chemical reactivity of various molecules on the surfaces of III–V semiconductors. We found that ethylene molecules are stable on GaP(110)
only upon adsorption at low temperatures (with the sample staying at or below 15K). High-resolution STM images, in combination with DFT calculations, enabled us to determine the ethylene/GaP(110) adsorption geometry, revealing that individual ethylene molecules physisorbed to the surface. Using scanning tunneling spectroscopy (STS) we probed the local electronic structure of the ethylene/GaP(110) system and found it to be consistent with theoretically predicted energy level alignments. The weak chemical reactivity observed for ethylene on the GaP(110) surface differs significantly from ethylene's behavior on other metallic [95, 97, 5], semiconducting [37, 81, 92, 24, 22], and insulating surfaces [55].

Figure 4.1: 335Å x 335Å STM image of GaP(110) after in-situ UHV cleavage. One surface defect, as well as several subsurface defects/dopants, can be seen. V=2.9V, I=30pA, T=8K [126].

Our GaP(100) wafers were p-type, doped with Zn atoms at a concentration of $2 \times 10^{18} \text{cm}^{-3}$. The GaP(110) surfaces were obtained by cleavage in UHV conditions at room temperature and were subsequently transferred in-situ to a home-built UHV cryogenic (8 K) scanning tunneling microscope. Each surface was exposed to ethylene either at room temperature or at low temperature (15 K). STS spectra were obtained using a lock-in amplifier ($f = 837 \text{ Hz}$, $V_{\text{mod}} = 5 \text{ mV}$) at variable tip–sample separations. This method is useful for increasing the dynamic range of the STS measurement when dealing with large gap semiconductors. During the bias sweep, the tip-sample distance is smoothly changed, reaching a minimum when the bias voltage is 0V. With this method, we are able to resolve features in the valence and conduction bands, as well as the band edges in
4.2. ETHYLENE / GAP(110)

one single spectrum. All STS curves were normalized following the method described by
Martensson et al. Our DFT calculations were performed within the generalized gradient
approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) using VASP and PAW pseudopotentials with a 540 eV planewave cutoff. For selected geometries optimized with PBE, single-point DFT calculations with the vdW-DF2 functional were used to assess the magnitude of van der Waals dispersion interactions on computed binding energies. A 6 x 6 x 6 Γ-centered k-point grid was utilized for bulk calculations, while a 2 x 2 x 1 Γ-centered k-point grid was used for slab supercell calculations. Calculations included one molecule per 3 x 4 unit cell (a surface coverage similar to our experiments) with supercells consisting of nine layers of GaP and 12 Å of vacuum. To compare with STS measurements, we further augmented our DFT calculations with self-energy corrections within the GW approximation. Simulated STM images were calculated using the Tersoff–Hamann approximation.

Fig. 4.1 shows a typical STM image of GaP(110) after cleavage in UHV conditions. The most common defects in our GaP(110) samples are atomic vacancies and dopants, which are generally created and exposed by cleavage, respectively. Our STM images show very flat GaP(110) surfaces with terrace widths greater than a micrometer.

Fig. 4.2a shows atomically resolved STM images of the GaP(110) surface acquired at different bias voltages. Although the interpretation of the STM images is not straightforward, unoccupied state images (positive bias) and occupied state images (negative bias) show cation (Ga\(^{+}\)) and anion (P\(^{-}\)) sites, respectively, consistent with the charge transfer from Ga to P upon surface relaxation. Fig. 4.2b shows a typical normalized dI/dV curve acquired on bare GaP(110). The spectrum exhibits a 2.1 V wide gap bounded by three reproducible resonances.

We explored the chemical reactivity of ethylene molecules on GaP(110) by dosing them in UHV at two different substrate temperatures: room temperature and 15 K. STM inspection of GaP(110) dosed with 0.1–10 Langmuir (L) at room temperature revealed pristine surfaces with no adsorbed ethylene molecules. Even after doses as high as 10 L the GaP(110) surface remained free of adsorbates. However, ethylene dosing performed with the sample held at 15 K led to the adsorption of ethylene on the surface, as shown in fig. 4.3a where the surface is observed to be decorated with ethylene molecules. High-resolution unoccupied state images of ethylene/GaP(110) show an elongated eye-shaped feature with an apparent height of 1 Å (fig. 4.3b). At this bias polarity, ethylene adsorbates appear to be nearly centered on top of the visible Ga atoms but with the maximum intensity shifted by 1 Å along the [001] direction (a white arrow in fig. 4.3b) indicates the direction of the shift). Occupied state images (fig. 4.3c) show ethylene adsorbates as more square-shaped and located midway between the visible P atomic rows in both lattice directions ([1-10] and [001] directions). Fig. 4.4a shows dI/dV curves acquired consecutively on both clean GaP(110) (red) and ethylene/GaP(110) (green). Both spectra show a similar energy gap, and the spectrum acquired on ethylene/GaP(110) does not exhibit any features which can be associated with molecular resonances. The only significant difference between the two spectra is an attenuation of the resonance seen on bare GaP(110) at +2 V when the tip is held above an ethylene molecule.
Figure 4.2: (a) Experimental STM images of GaP(110) acquired at 8K (left panels) (experimental parameters: +3.2V, 18pA; +2.3V, 19pA; -2.7V, 30pA) compared to corresponding simulated STM images (right panel). All images are 21Å x 21Å. (b) Experimental dI/dV acquired on GaP(110) (top panel) and calculated projected density of states (PDOS) for bare GaP(110) (lower panel). The red line shows PDOS for GaP(110) surface states, while the PDOS derived from bulk bands is shown in gray. (c) Sketch of the relaxed GaP(110) surface used in our ab-initio calculations. (d) Calculated band structure of relaxed GaP(110) along high symmetry lines in the surface Brillouin Zone. Surface bands are in red while bulk bands are in gray. Reproduced from [126].

Attenuation of this particular feature was also observed in height-dependent STS measurements on bare GaP(110), indicating a strong height-dependent tunneling conductance at this energy.

To better understand our experimental observations for our ethylene/GaP(110) system, we investigated it using DFT calculations, directly comparing them to our STM/STS measurements. Our DFT-PBE structural optimization of the GaP(110) surface (fig. 4.2c) yielded a surface buckling of 0.63 Å relative to the truncated bulk structure and a unit cell of 5.50 Å along the [001] direction and 3.89 Å along the [1-10] direction, in good agreement...
Figure 4.3: (a) Typical STM image of GaP(110) after dosing with ethylene at 15K. Image size: 84\,\text{Å} \times 84\,\text{Å}. Parameters: V=+2.7V, I=15pA. High resolution STM images of a single ethylene molecule are shown in (b) at +2.8V and (c) at -3.0V. The white arrow in (b) indicates an experimental shift of image intensity away from the underlying Ga atom center. Simulated STM images of a single ethylene molecule on GaP(110) are show in (d) for unoccupied states and (e) for the occupied states. The white arrow in (d) shows a theoretical shift of image intensity away from the underlying Ga atom center. (f) Side and (g) top views of the simulated relaxed structure for an ethylene molecule on GaP(110) in the most stable binding configuration. Reproduced from [126].

with previous calculations [38]. Simulated images of the surface at different experimental biases are shown in fig. 4.2a and accurately reproduce all of the features observed in the STM images at both bias polarities. The band structure obtained using an additional GW-based correction is shown in fig. 4.2b. Bands originating from the bulk along high-symmetry directions of the (110) surface Brillouin zone are depicted in gray, while the electronic features due to the surface are in red. Surface features include resonances degenerate with projected bulk bands, as well as surface state bands labeled C$_3$ and A$_5$ (following established notation [19]) that exist in the k-dependent gap region. From this band structure, we computed the density of states (DOS) of the (110) surface, as seen in the lower panel of fig. 4.2b. Here the integrated DOS from surface atoms is in red and from bulk atoms is in gray. According to the electronic band structure, the main contribution from the unoccupied (occupied) states to the surface DOS can be attributed to the bulk conduction (valence) band, while the small peak located at +2.2 V can be ascribed to the C$_3$ surface state. This can be seen clearly in the theoretical DOS of fig. 4.2b, which compares favorably to the STS data. The experimental gap is seen to be about 0.15 eV smaller than the bulk band gap due to the presence of the C$_3$ surface state just below the conduction band edge. The proximity of the Fermi energy (E$_F$) to the valence band edge is due to the high p-doping of the samples.
Theory allows us to examine the energetics of the many possible adsorption sites and geometries for ethylene on GaP(110). Such analysis reveals two potentially stable configurations with DFT-PBE binding energies of 180 meV/molecule and 241 meV/molecule, respectively. van der Waals corrections can enhance these binding energies – see below. In both cases the ethylene molecule is adsorbed on an equivalent site within the unit cell with the plane of the molecule forming a 30° angle with the surface, but the molecule has two different rotational orientations. The distance from the closest surface atom (Ga) to the molecular C–C bond is 2.80 Å and 2.95 Å for the two configurations, respectively. The most energetically favorable configuration (241 meV/molecule) is when the C–C double bond is...
oriented parallel to the [1-10] direction, whereas in the other configuration it is rotated by 90°, parallel to the [001] direction. Figs. 4.3g show a structural model of the most energetically favorable configuration of the system. Single-point calculations with the vdW–DF2 functional provide an assessment of the magnitude of van der Waals dispersion to adsorbate binding energetics. Our dispersion-corrected vdW–DF2 calculations increase the binding energies of these adsorbate sites to 325 and 395 meV/molecule, respectively, and preserve the relative stability of these geometries predicted with DFT-PBE. On the basis of the computed forces for this system (< 0.5 eV/Å), geometry optimizations for these two binding configurations are expected to lead to small changes in bond lengths, consistent with prior calculations on related systems [66, 8], suggesting that van der Waals corrections will have a modest quantitative impact on the interfacial electronic structure reported here. Thus, in what follows, we use DFT–PBE geometries when comparing our calculations to measured STM images and STS.

Because of the low predicted binding energies, ethylene molecules are expected to be stable on the surface only at relatively low temperatures, consistent with the observed absence of molecular adsorption at room temperature. We compared simulated STM images of the two predicted stable adsorption configurations with experimental STM images of ethylene/GaP(110). Despite the small size of the ethylene molecule and its weak interaction with the substrate, the computed STM images present several subtle differences that allow us to unambiguously identify the species on the surface as ethylene molecules adsorbed in the largest binding energy configuration. Figs. 4.3d and 4.3e show the simulated STM images of the ethylene molecule on GaP(110) in the highest binding energy configuration for unoccupied and occupied states, respectively. This geometry accurately reproduces not only the experimentally observed molecular adsorption site on the substrate but also the shape of the molecule at both polarities: an asymmetric eye-shape for unoccupied states and a square-shape for occupied states (figs. 4.3b,c). This geometry also captures the previously mentioned shift in the maximum of intensity in experimental unoccupied state images (0.7 Å in the simulated images as shown by the arrow in fig. 4.3d).

Lastly, to understand our STS measurements of ethylene/GaP(110), we computed the adsorbate frontier orbital energies using an efficient, empirical, parameter-free GW self-energy approach [93, 135]. With this self-energy correction, the adsorbate frontier energy levels are evaluated to be several eV outside of the GaP(110) band edges (see fig. 4.4b). Also, no significant charge transfer is found via Bader analysis [119, 22]. These calculations are consistent with the experimental absence of hybridized frontier molecular orbitals in the energy range explored by STS (fig. 4.4a). This also allows us to rule out hybridization of the C3 surface state with molecular orbitals as an explanation for the observed attenuation in ethylene/GaP(110) conductance around +2 V (fig. 4.4a). We believe this attenuation is due to the larger tipGaP(110) distance that occurs when the STM tip is held above an ethylene molecule. The C3 surface state decays faster into the vacuum than other band structure features due to its larger k|| components.

In conclusion, our combined experimental and theoretical analysis of ethylene/GaP(110) indicates that ethylene molecules physisorb onto GaP(110) primarily via a weak hybridization...
tion of the ethylene $\pi$-orbital with Ga p-states, with additional van der Waals dispersive contributions. The low reactivity of ethylene on GaP(110) is in clear contrast to alkenes adsorbed onto other metallic and semiconducting surfaces. For example, ethylene is found to chemisorb or decompose on Pd, Pt, Rh, and Ni [95, 97, 5]. On Si(001), ethylene chemisorbs via a [2 + 2] cycloaddition reaction that evolves from a weakly bound intermediate state [81, 92] that is very similar to the physisorbed state seen here for ethylene/GaP(110). The difference seen here for ethylene/GaP(110), however, is that when thermal energy is added to this physisorbed system, the molecule desorbs rather than undergoing further chemical reaction.

### 4.3 PFPA/PFPN

Another promising approach to functionalizing the (110) surfaces of III–V semiconductors involves reactions of organothiols with the surfaces [96, 16, 107, 89, 106]. The molecular basis for the resulting molecule–surface bonds, however, remains elusive. In addition, the weak stability of the thiol-derived layers at room temperature [16, 107, 31], their incommensurability and rather short-range order [89] limit the applicability of this functionalization strategy.

![Perfluorophenyl azide (PFPA) molecule stick figure.](image)

In this work, we exploited the slight polar character of the GaP(110) surface to design a chemical reaction leading to strong, covalent molecule-surface bonds. Our motivation is the reactivity of tertiary phosphines, which resembles the P sites of GaP(110). Tertiary phosphines can undergo a Staudinger reaction [118] with azide molecules to afford a phosphine imide with the loss of dinitrogen ($N_2$). Thus, we envision a heterogeneous version
Figure 4.6: a) A Staudinger-type reaction of perfluorophenyl azide on the GaP(110) surface to form Lewis acidic surface Ga-stabilized phosphine imides. Molecular analogue of such species, including B and Ga-stabilized phosphine imides, are also shown. b) Sketch of the relaxed GaP(110) surface. The lone pair on the anion ($P^-$) and the empty $p_z$ orbital at the cation ($Ga^+$) that provides the polar character to the (110) surface is depicted. c) Atomically resolved STM image of the bare GaP(110) surface before the PFPA adsorption (size: 10 x 10 nm$^2$, $V_s = +3$ V, $I_t = 30$ pA, $T = 7$ K).

of the Staudinger reaction on the GaP(110) surface (fig. 4.6a): the reaction of an azide molecule with the P sites on GaP(110) should yield phosphine imide moieties containing P–N molecule–surface bonds. Moreover, the Lewis acidic Ga atoms, adjacent to the P sites, might interact with the Lewis basic N of the phosphine imide to form Ga–N bonds. Remarkably, molecular examples of phosphine imides displaying such bonding interaction between Lewis basic N and certain Lewis acids, including triaryl gallium, have been reported [132]. Here we present a scanning tunneling microscopy (STM) study combined with computational DFT calculations on the thermally activated surface reaction between perfluorophenyl azides ($C_6F_5N_3$, PFPA in the following) and GaP(110), which supports the formation of covalent molecule–surface bonds in a three-membered ring configuration (P–N–Ga) featuring...
4.3. PFPA/PFPN

both P–N and Ga–N interactions. Our findings are consistent with a Staudinger-type reaction on the (110) surface of this III–V semiconductor. Interestingly, the non-covalent molecule-molecule $\pi$ interaction between aromatic perfluorophenyl units ($C_6F_5^-$) also plays an important role in this surface reaction, by driving molecular assembly to form a long-range, well ordered supramolecular structure on the surface (one molecule per surface unit cell). In addition, we have found an intermediate state of this reaction at room temperature in which the molecular units form one dimensional (1D) chains, composed of PFPA and PFPN (perfluorophenyl nitrene - PFPA without the N$_2$ group).

GaP(110) surfaces were obtained by mechanical cleavage in UHV conditions at room temperature. This procedure yields high-quality flat surfaces with a low density of intrinsic...
4.3. PFPA/PFPN

defects \cite{126}, which is particularly convenient for their chemical functionalization. PFPA molecules were subsequently deposited in situ onto the GaP(110) surfaces held at room temperature. The STM image in fig. 4.7a shows the typical morphology of the GaP(110) surface after dosed with 0.7 Langmuir of PFPA. Under these conditions, the aromatic molecules are mobile to diffuse along the surface to form 1D wheat-spike chains along two equal orientations with respect to the crystal lattice. Both orientations form an angle of $54^\circ$ with respect to the [001] direction. The molecular chains are typically composed of 2 – 10 repeating units with spacing between them of 9.2 Å. Both the orientation and spacing observed in the chains are coincident with a commensurate periodicity along $\vec{A} = 2\vec{a} + \vec{b}$, with $\vec{a} = (1, -1, 0)$ and $\vec{b} = (0, 0, 1)$ the surface unit cell vectors. Fig. 4.9a shows a large-scale STM image (135 x 135 nm$^2$) of GaP(110) after 0.8 Langmuir exposure of PFPA. Fig. 4.9c shows the $54^\circ$ angle between the chains and the [001] direction. This model, sketched in fig. 4.9c, shows good agreement with the experimental periodicities and orientation angles. Please note that the position of the red dots does not indicate the adsorption sites of the PFPA molecules. The apparent height of the chains is approximately 5 Å, which suggest a rather vertical configuration of the molecules. This is supported by the comparison of this apparent height with that observed for the nearly lying-flat iodobenzene molecule (C$_6$H$_5$I) on GaP(110), for which we measured an apparent height of 1.3 Å (see fig. 4.11). A close-up view of the molecular chains as seen with the STM for both bias polarities is presented in figs. 4.8a and b. High-resolution occupied state STM images of the chains exhibit two parallel sets of protrusions arranged in a wheat-spike configuration (fig. 4.8a). At this bias polarity, both types of protrusions appear as a slightly different height, as can be seen in fig. 4.8a. Unoccupied STM images show, however, a single set of protrusions along the molecule chain (fig. 4.8b).

In order to test the stability of the wheat-spike phase and obtain information regarding the bonding between the molecules and the substrate, we gently annealed the PFPA/GaP(110) samples at approximately 50°C. This temperature was enough to induce structural changes in the 1D phase that lead to a new molecular arrangement on the surface. Fig. 4.7b shows an STM image of the surface obtained after annealing. The molecules on the surface have formed two-dimensional (2D) islands from the initial chain configuration. A more detailed view of these islands is shown in fig. 4.10. Similar to the case of the intermediate wheat-spike phase, bias-dependent STM images of the 2D phase reveal different atomic-scale features. For occupied states, the molecular islands in the STM images (fig. 4.10a) appear stripped with straight rows running along the atomic Ga–P rows parallel to $\vec{a}$ ([1-10]). These rows are equally spaced by 5.5 Å perpendicular to $\vec{b}$ ([110]), a value coincident with the surface atomic lattice periodicity in that direction. Unoccupied state STM images resolve the internal structure of the rows to reveal elongated protrusions separated by 3.9 Å, which is also coincident with the atomic lattice spacing along $\vec{a}$. Remarkably, these protrusions show a tilt of $20^\circ \pm 3^\circ$ from the [001] direction, as marked fig. 4.10b. This 2D phase appears formed by molecule units in a highly packed (1 x 1) configuration.

To better understand and interpret the structure and chemical stability of the intermediate and product molecular phases on the GaP(110) surface, we performed accurate DFT
calculations including Van der Waals interactions. First, we address the study of the highly packed molecular phase observed after annealing. To study this phase, we have simulated one PFPN molecule per surface unit cell (1 x 1). As mentioned previously, PFPN (perfluorophenyl nitrene) is PFPA without the N$_2$ group. This is justified since, upon thermal activation, phenyl azide releases N$_2$ to form the highly reactive singlet phenyl nitrene [102]. Figs. 4.10e-f show the optimized structure for the 1 x 1 PFPN/GaP(110) calculation. This
compact PFPN stacking is stable with the phenyl rings vertically oriented and anchored to the surface through the remaining N atom. For this configuration, each PFPN molecule is bonded to the surface via the formation of three-membered ring [Ga–N–P], in which N forms two covalent bonds, P–N and Ga–N. Despite the dominant role of the covalent molecule-substrate interaction on the molecular assembly, intermolecular interactions define the orientation of the phenyl rings, which are aligned parallel to one another along the [1-10] direction, with a 20° tilt.

The calculated structure of the 2D molecular assembly that covalently functionalizes the GaP(110) surface is corroborated by comparing our experimental STM images (figs. 4.10a-b) with simulated images (figs. 4.10c-d) in the Tersoff-Hamann approximation [122]. According to our calculations, the occupied electronic bands in this system arise primarily from the hybridization of molecular orbitals (MO) with p character, which spatially extend perpendicular to the phenyl rings. Due to the parallel stacking of the phenyl rings, the MOs overlap and localize the charge density along the [1-10] direction. Therefore, the calculated STM image for occupied states (fig. 4.10c) shows 1D chains of charge density along the
Figure 4.11: a) Height profiles of 1D PFPA/PFPN chains (black), 2D PFPN islands (blue) and isolated iodobenzene molecules (red). High-resolution STM images of b) 1D molecular chain on GaP(110) (size: 7.3 x 5.3 nm², Vₛ = -3.2 V, Iₜ = 100 pA), c) 2D molecule island on GaP(110) (Vₛ = -2.5 V, Iₜ = 40 pA, T = 7 K), and d) individual iodobenzene molecules on GaP(110) (Vₛ = +2.3 V, Iₜ = 26 pA, T = 7 K). The inset in d) shows the relaxed structure of the iodobenzene on GaP(110).

stacking direction and equally spaced by 5.5 Å, in good agreement with the corresponding experimental STM images (fig. 4.10a). However, experimentally we did not observe internal structure within the chains. For unoccupied states, the contrast in the calculated STM images is dominated by MOs with s and p character that show two charge density lobes localized in the phenyl ring. Therefore, the simulated images (fig. 4.10d) show the PFPN molecules as individual elongated features oriented along the phenyl rings, thus also tilted (20°) from the [001] direction. These features nicely reproduce our experimental images for unoccupied states, and therefore allow us to identify the observed elongated protrusions with individual PFPN molecules. Since the optimized geometry accurately reproduces both the experimentally observed molecular adsorption site on the substrate and the main features of the STM images at both polarities, we can conclude that the adsorption and thermal activation of PFPA molecules leads to a successful covalent functionalization of the GaP(110) surface with PFPN units.

Lastly, we address the nature of the wheat-spike nanostructures observed as the intermediate state for the surface reaction of PFPA on GaP(110). Although bias-dependent STM imaging of the 1D chains (figs. 4.8a-b) precludes the straightforward identification their molecular arrangement, it indicates a more complex molecular structure than a 1D - stack of molecules, as previously reported for similar phenyl groups on silicon surfaces [79, 52]. We
calculated several possible configurations involving PFPA and PFPN molecules compatible with the observed orientation of the molecular chains on the GaP(110) surface. Among them, we found one compatible nanostructure that contains one PFPA molecule and one PFPN molecule per unit cell. Calculated images of this structure show a good qualitative comparison with the STM images of the chains. Figs. 4.12b-c show two calculated STM images from the relaxed 4 x 2 PFPA-PFPN/GaP(110) structure. For occupied states, the calculated image shows both kinds of molecules as protrusions showing internal structure (fig. 4.12b). The PFPN molecules appear brighter than the PFPA molecules due to the higher vertical position. This fairly well reproduces the experimental STM images at this polarity (fig. 4.12d), for which two sets of protrusions with internal structure (not as pronounced as that of the calculated images) are also clearly observed along the same crystal direction. For unoccupied states, the calculated STM images show the chains as independent parallel pairs of PFPA-PFPN molecules. Each pair shows two featureless protrusions on each type of molecule with the PFPN molecules still brighter than the PFPA molecules (fig. 4.12c). The experimental images also show independent featureless structures on along the chains, although these are seen as single protrusions, unlike in the calculated images. The simultaneous presence of PFPA and PFPN molecules in this intermediate phase would be compatible with two experimental observations: i) the requirement of thermal activation to form the covalent PFPN phase and ii) a small energy barrier required from room temperature (annealing at 50°C) to start the substrate-induced N_2 detachment from the PFPA and following PFPN covalent anchoring to GaP(110). According to our theoretical model, the formation of the 1D chains likely implies a larger role of molecule-molecule interaction than molecule-substrate interaction, which rules out a fully covalent chemical functionalization of the surface in the intermediate state of the reaction. Although the model presented reasonably reproduces the experimental observations, the large number of possible transient intermediates [73] and reaction pathways of phenyl azides on the surface unavoidably limits our theoretical analysis and, therefore, our understanding regarding the intermediate state of the reaction.

In conclusion, we have shown a well-defined chemical reaction of perfluorophenyl azide on the GaP(110) surface, a prototypical III-V semiconductor. This heterogeneous surface reaction, derived from a Staudinger reaction, lead to the molecular functionalization of the surface stable at room temperature. The molecule-surface linkage, combining P–N and Ga–N bonding interactions, ensures covalent attachment of molecules on the surface. Moreover, the molecule–molecule interaction promotes molecular organization on the surface to form long-range and well-packed, ordered structures. Considering the wide range of azide molecules available, this novel strategy should open up the opportunity for the modification of this kind of semiconducting surfaces for a vast array purposes.
Figure 4.12: Evolution of the thermally-activated chemical reaction: a) intermediate state after the PFPA deposition on GaP(110) at room temperature ($V_s = -2.7$ V, $I_t = 15$ pA). b) Early stage of the reaction toward the final product after annealing the sample in a) at 50°C for 180 s ($V_s = -2.6$ V, $I_t = 40$ pA). c) Final stage of the reaction after further annealing the sample in b) at 50°C for another 420 s ($V_s = -2.7$ V, $I_t = 30$ pA). All the images shown have a size of 40 x 40 nm$^2$ and were acquired at $T = 7$ K.
Figure 4.13: a) Simulated relaxed structure for the PFPA/PFPN nanostructure on GaP(110). Calculated STM image of the PFPA/PFPN nanostructures on the GaP(110) surface are shown in c) for occupied states ($V_s = -3 \text{ V}$) and d) for unoccupied states ($V_s = +3 \text{ V}$). High-resolution STM images taken at $T = 7 \text{ K}$ (size: $7.3 \times 5.3 \text{ nm}^2$) of a molecular chain are shown in d) $V_s = -3.2 \text{ V}$, $I_t = 100 \text{ pA}$ and e) $V_s = +2.8 \text{ V}$, $I_t = 15 \text{ pA}$. 
5.1 Introduction

Owing to their inherently 2-dimensional nature, few-layer semiconducting TMDs exhibit a number of unique physical attributes that are extremely sensitive to the number of TMD layers present \[83, 47, 116, 14, 139, 125\]. This provides new opportunities for creating van der Waals heterostructures with tailored properties and designed functionalities. For example, few-layer TMDs have been shown to support larger current densities than single layer electronic nanodevices \[130\], and the photovoltaic response of van der Waals p-n junctions has been shown to be sensitive to the number of TMD layers \[68\]. Despite the promise of few-layer TMDs for electronic and optoelectronic applications, however, there is so far little understanding of how the overall electronic structure evolves with layer number in the 2D limit. Most previous spectroscopic studies of few-layer TMD semiconductors have been via optical measurements \[17, 57, 85, 84, 136\] that only indirectly measure band-structure, as well as photoemission \[139, 56\] studies that primarily focus on states near the Fermi energy and in the valence band. While many theoretical studies have been performed \[13, 62, 103, 27, 48, 91\], a consistent picture has not yet emerged and many critical parameters, such as bandgaps and conduction band structure, remain ambiguous.

5.2 Growth and Structural Characterization

Single layers of MoSe\(_2\) were grown on bilayer graphene (BLG) and HOPG substrates in a molecular beam epitaxy (MBE) chamber with a base pressure of \(2 \times 10^{-10}\) Torr at the HERS endstation of beamline 10.0.1, Advanced Light Source, Lawrence Berkeley National Laboratory. A reflection high-energy electron diffraction (RHEED) system was used to monitor the growth of MoSe\(_2\) layers in-situ. BLG substrates were obtained by flash annealing SiC(0001) substrates to 1600 K \[131\] while HOPG substrates were cleaved under ambient conditions before being placed in the vacuum chamber. Sharp RHEED (fig. 5.2a) and
5.2. GROWTH AND STRUCTURAL CHARACTERIZATION

Figure 5.1: a) Schematic representation of the formation of the quasi-commensurate superperiodicity (i.e. moiré pattern) due to the atomic lattice mismatch between MoSe$_2$ and graphene (3:4). b) Example of a small rotational misalignment ($\theta = 1.5^\circ$) between MoSe$_2$ and graphene showing the large effect on $\alpha$. c) Atomic-resolution STM image of monolayer MoSe$_2$ showing an incommensurate 9.65 Å x 9.65 Å moiré pattern with an angle of $\alpha = 6^\circ$. The rotational misorientation between MoSe$_2$ and graphene lattices is $\approx 1.5^\circ$ (75 Å x 75 Å, $V_s = +0.5$ V, $I_t = 40$ pA, $T = 5$ K). d) Moiré superlattice periodicity plotted as a function of the measured angle $\alpha$ between the atomic lattice vectors and the moiré unit vectors for different regions and samples.

Low-energy electron diffraction (LEED) patterns (fig. 5.2c) of the BLG substrates indicate their high-quality epitaxy and cleanliness. High-purity Mo and Se were evaporated from an electron-beam evaporator and a standard Knudsen cell, respectively. The flux ratio of Mo to Se was controlled to be 1:8. The growth rate was 0.12 ML per minute. During the growth process the substrate temperature was kept at 530 K, and after growth the sample was annealed to 900 K for 30 minutes. Fig. 5.2b shows the RHEED pattern of a MoSe$_2$/BLG layer with 0.8 ML coverage. A distinct MoSe$_2$ (1 x 1) pattern can be observed, while the graphene pattern is almost invisible. Fig. 5.2d shows the co-existing LEED pattern of
both the BLG substrate (red circles) and MoSe₂/BLG film (green circles). This LEED pattern indicates that MoSe₂ layers grow with approximately the same lattice orientation as graphene. However, a more detailed analysis of the diffraction spots of MoSe₂/BLG reveals that their intensity is slightly stretched along the rotational direction, indicating that monolayers of MoSe₂ also show small rotational misaligned domains \( \theta < \pm 4^\circ \) (red and green dashed lines in fig. 5.2d). This is consistent with the moiré patterns observed in the STM images of MoSe₂/BLG (fig. 5.1). After growth, the sample was transferred directly into the analysis chamber (base pressure of \( 3 \times 10^{-11} \) Torr) for low temperature (40 K) core level spectroscopy experiments. The photon energy was set at 70 eV, with energy and angular resolution of 25 meV and 0.1°. Fig. 5.2e and the zoom-in inset show the characteristic core levels of Mo (36.4 eV of 4p\(_{3/2}\) orbit and 38.2 eV of 4p\(_{1/2}\) orbit) and Se (54.7 eV of 3d\(_{5/2}\) orbit and 55.5 eV of 3d\(_{3/2}\) orbit) of MoSe₂. We have also characterized the MoSe₂ layers by Raman spectroscopy at room temperature. Raman measurements were performed using continuous wave excitation centered at 488 nm, with the power of 920 \( \mu \)W and a focused spot about 1 \( \mu \)m in diameter. Fig. 5.2f shows a typical Raman spectrum showing distinctive [123] peaks for MoSe₂/BLG at 241.0 cm\(^{-1}\) (A\(_{1g}\), out of plane) and 287.5 cm\(^{-1}\) (E\(_{2g}\), in plane) with FWHM (full-width-at-half-maximum) of 5.2 cm\(^{-1}\) and 4.0 cm\(^{-1}\), respectively.

In order to protect the film from contamination and oxidation during transport through air to the UHV-STM chamber, a Se capping layer with a thickness of 10 nm was deposited on the sample surface after growth. For subsequent STM experiments, the Se capping layer was removed by annealing the sample at 600 K in UHV for 30 minutes. After this final annealing, the samples were transferred, without breaking UHV conditions, into the cryogenic STM for surface imaging and spectroscopy. The STM image in fig. 5.3 shows the typical morphology of a 0.8ML MoSe₂/BLG sample.

### 5.3 STM/STS

We performed a combined STM/STS/theory study of few-layer MoSe₂ on bilayer graphene, where we characterized how the electronic bandgap \( (E_g) \), the valence band local density of states (LDOS), and the conduction band LDOS change with the number of MoSe₂ layers between 1 (monolayer – ML), 2 (bilayer – BL) and 3 (trilayer – TL). These measurements compare favorably with \textit{ab initio} GW calculations, revealing the important influence of interlayer coupling and Coulomb interactions on these properties, as well as the relative contributions from different parts of the Brillouin zone.

The STM/STS experiments were carried out on high quality MoSe₂ grown on bilayer graphene (BLG) on 6H-SiC(0001) substrates via molecular beam epitaxy [139]. A sketch of the structure of few-layer MoSe₂ is shown in fig. 5.4a. Fig. 5.4b depicts the 2H stacking arrangement for MoSe₂, which we have confirmed in this study based on comparison between experiment and theory (see SI for a detailed discussion of the stacking). Samples grown with an average MoSe₂ coverage ranging between 0.8 ML and 2 ML exhibit co-existing regions of
ML, BL, and TL MoSe$_2$, as well as bare BLG substrate, as shown in the STM image of fig. 5.4c. While the TL regions in fig. 5.4c are relatively small compared with the ML and BL regions, we are able to tune the sizes of the different layered regions by altering the MoSe$_2$ coverage.

Variations in the electronic structure between ML, BL, and TL MoSe$_2$ films on BLG were experimentally determined via STS using standard lock-in techniques [125]. All STS data were acquired at least 5nm away from step edges, defects, and domain boundaries. Figs. 5.5a-c show typical STM dI/dV spectra for ML, BL, and TL MoSe$_2$, respectively. Each spectrum reveals a relatively wide bandgap surrounded by features in both the valence and conduction bands. Prominent features that determine the band edges ($V_1, C_1$), as well as newly discovered features in the conduction band ($C_1, C_2$) are marked in the spectra. Bandgap values were determined by examining the dI/dV spectra on a logarithmic scale (figs. 5.5d-f) and following the statistical analysis procedure described in ref [125]. For ML, BL, and TL MoSe$_2$/BLG we determine bandgap values of $E_{g,ML} = 2.18 \pm 0.04$ eV,
Figure 5.3: STM image showing the typical morphology of an MoSe$_2$/BLG sample studied in our work. [14]

$E_{g, BL} = 1.56 \pm 0.04$ eV, and $E_{g, TL} = 1.32 \pm 0.04$ eV, respectively. Uncertainty in the values of $E_g$ arises mainly due to lateral spatial inhomogeneity and tip-induced band bending [125, 35]. Lateral inhomogeneity causes band edges to rigidly shift by 10s of meV from point to point in both the bilayer and trilayer, while lateral variations in ML MoSe$_2$ are smaller by an order of magnitude. These rigid shifts are presumably due to inhomogeneous doping effects and do not significantly affect the measured energy gap values. The position of the Fermi energy ($V_{bias} = 0$V) with respect to the band edges indicates that these samples have very low n-type doping.
Figure 5.4: (a) Sketch of few-layer MoSe$_2$. Se atoms are shown in green, while Mo atoms are in purple. (b) 2H stacking configuration of MoSe$_2$ with both the Se and the Mo atoms in an AB1 stacking pattern. (c) Typical STM image of MoSe$_2$/BLG ($V_{\text{bias}} = +1.5V$, $I_t = 30pA$). Reproduced from [14].

5.4 Theory

In order to interpret our experimental results, we performed *ab initio* simulations of the electronic structure of ML, BL, and TL MoSe$_2$. These simulations allowed us to system-
Figure 5.5: Representative STS spectra obtained for (a) ML MoSe$_2$/BLG (lockin wiggle voltage: $\delta V = 4$ mV, $f = 872$ Hz, set point current: $I_t = 5$ nA), (b) BL MoSe$_2$/BLG (lockin wiggle voltage: $\delta V = 5$ mV, $f = 871$ Hz, set point current: $I_t = 100$ pA), and (c) TL MoSe$_2$/BLG (lockin wiggle voltage: $\delta V = 5$ mV, $f = 871$ Hz, set point current: $I_t = 5$ nA). (d-f) Same STS curves shown on a logarithmic scale to highlight the electronic band edges (band edges are marked by dashed lines). Reproduced from [14].

atically study how the electronic structure of few-layer MoSe$_2$ is affected by the following factors: (1) different multilayer stacking configurations; (2) many-electron interactions; (3) interactions with the substrate; and (4) the spatial distribution of electronic states. We start by discussing the role of the stacking configuration. Five possible stacking configurations exist for two layers of MoSe$_2$. Three of these have an inversion center and two do not. We performed density functional theory (DFT) simulations for all five stacking configurations and determined that the stacking labeled AB1 (fig. 5.4b) is the correct stacking sequence based on both its calculated stability and its match with experimentally observed spectroscopic features (see sec. 5.4.1 for more details). All calculations for BL and TL MoSe$_2$ were therefore performed using the AB1 structure.

Many-electron interactions were included in our calculations through the \textit{ab initio} GW [54] technique [108, 28] as implemented using the BerkeleyGW package [28] (this was necessary since bare DFT does not yield accurate quasiparticle energies). In the first stage of the calculations we neglected the effect of the substrate by considering free-standing ML,
BL, and TL MoSe\textsubscript{2}. In order to speed the convergence with respect to k-point sampling, we employed non-uniform sampling of the Brillouin zone, where the smallest q-vector corresponds to 1/1150th of a reciprocal lattice vector (more details in sec. 5.4.2). To address the role of the substrate we then calculated the effect of a doped bilayer graphene substrate on few-layer MoSe\textsubscript{2} (the SiC was ignored since it is much less polarizable than BLG and is further away from the MoSe\textsubscript{2} layers). BLG screening of the MoSe\textsubscript{2} layers was calculated following the same method as in ref. 125.

The final calculated quasiparticle band structure (including screening contributions from the BLG substrate) for ML, BL, and TL MoSe\textsubscript{2} is plotted in the right panels of fig. 5.6. This electronic structure was used to simulate the STM differential conductance (dI/dV) via a WKB approximation having no adjustable parameters (see sec. 5.4.3 for technical details), and the simulation results are compared with the experimental STS spectra in the left panels of fig. 5.6. We observe good agreement between the theoretical and experimental dI/dV curves, especially near the valence band maxima (VBM) and conduction band minima (CBM). This procedure allows us to identify the reciprocal-space origin of the experimental features \( V_1 \), \( C_1 \), and \( C_2 \) in fig. 5.5 by calculating the contributions of different regions of the Brillouin zone. We are thus able to conclude that the experimental valence band feature \( V_1 \) originates from the K point for the ML, and from the \( \Gamma \) point for the BL and TL structures. The experimental conduction band features \( C_1 \) and \( C_2 \) are seen to arise from both the \( \Lambda_{\text{min}} \) and \( \Sigma_{\text{min}} \) points of reciprocal space, where \( \Lambda_{\text{min}} \) is the point halfway between \( \Gamma \) and K, and \( \Sigma_{\text{min}} \) is the point halfway between \( \Gamma \) and M (see inset in fig. 5.6). The general good agreement between theory and experiment (for both the valence and conduction bands) is strong evidence that the main features seen in the experimental STS spectra come from the intrinsic electronic structure of MoSe\textsubscript{2} and not from extrinsic effects, such as defect states.

A comparison of experimental and theoretical bandgaps for few-layer MoSe\textsubscript{2} can be seen in fig. 5.7. The most accurate calculated bandgaps (taking into account both GW and substrate corrections) for the ML, BL, and TL structures are \( 2.05 \pm 0.15 \) eV, \( 1.65 \pm 0.15 \) eV, and \( 1.46 \pm 0.15 \) eV respectively, well within the experimental error bars. While the magnitude of the calculated gap varies with theoretical formalism, all levels of theory predict that monolayer MoSe\textsubscript{2} is a direct bandgap material at the K point of the Brillouin zone, whereas BL and TL MoSe\textsubscript{2} have indirect gaps spanning \( \Gamma_v \) to \( \Lambda^\text{min}_{c} \). These indirect transitions are also corroborated by the experimental dI/dV curves since the valence band edge signal is stronger in the BL and TL structures than in the ML structure, indicating that the valence band edge is likely closer to the \( \Gamma \) point in BL and TL MoSe\textsubscript{2}. The effect of the substrate reduces the energy gaps inhomogeneously in reciprocal space, but the indirect gap is slightly more affected. In all cases the substrate plays a decreasing role as the number of layers is increased, as expected.

We are able to gain further insight into the electronic structure of few-layer MoSe\textsubscript{2} by examining how the spatial dependence of the simulated electronic states changes with layer number. Fig. 5.8 shows the modulus squared of ML and TL wavefunctions at the \( K_c \), \( \Gamma_v \), and \( \Lambda^\text{min}_{c} \) points in the bandstructure. The major contribution to the conduction band state at \( K_c \) (upper left panel) is from the Mo d orbital, so it is not expected to hybridize significantly
Figure 5.6: Right panels: *ab initio* GW band structure of ML, BL, and TL MoSe$_2$, including screening effects from the BLG substrate. Left panels: corresponding simulated STM dI/dV spectra (solid blue lines) along with experimental STM dI/dV spectra for ML (dark red), BL (orange) and TL (yellow) MoSe$_2$. The horizontal solid lines mark the experimental VBM and CBM, and the dashed lines denote the experimental Fermi energy. [14]
as we add more layers. Indeed, the corresponding state at $K_c$ in the TL structure (lower left panel) looks very similar to the ML state. The valence $K_v$ states (not shown) also display little hybridization, and so we conclude that the direct bandgap at $K$ is not significantly affected by hybridization between different layers. This picture is consistent with the fact that the direct gap at $K$ predicted by DFT is constant with the number of layers (green line in fig. 5.7 left panel). The picture is different for the indirect gap. The $\Gamma_v$ state on ML MoSe$_2$ (upper middle panel in fig. 5.8) has a significant contribution from Se p states which are able to interact with Se atoms in adjacent layers. Indeed, the corresponding state $\Gamma_v$ on TL MoSe$_2$ (lower middle panel) displays significant hybridization. The conduction band state at $\Lambda_c^{\text{min}}$ is qualitatively different in the degree to which it is highly delocalized. This state is strongly modified as its spatial confinement is decreased by going from the ML to the TL structure (right panels). These differences in the character of the $\Gamma_v$ and $\Lambda_c^{\text{min}}$ states are responsible for driving the direct-to-indirect transition in MoSe$_2$ as layer number is increased.

Figure 5.7: Direct and indirect bandgaps for few-layer MoSe$_2$ calculated within different levels of theory (triangles and squares) and obtained from experimental STS measurements (diamonds). The shaded regions mark the theoretical uncertainty in the GW calculations. All levels of theory predict a crossover from direct to indirect bandgap as the number of layers is increased from one to two. The theoretical uncertainty arises primarily due to the GW approximation of the electronic self-energy and the approximate treatment of the substrate. [14]
Figure 5.8: Modulus squared of calculated electronic wave functions for different Bloch states for ML and TL MoSe$_2$. The horizontal axis follows the [110] direction (same as Fig. 5.4a), the vertical axis points in the out-of-plane direction, and the wave functions have been integrated in the direction perpendicular to the page. Se atoms are shown in green, while Mo atoms are in purple.
5.4.1 Stacking Details

There are five possible commensurate stacking configurations for bilayer MoSe\textsubscript{2} (figs. 5.10a-e). Of these, three stacking configurations, referred to as AB–stacked, have an inversion center and two configurations, referred to as AA–stacked, do not. There are two configurations (AA1 and AB1) where a Mo atom in the top layer is above a Se atom in the bottom layer. There is one configuration (AB2) where a Se atom in the top layer is above the hexagon center of the bottom layer, and two configurations (AA3 and AB3) where a Se atom in the top layer is directly above a Se atom in the bottom layer. To determine the stacking configuration of our samples, we performed fully relativistic density functional theory (DFT) calculations using the local density approximation (LDA) and scalar relativistic DFT calculations using both LDA and the van der Waals density functional with Cooper exchange (vdW–DF–c09x) \[29, 25\]. We find that AA1 and AB1 are the most stable stacking configurations. AA1 and AB1 also minimize the interlayer distance, suggesting that steric repulsion effects determine the stability of MoSe\textsubscript{2} stacking configurations, as is also the case in MoS\textsubscript{2} \[78\]. The other stacking configurations, AA3, AB2, and AB3, are between 0.03 and 0.09 eV/(unit cell) higher in energy than AB1 and AA1. The band gaps and total energies of the different MoSe\textsubscript{2} stacking configurations are reported in the table in fig. 5.9.

Since AA1 has no inversion symmetry, spin-orbit coupling splits the valence bands near the K point into four bands that are roughly equally spaced (fig. 5.10f). In the bandstructure of AB1 (fig. 5.10g), however, time reversal and inversion symmetries ensure that the four highest valence bands become two doubly degenerate bands, which are separated by 0.23 eV. Our STM data (fig. 5.11b) and previously published ARPES measurements of our bilayer MoSe\textsubscript{2} samples \[139\] show two valence bands at the K point separated by 0.2 eV. This strongly suggests that our sample has AB1 stacking. AB1 is also the bulk stacking configuration of 2H–MoSe\textsubscript{2}. Hence, all our GW calculations are done on AB1–stacked MoSe\textsubscript{2}.

5.4.2 Electronic Structure Calculation Details

Mean-field density functional theory (DFT) calculations in the local density approximation (LDA) were performed by Steve Louie’s group using the Quantum Espresso code \[11\]. The calculations were done in a supercell arrangement with a plane-wave cutoff basis using norm-conserving pseudopotentials with a 125 Ry wave function cutoff. We included the Mo semicore 4d, 4p and 4s states as valence states for our DFT and GW calculations. The distance between repeated supercells in the out-of-plane direction is 50 Å. We fully relaxed the few-layer MoSe\textsubscript{2} structures including the bilayer graphene substrate, and included spin-orbit interactions as a perturbation as in ref. \[103\]. We calculated the substrate screening due to the bilayer graphene following the same procedure as in ref. \[125\].

As mentioned previously, we found the GW quasiparticle bandgap to converge very slowly with respect to the number of k-points in the Brillouin zone. This slow convergence originates from the large lattice constant in the out-of-plane direction, which leads to a
### Fully-relativistic with LDA functional

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<td>$\Gamma$</td>
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### Scalar relativistic with vdW-DF-c09x functional

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<th>$E_{\text{tot}} - E_{\text{tot}(AB1)}$ (eV/unit cell)</th>
<th>$E_{\text{gap}}$ (eV)</th>
<th>VBM</th>
<th>CBM</th>
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Figure 5.9: Total energy, band gap, valence band maximum (VBM), conduction band minimum (CBM), and gap at K point for different bilayer MoSe$_2$ stacking configurations as calculated with different DFT functionals (total energy is relative to energy of AB1-stacked bilayer). Reproduced from [14].

A sharp variation in the dielectric matrix $\epsilon_{GG'}(q)$ for small wave vectors $q$. A Monkhorst-Pack grid of at least a 60 x 60 x 1 k-points was necessary to converge the quasiparticle bandgap to within 100 meV. In order to address this computational challenge, we employed a non-uniform sampling scheme for the Brillouin zone. We first set up a regular 6 x 6 x 1 Monkhorst-Pack k-grid, and we then overlaid an extra set of 10 q-points around $\Gamma$ to accurately capture the long wave length behavior of the screening for few-layer MoSe$_2$. This non-uniform approach yields the same gaps as those obtained on regular 60 x 60 x 1 k-grids, but at a small fraction of the computational cost.

We estimate our quasiparticle band structures to be converged to within 100 meV for our GW calculations. The error arises mainly from the cutoff of the dielectric matrix (20 Ry) and number of bands (5000) included in the expression for the self-energy operator. We estimate the error as roughly 150 meV for our GW calculations that include substrate
Figure 5.10: MoSe$_2$ stacking configurations: (a) AA1, (b) AA3, (c) AB1, (d) AB2, (e) AB3. (f) Bandstructure of AA1-stacked bilayer MoSe$_2$ from fully-relativistic LDA calculation. (g) Bandstructure of AB1-stacked bilayer MoSe$_2$ from fully-relativistic LDA calculation. Reproduced from [14].
screening. The extra error of around 50 meV is estimated from neglecting hybridization between MoSe$_2$ and BLG, as well as from the discretized frequency sampling employed to calculate the dielectric response from BLG.

### 5.4.3 Theoretical $dI/dV$ Calculation Details

![Figure 5.11: Theoretical $dI/dV$ (blue) for the (a) ML, (b) BL, and (c) TL with partial contributions from several different points in the Brillouin zone: $\text{K}$ (green), $\Gamma$ (red), $\Lambda_{\text{min}}$ (purple), and $\Sigma_{\text{min}}$ (yellow). Reproduced from [14].](image)

We theoretically simulated the MoSe$_2$ LDOS using the Tersoff-Hamann formalism [122]. For each MoSe$_2$ structure, we used a spherically localized tip 4 Å above the top Se atom. The tip position was averaged in a plane parallel to the MoSe$_2$ surface to reduce numerical noise. Fig. 5.11 shows partial contributions to the theoretical $dI/dV$ from the $\Gamma$, $\text{K}$, $\Lambda_{\text{min}}$, and $\Sigma_{\text{min}}$ points in the Brillouin zone. For an MoSe$_2$ ML, this wavevector-resolved $dI/dV$ break-down indicates that the feature labeled $V_1$ comes from the K-point (not visible in the scale), and that the feature labeled $C_1$ comes from states from $\Lambda_{\text{min}}$ and $\Sigma_{\text{min}}$. For BL MoSe$_2$, feature $V_1$ comes from $\Gamma$, $C_1$ comes from $\Lambda_{\text{min}}$, and $C_2$ comes from $\Sigma_{\text{min}}$. For the TL, feature $V_1$ comes from $\Gamma$, $C_1$ comes from $\Lambda_{\text{min}}$, and $C_2$ comes from a combination of $\Lambda_{\text{min}}$ and $\Sigma_{\text{min}}$.

### 5.5 Conclusion

In conclusion, we measured the electronic structure of semiconducting MoSe$_2$ as a function of layer number for monolayer, bilayer, and trilayer stacking. We find that the addition of layers in the 2-dimensional regime causes the electronic bandgap to significantly shrink in size while simultaneously creating new features in both the valence and conduction bands. These experimental results are consistent with theoretical GW calculations that take into account stacking geometry, wavefunction hybridization, electron-electron interactions, and substrate screening, thus providing new insight into how different electronic structure features arise.
from various Bloch state properties within the Brillouin zone. Such deeper understanding of the electronic properties of few-layer TMD materials will help in the creation of next-generation 2D nanodevices.
6.1 Excitons

Exciting electrons across an energy gap in a semiconductor is an overall charge-neutral process. However, the electron that gets excited will in general feel a weak Coulomb attraction to the hole that it left behind, similar to how the electron in a hydrogen atom feels an attraction to the proton. In condensed matter parlance, we call this two-particle entity an exciton. These excitons occur in all materials exhibiting a bandgap, but the attraction between the electron and hole is often negligible.

Figure 6.1: Exciton energy levels in a simple semiconductor. The excited electron is lower in energy than the bottom of the conduction band due to the attractive potential from the hole. Reproduced from [60].
The strength of the interaction between the electron and the hole is described in terms of the exciton binding energy. This is the energy that must be supplied to break apart the exciton into individual free charge carriers. In an admittedly misleading way, we experimentalists tend to think of excitons in an inherently single-particle picture, where the exciton has energy levels corresponding to states in which the electron can exist (think of the electron in hydrogen again). We often sketch these states on a bandstructure diagram (fig. 6.1), with the spectrum of bound states lying in the gap below the onset of the conduction band. The value of the exciton binding energy is important for optoelectronics applications, as the exciton states can actually show up in absorption and photoluminescence experiments. In fact, in 2D TMD semiconductors, the rich variety of exciton states appearing in the optical absorption spectra tend to obscure all-optical measurements of the band edges (fig. 6.2).

![Figure 6.2](image)

Figure 6.2: Left: Sketch of the optical absorption of a conventional semiconductor. In both 2D and 3D, the bulk band edge can be determined optically. Right: Theoretical optical absorption in a 2D TMD semiconductor. The rich exciton structure obscures optical measurements of the band edge. (left reproduced from [23], right reproduced from [103]).

In keeping with our comparison between excitons and hydrogenic systems, the exciton levels can often be described as a Rydberg-like series, with the lowest level state corresponding to the exciton ground state, and the other levels to various excited states. Following ref. [23], the hydrogenic Rydberg series comes from a 2D model with the effective mass Hamiltonian

$$H = -\frac{\hbar^2}{2\mu} \nabla_r^2 + V_{eh}(r)$$  \hspace{1cm} (6.1)
where
\[ \mu = \frac{m_e m_h}{m_e + m_h} \]  \hspace{1cm} (6.2)
is the exciton reduced mass, and
\[ V_{eh}(r) = -\frac{e^2}{er} \]  \hspace{1cm} (6.3)
is a screened Coulomb potential created by the electron and hole. The energy of the exciton
states from this model, referenced to the bottom of the conduction band (in hydrogen this
would be equivalent to giving the energy differences between the states and the continuum)
is found to be
\[ E_b^{(n)} = \frac{\mu e^4}{2\hbar^2 c^2(n - 1/2)^2} \]  \hspace{1cm} (6.4)
for a given quantum number n (n=1 for the ground state). In many conventional 3D
semiconductors, this model holds well and predicts the progression of exciton states. In 2D,
however, the model tends to break down. If you are dealing with a single layer, or a few
layers, of atoms, then this effective mass Hamiltonian is no longer valid, as the screened
Coulomb potential becomes significantly anisotropic. When the electric field lines between
the electron and the hole pass through the plane of the material, they will be screened by
the charge carriers. However, when the field lines protrude above or below the plane of the
material, they will not be effectively screened, behaving similar to field lines in vacuum.
Including substrates makes the situation even more complicated. This winds up causing
the exciton energy levels in 2D TMD semiconductors to behave in a distinctly non-Rydberg
fashion.

6.2 How to Measure the Exciton Binding Energy

In order to determine the exciton binding energy, two quantities are needed. The first is
the electronic (or quasiparticle) bandgap. This is the energy required for the onset of direct
band-to-band transitions in the semiconductor. In many systems, this can be measured
optically (see fig. 6.2). However, in the few-layer TMDs, this is a difficult quantity to
extract from all-optical measurements. STM, on the other hand, provides a perfect solution.
Through dI/dV spectroscopy, the electronic bandgap can be directly determined. Because
STS is not a charge-neutral excitation spectroscopy, it is not complicated by the exciton
physics. The bandgap measured in STS is the single-particle electronic bandgap that we
desire.

The second quantity needed to extract the exciton binding energy is the optical bandgap.
This is the minimum photon energy needed to excite an electron from the top of the valence
band. While this value can be extracted directly from optical absorption measurements,
it is often difficult to do this in TMDs because the absorption peaks sit on top of a large
polynomial background signal, making their peak energies difficult to determine. Photo-
luminescence spectroscopy, however, is a nearly background-free measurement technique.
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which can give reliable values for the optical bandgap, provided the material is a direct-gap semiconductor. To perform this experiment, a laser whose photon energy is higher than the electronic bandgap is used to illuminate the surface, exciting electrons from the valence band to the conduction band. These excited electrons start high in the conduction band, but fall through generally non-radiative channels to the bottom of the conduction band, where they can then radiatively decay by recombining with a hole in the top of the valence band (assuming a direct bandgap). The photon given off in the recombination process gives the energy of the bandgap. In the case of excitons, this energy is decreased by the exciton binding energy. Thus the photoluminescence spectrum directly provides the optical bandgap. In the case of semiconducting TMD monolayers, there are often two peaks seen in absorption and PL studies, the so-called A and B excitons (see fig. 6.9d). These come about because the top of the valence bands at the K point are split by the spin-orbit interaction. In the case of a PL measurement, the A exciton comes from an excited electron recombining with a hole in the top spin-split band at the K point, while the B exciton comes from recombination with a hole in the bottom spin-split band. By measuring the difference between the A and B excitons, one can quickly determine the magnitude of the spin splitting of the states at the top of the valence band.

The exciton binding energy that we are after is the difference between the electronic bandgap and the optical bandgap (see fig. 6.3). In determining this value, it is important to perform the STS and PL measurements on the same samples. If a parameter changes between the two measurements (such as the substrate or the dielectric screening environment), then the comparison between the two values becomes meaningless.

6.3 Exciton Binding Energy in Single Layer MoSe$_2$

As mentioned in the previous section, reduced screening in two dimensions results in enhanced electron–electron interactions, which can generate large bandgap renormalization and exotic excitonic effects [18, 105, 52, 103]. We performed a rigorous experimental study of the extraordinarily large exciton binding energy in 2D semiconducting MoSe$_2$. We determined the single-particle electronic bandgap of single-layer MoSe$_2$ via scanning tunnelling spectroscopy, as well as the two-particle exciton ground state energy using photoluminescence spectroscopy. Combining these yields an exciton binding energy of 0.55 eV for monolayer MoSe$_2$ on bilayer graphene – orders of magnitude larger than what is seen in conventional 3D semiconductors and significantly higher than what we see for MoSe$_2$ monolayers in more highly screening environments. This finding is corroborated by our ab initio GW and Bethe–Salpeter equation calculations [54, 108] which include electron correlation effects. The renormalized bandgap and large exciton binding we observed will have a profound impact on electronic and optoelectronic device technologies based on single-layer semiconducting TMDs.

The remarkable properties of atomically thin semiconducting TMD layers include an indirect-to-direct bandgap crossover when going from bulk to monolayer [83, 116, 139],
Figure 6.3: In order to determine the magnitude of the exciton binding energy, it is necessary to know both the electronic bandgap ($E_g$) and the optical bandgap ($E_{\text{opt}}$). The difference between these two quantities yields the exciton binding energy ($E_b$).

field-induced transport with high on–off ratios [104], valley-selective circular dichroism [85, 136, 17, 57], and a strong photovoltaic response [9, 45]. Enhanced Coulomb interactions due to low-dimensional effects tend to increase the quasiparticle bandgap through a process known as bandgap renormalization, as well as to cause electron–hole pairs to form more strongly bound excitons [18, 103, 62, 103]. Such effects have been observed previously in other reduced dimensionality systems, including carbon nanotubes [129] and nanostructured materials [112]. The electronic bandgap ($E_g$) characterizes single-particle (or quasiparticle) excitations and is defined by the sum of the energies needed to separately tunnel an electron and a hole into monolayer MoSe$_2$. The optical bandgap ($E_{\text{opt}}$) describes the energy required to create an exciton, a correlated two-particle electron–hole pair, via optical absorption. The difference in these energies ($E_g - E_{\text{opt}}$) directly yields the exciton binding energy ($E_b$) with no need for further modelling. We found evidence of significant Coulomb-driven quasiparticle bandgap renormalization and unusually strong exciton stability in 2D MoSe$_2$ through the independent determination of $E_g$ and $E_{\text{opt}}$ using STS and PL spectroscopy, respectively. Using this technique we also directly observed a reduction in exciton binding energy as substrate screening was increased.
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Figure 6.4: a) Top and side view sketches of monolayer MoSe$_2$ including the substrate. b) High resolution STM image of MoSe$_2$/BLG ($V_{\text{bias}} = -1.53$V, $I_t = 20$pA). Approximate moiré unit cell marked in orange, unreconstructed unit cell are marked in green. c) Typical STM image of monolayer MoSe$_2$ showing a 9.7 Å x 9.7 Å moiré pattern ($V_{\text{bias}} = -0.9$V, $I_t = 20$pA). d) High resolution STM image of bare bilayer graphene, showing a characteristic moiré pattern between the two graphene layers. Unreconstructed unit cell shown in red. Reproduced from [125].

6.3.1 STM/STS

STS and PL measurements were both carried out on the same high-quality submonolayer MoSe$_2$ films grown on epitaxial bilayer graphene (BLG) on 6H-SiC(0001), as well as on cleaved graphite (HOPG) substrates. Because the MoSe$_2$ surface coverage for our samples was typically around 0.8 ML, we were able to simultaneously image the MoSe$_2$ monolayer and the underlying substrate using scanning tunnelling microscopy (STM). Figs. 6.4b,d shows atomically resolved STM images taken of an MoSe$_2$ monolayer region and a BLG substrate region, respectively. The BLG substrate (fig. 6.4d) shows typical hexagonal atomic contrast due to the Bernal AB stacking overlaid with the $(6\sqrt{3} \times 6\sqrt{3})$ SiC reconstruction [80]. The high-resolution STM image acquired on MoSe$_2$ (fig. 6.4b) shows a honeycomb atomic lattice with one sublattice appearing brighter than the other. Both sublattices show a unit cell of 3.3Å, corresponding to the interatomic spacing in both the basal Se and Mo planes of MoSe$_2$. The larger-scale MoSe$_2$/BLG image (fig. 6.4c) shows only one sublattice owing to a slightly lower (and more typical) spatial resolution. The atomic registry of the MoSe$_2$ lattice was often oriented precisely with the graphene lattice (yellow arrows in figs.
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but also frequently showed a slight rotation angle (dashed purple lines in fig. 6.4c). An additional periodic superlattice was always visible in the STM images (figs. 6.4b,c). This superlattice is explained by the fact that when the MoSe₂ and graphene lattices are overlaid, four graphene unit cells accommodate three unit cells of MoSe₂, thus forming a quasicommensurate 9.87 Å x 9.87 Å superstructure (a moiré pattern) as observed in the STM images of MoSe₂. Rotationally misaligned MoSe₂ domains show slightly smaller incommensurate moiré patterns. Similar structure was seen in STM images of a single layer of MoSe₂ grown on HOPG.

Figure 6.5: a) Energy diagram schematically indicating the electronic bandgap (E₁), optical bandgap (E₂), and exciton binding energy (E₃). b) STM dI/dV spectrum acquired on monolayer MoSe₂/BLG showing the electronic bandgap and nearby electronic features: V₁₋₄ in the valence band and C₁ in the conduction band (f=871 Hz, I=5nA, Vwiggle=3mV). c) Close-up view of MoSe₂ STS (boxed region in b and d) showing the valence band maximum and V₁ feature. d) Logarithm of a typical dI/dV spectrum used in the statistical analysis to obtain E₁. Reproduced from [125].

We experimentally investigated both the electronic structure and optical transitions in monolayer MoSe₂ by combining STS and PL spectroscopy. Fig. 6.5b shows a typical STM dI/dV spectrum acquired on monolayer MoSe₂/BLG. The observed electronic structure is dominated by a large electronic bandgap surrounded by features labelled V₁₋₄ in the valence band (VB) and C₁ in the conduction band (CB). The MoSe₂ band edges are best determined by taking the logarithm of dI/dV, as shown in fig. 6.5d. There the VB maximum (VBM)
for monolayer MoSe$_2$ is seen to be located at $1.55 \pm 0.03$ V and the CB minimum (CBM) at $0.63 \pm 0.02$ V. The relative position of $E_F$ ($V_{bias} = 0$V) with respect to the band edges reveals n-type doping for our samples, although with a very low carrier concentration. We tentatively attribute the n-doping of our MoSe$_2$ samples to intrinsic point defects such as vacancies and/or lattice antisites, which have been found to be responsible for n-doping in similar materials [51]. Our STS measurements yield a value for the single-particle electronic bandgap for MoSe$_2$/BLG of $E_g = E_{CBM} - E_{VBM} = 2.18 \pm 0.04$eV. Similar behaviour is seen for MoSe$_2$/HOPG, except that the electronic bandgap is reduced by 11% owing to the different dielectric screening properties of the two substrates.

Figure 6.6: The bandgap of monolayer MoSe$_2$ was determined from the logarithm of 57 individual STS curves. One such curve is shown in purple. The logarithm of the mean of the signal within the bandgap is depicted in blue as $C_{g,av}$. The green line is two standard deviations above $C_{g,av}$. The red lines on either side of the curve are linear fit lines to the band edges. The gap edges are defined as the energies at which the linear fit lines cross $C_{g,av}$. Reproduced from [125].

The electronic bandgap value of $E_g = 2.18 \pm 0.04$ eV obtained for monolayer MoSe$_2$/BLG was determined through a statistical analysis of 57 individual STS curves obtained on multiple MoSe$_2$/BLG samples with multiple STM tips. These STS curves were all acquired far from the edges of monolayer MoSe$_2$ patches ($d > 1$ nm). Due to the wide variation in signal strength near a band edge, it was necessary to use the logarithm of the $dI/dV$ curves for accurate gap determination. For each curve, the same procedure was utilized, as follows: we first vertically offset all the data by a factor of 1.1 times the absolute value of the overall minimum value of the spectrum in order to make sure that we could take the logarithm without running into any negative numbers (we tried varying the amount of the
offset between 1.1 and 10 times the minimum value and observed no significant change in the final gap value). We then calculated the mean value of the signal within the bandgap to determine the average floor of the spectrum ($C_{g,av}$), as well as the standard deviation ($\sigma$) for signal fluctuations around $C_{g,av}$. After taking the logarithm of the curve, we determined the energies at which the CB and VB edges in the $dI/dV$ signal approached to within $2\sigma$ of $C_{g,av}$. These energies are labelled $E_{\text{VB},2\sigma}$ and $E_{\text{CB},2\sigma}$ (see fig. 6.6). Linear fits were then made to the log($dI/dV$) spectrum for energies $E_{\text{VB},2\sigma} - \Delta E < E < E_{\text{VB},2\sigma}$ (the VB fit) and for energies $E_{\text{CB},2\sigma} < E < E_{\text{CB},2\sigma} + \Delta E$ (the CB fit). $\Delta E = 150 \text{ mV}$ was determined as the largest energy range over which the linear fit of to the log($dI/dV$) signal yielded an $R^2$ value (the coefficient of determination, which indicates how well data is fit by a regression [127]) greater than 0.95 (we find that any value of $\Delta E$ in the range $100\text{ mV} < \Delta E < 300 \text{ mV}$ results in a mean bandgap well within our error bars). The bandgap edges ($E_{\text{VBM}}$ and $E_{\text{CBM}}$) were then determined as the points where the VB and CB linear fit lines intersect the bandgap floor determined by $C_{g,av}$. Our reported value of $E_g = 2.18 \pm 0.04 \text{ eV}$ is the average value of $E_{\text{CBM}} - E_{\text{VBM}}$ determined in this way for the 57 STS curves. The uncertainty was determined by adding the standard errors (i.e. standard deviations of the mean) of the VBM and CBM in quadrature, as well as including the effects of band bending. There is some slight ambiguity regarding the precise band edge location due to quasiparticle lifetime broadening effects [61]. A simple analysis using conventional tunnel current expressions [35, 113, 65] shows that our algorithm (above) captures the band edge within this broadening limit. Such energy broadening is expected to be significantly less than the photoluminescence FWHM, which puts it well within our stated error bars.

The uncertainty in $E_g$ arises from both lateral positional variations as well as tip-induced electronic artifacts (which we broadly refer to as tip-induced band bending (TIBB)). TIBB can arise owing to poor screening of electric fields at a semiconducting surface [35]. We are able to rule out TIBB as a significant source of error in our measurements by two methods: tip-sample distance variation (which allows us to access different electric field values) and comparison of our spectra with our angle-resolved photoemission spectroscopy (ARPES). Although TIBB effects can only be roughly estimated by numerical models [35, 26, 80], they are strongly dependent on accessible experimental parameters such as tip-sample distance (or, equivalently, open-loop tunnel current, $I_t$), tip-sample work function differences, and doping concentration. In order to estimate the influence of TIBB and related electron-hole interactions in the tip-sample junction on our STS measurements of single-layer MoSe$_2$, we obtained $dI/dV$ curves at a number of different tip-sample distances, as indicated by the initial tunnel current set-point $I_t$ (always obtained using the same initial set-point voltage, $V_{\text{bias}} = +1.5 \text{ V}$). In fig. 6.7 we show spectra obtained with a range of initial $I_t$ values covering more than 4 orders of magnitude, equivalent to a variation in tip-sample distance close to 5 Å.

For measurement of TIBB effects on the VBM we focused on the STS feature $V_2$. The reason for this is that the amplitude of feature $V_1$ is too strongly tip-height dependent (i.e. it disappears for larger tip-height distances) since $V_1$ derives from a K-point state in reciprocal space, whereas feature $V_2$ has a more robust tip-height amplitude dependence.
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Figure 6.7: $dI/dV$ spectra acquired at different initial tunnelling set-point currents ($f = 873$ Hz, $V_{\text{rms}} = 2.8$ mV, and starting set point voltage = +1.5 V). All curves were taken consecutively with the same tip apex. Reproduced from [123].

since it derives from a $\Gamma$-point feature (see previous section). Feature $V_2$ is thus the nearest spectroscopic feature to the VBM whose height-dependent energy shifts we can resolve with high accuracy. Since $V_2$ occurs at a higher magnitude of voltage than the VBM, TIBB-induced variation in the location of $V_2$ puts an upper bound on TIBB-induced variation of the VBM. We find that for tunnel current set points ranging over 0.01 nA to 500 nA (fig. 6.7) the energy variation in the location of $V_2$ is $\Delta V < 25$ mV. TIBB-induced error in the location of the VBM is thus $\Delta E_{\text{VBM}} < 25$ meV.

In order to deduce the TIBB-induced error in our measured value of the CBM, we directly applied our band-edge finding algorithm (described in the previous section) to determine $E_{\text{CBM}}$ in spectra measured for tunnel current set-points ranging over 0.01 nA to 500 nA. For this range of tip-sample distances we see no systematic TIBB-induced shift in $E_{\text{CBM}}$ and the fluctuations we observe are well within the fluctuation limits that we observed previously.
The total TIBB-induced error in our experimental determination of $E_g$ is thus $\Delta E_{g,TIBB} < 25$ meV. This TIBB-induced uncertainty is accounted for in the total uncertainty that we report for our measured value of $E_g$ for single layer MoSe$_2$: $E_g = 2.18 \pm 0.04$ eV.

The spectroscopic features $V_{1-4}$ observed in our STS experiments on MoSe$_2$/BLG (fig. 6.8a) can be interpreted with the aid of the VB electronic structure revealed by ARPES measurements performed previously by some of us [139]. Fig. 6.8b shows a typical ARPES spectrum of a 0.8 ML MoSe$_2$ sample grown on BLG on SiC(0001). The VB energy region of monolayer MoSe$_2$ is dominated by three dispersive bands with hybridized Mo-d and Se-p character (bands labelled in fig. 6.8b as 1-3). In addition to the characteristic MoSe$_2$ electronic features, linear bands from graphene are also visible in the spectrum and mostly
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The VBM of single-layer MoSe$_2$ is located via ARPES at the onset of the split band 1 (-1.53 eV relative to E$_F$) at the K-point, which unambiguously characterizes a single layer of MoSe$_2$ [139]. Similarly, STS experiments show the VBM at $-1.55 \pm 0.03$ eV, which is the onset of the STS feature V$_1$ (fig. 6.5c and 6.8a). Therefore, we can identify the feature labeled V$_1$ with the spin-split band that occurs at the K point of 2D semiconducting TMDs. The other main STS features in the VB energy range (V$_2$ - 4) are located 0.44 eV (V$_2$), 1.10 eV (V$_3$) and 1.42 eV (V$_4$) below the VBM. A simple comparison with the ARPES spectrum enables us to identify these features with dispersionless regions of bands 1-3 close to the Γ symmetry point. Dispersionless regions of electronic bands lead to van Hove singularities in the density of states which are often easily detectable via STS. Bands 1 and 3 show no dispersion at the Γ point (0.39 eV and 1.08 eV, respectively, below the VBM) (fig. 6.8a). This is in good agreement with the position of the STS peaks V$_2$ and V$_4$. The feature V$_3$, which is more broadened than V$_2$ and V$_4$, corresponds to the slightly dispersive band 2 along Γ–K. This band shows two dispersionless regions at 1.08 eV and 1.20 eV below the VBM, which is also in good agreement with the STS V$_3$ peak maximum at 1.10 eV below the VBM. The much larger conductivity of peaks V$_2$ - 4 compared to peak V$_1$ is due to k-parallel dependence of the tunneling probability (larger k-values lead to lower tunneling probability due to reduced extension of the wavefunction into the vacuum).

6.3.2 Photoluminescence Spectroscopy

Measurement of the optical bandgap (E$_{opt}$), the electron-hole excitation energy, was performed using PL spectroscopy in Feng Wang’s laboratory. PL from single-layer MoSe$_2$ on either graphene or HOPG is strongly quenched by non-radiative channels opened by the substrate, but the PL signal is still clearly observable as a well-defined peak. A representative set of data taken at two different temperatures for MoSe$_2$/BLG is shown in fig. 6.9. At room temperature, the PL spectra show a clear Lorentzian shape centered at $1.55 \pm 0.01$ eV. At 77 K, the peak position of the PL is shifted to $1.63 \pm 0.01$ eV. This decrease of photon energy at high temperature has been observed previously [109] and is attributed to thermal reduction of the MoSe$_2$ electronic bandgap. As previous studies [109] have shown that PL does not shift significantly when the temperature drops below 77 K, we determined the low-temperature MoSe$_2$/BLG optical bandgap to be E$_{opt} = 1.63 \pm 0.01$ eV (uncertainty here arises from spatial variations and temperature dependence). The optical bandgap rises only slightly (by 2%) for MoSe$_2$/HOPG.

The MoSe$_2$/BLG optical bandgap of E$_{opt} = 1.63$ eV differs from the electronic bandgap E$_g = 2.18$ eV by the amount $0.55 \pm 0.04$ eV, which corresponds to the binding energy of the MoSe$_2$/BLG electron-hole excitation. For MoSe$_2$/HOPG we find that the exciton binding energy is reduced by 51% compared to MoSe$_2$/BLG, which shows directly how increased environmental screening reduces this quantity. The exciton binding energy seen for single-layer MoSe$_2$/BLG is two orders of magnitude higher than the binding energy seen in conventional semiconductors such as Si or Ge.
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Figure 6.9: Representative photoluminescence spectra acquired at room temperature (black) and 77K (green) for 0.8 ML MoSe₂ on BLG. The PL signal at room temperature is centered at 1.55eV. The peak shifts to 1.63eV at 77K. The PL peak corresponds to the lowest-energy exciton transition \(E_{\text{opt}}\) in single-layer MoSe₂. Reproduced from [125].

### 6.3.3 Theory

To better understand and interpret our experimental findings, Steve Louie’s group performed *ab initio* GW [54] and GW plus Bethe-Salpeter equation (GW-BSE) calculations [108, 28] on MoSe₂ using the BerkeleyGW package [28]. This allowed computation of the monolayer MoSe₂/BLG quasiparticle structure and optical transitions, including electron-hole interactions. Within this approach we found that MoSe₂ monolayers are direct gap semiconductors at both the DFT and GW levels of theory. For quantitative comparison between experiment and theory we had to take into account the screening of the MoSe₂ layer by the BLG underneath (the screening from SiC was neglected because its polarizability is much smaller than that of BLG). Substrate screening is expected to decrease both the quasiparticle bandgap and the exciton binding energy of an isolated MoSe₂ layer. To avoid the high computational demands of performing a highly converged calculation for the explicit MoSe₂/BLG supercell system, we developed a novel method to incorporate substrate screening. We first separated the total screening into the intrinsic MoSe₂ and the BLG substrate contributions [76]. We calculated within the random phase approximation (RPA) the intrinsic contribu-
Figure 6.10: a-c) Relevant energy levels sketched for GW-BSE calculation without substrate (a) and with bilayer graphene substrate (b) and experimental data (c). d) Calculated optical absorbance of single-layer MoSe$_2$ with and without electron-hole interactions. The shaded grey area corresponds to energies above the single-particle electronic gap. The experimental differential reflectivity spectrum measured at 77K is shown in green. e) Spatial map of the exciton wavefunction corresponding to the excitonic peak labelled A in a-d (wavefunction is shown with the hole - black circle - fixed in space). Mo atoms are small black square, Se atoms are not shown. Reproduced from [125].

...tion of MoSe$_2$ fully from first principles, including all local field effects. For the substrate contribution, we fully took into account the in-plane substrate long-wavelength screening and the full perpendicular component of the screening while neglecting in-plane local fields produced by the substrate (this is justified by the in-plane delocalization of the orbitals in graphene). Within this approach we calculated a quasiparticle bandgap of 2.13 ± 0.10 eV for MoSe$_2$/BLG, in good agreement with the experimental value of 2.18 ± 0.04 eV. The the-
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Theoretical uncertainty arises primarily as a result of the GW approximation of the electronic self-energy.

Louie’s group performed mean-field density functional theory (DFT) calculations in the local density approximation (LDA) using the Quantum Espresso code [41]. The calculations were done in a supercell arrangement with a plane-wave basis using norm-conserving pseudopotentials with a 125 Ry wave function cutoff. We included the Mo semicore 4d, 4p, and 4s states as valence states for our DFT, GW and GW-BSE calculations. The distance between repeated supercells in the out-of-plane direction was 25 Å. We fully relaxed the MoSe$_2$ geometry and included spin-orbit interactions as a perturbation as in a previous work [103]. Similar to previous calculations [103] on related MoS$_2$, we found it necessary to employ a large energy cutoff of 38 Ry and to use a large number (10,000) of unoccupied states to obtain well-converged quasiparticle energies.

In order to include the substrate screening from the bilayer graphene, we first relaxed a supercell structure with the van der Waals density functional [29] with Cooper exchange [25] and found a separation of 3.4 Å between the MoSe$_2$ layer and the upper graphene layer. We then calculated the irreducible RPA polarizability for the bilayer graphene alone in reciprocal space and mapped the sets of GG$'$ (reciprocal lattice vectors) and qq$'$ wave vectors that describe the polarizability $\chi_{0,\text{bilayer}}$ of bilayer graphene to the primitive unit cell of MoSe$_2$. In this process, we neglected local field components in the direction parallel to the substrate, i.e., we set

$$\chi_{0,\text{bilayer}}(\mathbf{q}) = \chi_{0,\text{MoSe}_2}(\mathbf{q})\delta_{G_xG'_x}\delta_{G_yG'_y}\delta_{G_zG'_z}$$

where $\nu$ is the truncated Coulomb interaction.

We then calculated a correction to the electronic self-energy of MoSe$_2$ using a correction to the screening,

$$\Delta\varepsilon_{GG'}^{-1}(\mathbf{q}) = [1 - \nu(\chi_{0,\text{MoSe}_2}(\mathbf{q}) + \chi_{0,\text{bilayer}}(\mathbf{q}))]_{GG'}^{-1} - [1 - \nu\chi_{0,\text{MoSe}_2}(\mathbf{q})]_{GG'}^{-1}$$

where $\nu$ is the truncated Coulomb interaction.

With this expression for $\Delta\varepsilon^{-1}$, we calculated the correction to the self-energy as $\Delta\Sigma = iG(\Delta\varepsilon^{-1})\nu$, where $G$ is the Greens function. The self-energy of intrinsic MoSe$_2$ was calculated using the GPP model [54], while the correction term was evaluated within the COHSEX approximation. The renormalization of the quasiparticle gap in MoSe$_2$ is not very sensitive to the amount of doping in the bilayer graphene substrate. When we dope the BLG substrate by lowering the Fermi energy by 300 meV, the renormalization of the fundamental gap in MoSe$_2$ differs by less than 10 meV. This justifies the use of undoped BLG substrates in our MoSe$_2$/BLG calculations.

For the GW calculations, the dielectric matrices were evaluated up to a cutoff of 38 Ry on a 12 x 12 x 1 k-grid. Additionally, we calculated a correction to the quasiparticle bandgap as the difference between the gap obtained on a denser k-grid of 21 x 21 x 1 and the gap obtained on a coarser k-grid of 12 x 12 x 1, where these two calculations were performed with a 15 Ry cutoff for the dielectric matrix. This procedure closes the
quasiparticle bandgap calculated without the bilayer graphene substrate by 142 meV, and the gap for the calculation with substrate by 34 meV. For the Bethe-Salpeter equation (BSE) calculation, we first evaluated the necessary matrix elements on a 21 x 21 x 1 k-grid and then interpolated them to a 90 x 90 x 1 k-grid, where we diagonalized the BSE Hamiltonian keeping two conduction and one valence bands. Further increasing the number of bands to three conduction and three valence bands does not change the absorption spectrum in the energy range from 0 up to 2.4 eV.

The uncertainty in the theoretical calculation arises primarily due to the approximation to the electronic self-energy within the GW approach. Our calculated quasiparticle bandgap is converged to within better than 50 meV, where the error arises primarily due to k-point sampling. However, the GW approximation is known to be accurate to within approximately 100 meV \[^{54}\]. So, we estimate that our theoretical quasiparticle bandgap should be accurate to within 100 meV. Similarly, one source of uncertainty when calculating the exciton binding energy is the approximation to the kernel of the electron-hole interaction in the BSE, which is typically a few percent \[^{108}\]. This uncertainty corresponds to at most 25 meV in MoSe\(_2\). On the other hand, we estimate that our numerical solution of the BSE is accurate to within 100 meV due to finite k-point sampling. Therefore, we estimate our exciton binding energy to be accurate to within roughly 100 meV.

Combining this screening approach with the GW-BSE method allowed Louie’s group to calculate the optical spectrum and the exciton binding energy of an MoSe\(_2\) monolayer both with and without BLG substrate screening. We find that the BLG substrate decreases the exciton binding energy from 0.65 ± 0.10 eV to 0.52 ± 0.10 eV, with the latter value in good agreement with the corresponding experimental MoSe\(_2\)/BLG value of 0.55 ± 0.04 eV. Similarly, the calculated optical gap for MoSe\(_2\)/BLG is found to be 1.61 ± 0.14 eV, in good agreement with the measured optical gap of 1.63 ± 0.01 eV. The calculated electronic bandgap, optical gap and exciton binding energies are all graphically compared with the experimental results in the energy level diagrams of fig. 6.10a-c. In fig. 6.10d, we compare our calculated optical absorption spectrum with experimental reflectivity data for MoSe\(_2\)/BLG. We observe good agreement between experiment and theory for the first two excitonic peaks (A and B). Higher energy excitonic states, such as A\(_0\) and B\(_0\), are known to be more affected by electron-phonon interactions \[^{103}\] (not included in the present calculation) and are more spectrally broadened. Fig. 6.10e shows the predicted spatial dependence of the lowest-energy bright exciton state.

### 6.3.4 Effects of Substrate Screening

Because of their two-dimensional nature, the electronic and optical properties of monolayer TMD films are extremely sensitive to the surrounding dielectric environment \[^{62, 87}\]. To investigate the role of substrate screening on the exciton binding energy, we performed STM/STS and PL measurements on monolayer MoSe\(_2\) grown on HOPG graphite and compared it to our measurements of MoSe\(_2\)/BLG. The structure of the MoSe\(_2\)/HOPG is similar to that on BLG. Fig. S8A shows an atomically resolved STM image of the MoSe\(_2\)/HOPG...
surface with a 9.5 Å moiré pattern.

Figure 6.11: a) Atomically resolved STM image of MoSe$_2$ on HOPG. A quasi-commensurate moiré pattern, due to lattice mismatch and rotation between MoSe$_2$ and HOPG, is visible. b) Representative STM dI/dV spectra for MoSe$_2$/BLG (purple) and MoSe$_2$/HOPG (blue) with electronic bandgap values indicated. (f = 873 Hz, I$_t$ = 10 nA, $V_{rms}$ = 3 mV, T = 5K). c) Energy level sketch for MoSe$_2$/HOPG. d) Representative photoluminescence spectrum for MoSe$_2$/HOPG acquired at 77K. The peak corresponds to the lowest-energy exciton transition. Reproduced from [125].
The electronic bandgap of MoSe$_2$/HOPG was measured using low temperature STS (fig. 6.11b). Following the same fitting procedure used as for MoSe$_2$/BLG, we find a bandgap value of $E_g = 1.94 \pm 0.04$ eV for MoSe$_2$/HOPG, an 11% reduction from the bandgap value seen for MoSe$_2$/BLG (spectra for both MoSe$_2$/BLG and MoSe$_2$/HOPG are shown in fig. 6.11b for comparison). The reduced electronic bandgap seen for MoSe$_2$/HOPG is consistent with the increased screening from the underlying graphite substrate [62]. In addition to exhibiting a smaller bandgap, MoSe$_2$/HOPG shows an even smaller amount of n-doping, as seen from the Fermi level location in fig. 6.11b.

Our PL measurements on MoSe$_2$/HOPG, performed at 77K, show a broad peak at a photon energy of 1.67 eV, indicating an optical bandgap of $E_{\text{opt}} = 1.67 \pm 0.03$ eV. This shows a very small 0.04 eV increase in the optical gap for MoSe$_2$/HOPG as compared to MoSe$_2$/BLG. The more significant difference in the PL for these two systems is that the PL signal broadened and quenched for MoSe$_2$/HOPG compared to MoSe$_2$/BLG. This arises mainly from the additional non-radiative channels that are opened by the more highly-conductive graphite substrate which reduces the overall PL signal as well as the quasiparticle lifetime. Combining our STS and PL measurements, we directly determine the exciton binding energy for MoSe$_2$/HOPG to be $E_b = E_g - E_{\text{opt}} = 0.27 \pm 0.05$ eV. This value is 51% smaller than the exciton binding energy found for MoSe$_2$/BLG.

The 51% reduction in exciton binding energy for MoSe$_2$/HOPG compared to MoSe$_2$/BLG qualitatively follows the expectation that increased substrate screening should lead to decreased exciton binding energy. Quantitatively accounting for this difference, however, is more difficult, as accurately calculating the excitonic response requires a many-body treatment that is significantly harder for a graphite substrate compared to a BLG substrate. We are, however, able to make a rough theoretical estimation of the expected change in the electronic bandgap seen for MoSe$_2$/HOPG compared to MoSe$_2$/BLG using ab initio techniques.

Since the graphite substrate is much thicker than bilayer graphene, it is not computationally feasible to construct a supercell large enough to contain both MoSe$_2$ and graphite. We therefore performed an additional approximation and neglected off-diagonal components of the screening perpendicular to the substrate. This allowed us to calculate the polarizability of graphite in a small unit cell and directly map the components of the polarizability to the unit cell of MoSe$_2$ as:

\[
\tilde{\chi}_{GG'}^{0,\text{graphite}}(q) = \frac{\chi_{GG'}^{0,\text{graphite}}(q)}{2} \delta_{G_xG'_x} \delta_{G_yG'_y} \delta_{G_zG'_z} \tag{6.7}
\]

Neglecting these extra off-diagonal matrix elements is roughly equivalent to placing MoSe$_2$ directly above the graphite substrate without any separation, which should overestimate the screening from the substrate. Indeed, we find within this model that the GW quasiparticle bandgap of MoSe$_2$/HOPG closes by $340 \pm 100$ meV with respect to MoSe$_2$ on bilayer graphene, which slightly overestimates the experimentally observed reduction of 240 meV.
6.3.5 Conclusion

Our theoretical and experimental results reveal that many-electron interactions are strong in MoSe$_2$/BLG and prominently affect the quasiparticle excitations and optical response of this system. The 51% reduction seen for the exciton binding energy in MoSe$_2$/HOPG arises from the stronger substrate screening, which reduces both the quasiparticle electronic gap and the exciton binding energy without significantly changing the optical gap. Our results directly demonstrate that increased free-carrier screening in graphite plays a large role in determining the TMD exciton binding energy [50, 138]. Similar behaviour on the quasiparticle electronic gap has indeed been observed in previous ARPES measurements on highly doped MoSe$_2$ [139]. The strong, environmentally dependent exciton binding energies observed here should play a significant role in the room-temperature performance of optoelectronic nanodevices composed of single-layer semiconducting TMDs as well as more complex layered heterostructures.


