Nanoscale Electronic Structure of Cuprate Superconductors Investigated with Scanning Tunneling Spectroscopy

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Tess Lawanna Williams
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Abstract

Despite 25 years of intense research activity, high-temperature superconductors remain poorly understood, with the underlying pairing mechanism still unidentified. Efforts are complicated by the remarkably complex phase diagram, rich in energy-dependent charge and spin orders.

In this thesis I describe the use of a Scanning Tunneling Microscope (STM) to study energy-dependent charge orders in Bi$_{2-y}$Pb$_y$Sr$_2$CuO$_{6+\delta}$, a cuprate high-temperature superconductor.

STM, a surface-sensitive probe used to map electronic structure with sub-meV energy resolution and sub-Å spatial resolution, has contributed greatly to our current understanding of the cuprate high-temperature superconductors. However, STM data is acquired with a constant-current normalization condition. The measured differential conductance, $g(x, y, V)$, is often taken to be proportional to the density of states at energy $eV$ (where $V$ is the voltage applied between tip and sample). In fact, due to the normalization condition, the measured $g(x, y, V)$ is actually the quotient of the density of states at energy $eV$ and the integrated density of states from the
Fermi energy to eV. This unavoidable quotient may fold electronic structure from its true energy range into other energies.

I discuss a new method to correct STM differential conductance spectra to remove the constant-current normalization condition. Using local work function measurements and the constant-current topograph, I create a map which does not suffer from the setpoint effect and contains a mixture of topographic information and properly normalized spectroscopic information. I apply this method to the extraction of the incommensurate charge modulation at $\vec{q} \sim \frac{3\pi}{4} a_0$.

I also extend the study of electronic nematic order, an atomic-lattice-periodic $C_4 \rightarrow C_2$ symmetry breaking, from highly underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [28] to overdoped Bi$_{2-y}$Pb$_y$Sr$_2$CuO$_{6+\delta}$. I find that the electronic nematic order parameter is robust to change of scan angle. I define and contrast three different electronic nematic orders with different phases with respect to the crystal. I discuss the effect of the choice of normalization and possible alternate explanations for the source of the calculated nematic order.

Finally, I discuss a drift-correction technique, which removes picometer scale drift that is introduced into a spectral map by experimental imperfections, and characterize the optimal algorithm and potential artifacts that drift-correction may introduce.
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Dedicated to Henri
Chapter 1

Principles of Scanning Tunneling Microscopy and Spectroscopy

Scanning Tunneling Microscopy (STM) was pioneered by Binnig and Rohrer at IBM in Zurich in 1982 [6, 7] and has been an instrumental tool in the study of the spatial variation in the electronic structure of a wide variety of interesting materials. An STM is a sharp conducting tip which is scanned over a surface of interest with an applied bias voltage between the two. In a world described by classical physics, no current will flow if there is no physical contact. However, if the separation distance is sufficiently small, on order half a nanometer, wavefunctions of the tip and sample overlap and electrons quantum mechanically tunnel through an energy barrier between the tip and the sample. The tunneling rate, typically on order picoAmps to nanoAmps, falls off exponentially with the tip-sample separation distance and is linearly proportional to the density of states (DOS) of the tip and the DOS of the sample. Thanks to the exponential falloff, STM can probe the spatial variation of
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the electronic structure of a material with picometer spatial resolution. This extraordinary precision enables study of atomic scale and even sub-atomic scale electronic structure. The energy resolution of a well-designed STM is limited only by the thermal smearing of the Fermi function at cryogenic temperatures; microelectronVolts to millielectronVolts precision is routinely attained. The principle technical difficulty of STM is the stable maintenance of such a small tip-sample separation distance while scanning with high precision in the plane of the sample. When Binnig and Rohrer solved that problem in the early 1980s, they launched a new age of the study of materials at previously unattainable length-scales.

1.1 Theory of Electron Tunneling

A detailed theory of electron tunneling was developed by Bardeen in 1960 [4] and applied to STM by Tersoff and Hamann in the early 1980s [51, 52]. A brief overview of the case of elastic tunneling will be given here.

Following Bardeen, if the tip and sample wavefunctions are modeled as separate systems and allowed to weakly overlap, then time dependent perturbation theory can be used to calculate the tunneling rate. The total current will be given by the rate of tunneling from sample to tip minus the rate from tip to sample, calculated using Fermi’s Golden Rule.

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} |M|^2 \text{DOS}_s(E_s) \text{DOS}_t(E_t) \{ f(E_s)[1-f(E_t)] - f(E_t)[1-f(E_s)] \} \, dE \tag{1.1}
\]

where \( e \) is the electron charge, \( \hbar \) is Planck’s constant, \( |M| \) is the tunneling matrix.
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Figure 1.1: Cartoon of the tunneling of electrons through an energy barrier as in an STM. Bias voltage $V_s$, applied to the sample, shifts the relative Fermi levels of the tip and sample. $\phi_t$ and $\phi_s$ are the work functions of the tip and sample, respectively and determine the height of the energy barrier. $z_\delta$ is the tip-sample separation distance and the physical width of the energy barrier. In this particular illustration, neither the tip DOS nor sample DOS depend on energy. This would be a very boring measurement. Usually STM is done when the sample DOS depends on energy in interesting ways.

The integral is taken over energy. If a bias voltage $V_s$ is applied to the sample with respect to the tip, then $E_t \equiv E$ with $E = 0$ referenced to the Fermi energy $E_f$ and $E_s = E - eV_s$. When a negative bias voltage is applied to the sample, electrons will tunnel from the occupied states of the sample to the empty states of the tip.

A series of approximations are typically made to arrive at a more tractable ex-
pression for the tunneling current.

First let us consider the Fermi function,

\[ f(\epsilon) = \frac{1}{1 + e^{\epsilon/k_B T}} \]  

where \( k_B \) is the Boltzmann constant and \( T \) is temperature. At the temperatures of the experiments presented in this thesis, 2 to 15 K, \( k_B T = 0.17 \) to 1.3 meV, and it is reasonable to approximate the Fermi function as a Heaviside step function, \( \Theta(-\epsilon) \). If we make this approximation, \( \{f(E_s)[1 - f(E_t)] - f(E_t)[1 - f(E_s)]\} = \{f(E - eV)[1 - f(E)] - f(E)[1 - f(E - eV)]\} \) is 1 within the range \(-eV\) to 0 and 0 elsewhere. The limits of the integral collapse from \( \pm \infty \) to \(-eV\) to 0 and explicit temperature dependence is eliminated.

Second, we choose a tip with a flat DOS in the energy range of interest (for example, \( \pm 100 \) mV, for cuprate superconductors discussed in this thesis), such as Tungsten or Platinum-Iridium. If the tip DOS does not depend on energy, it can be pulled out of the integral and ignored as an inert and uninteresting prefactor. (It is always the goal of the scanning tunneling microscopist to work with a tip that is as featureless as possible in every conceivable way.)

The third step requires the crucial approximation that in the energy range of interest (that is, sufficiently close to the Fermi energy) the tunneling matrix element does not depend on energy and can therefore can be taken outside the integral. This was shown by Bardeen to be a reasonable approximation for experimentally relevant regimes [4].

The tunneling matrix element \(|M|\) was calculated by Tersoff and Hamann (TH)
by using a variation on the WKB approximation [51]. This requires treating the energy barrier as a square. The tilt on the top (exaggerated in Figure 1.1) is on order the applied bias voltage, which does not typically exceed $\pm 100 \text{meV}$. The height of the barrier is the energy required to remove an electron from the material, otherwise known as the work function, $\phi$, and is on order $3 - 5 \text{eV}$.

TH start with the matrix element developed by Bardeen,

$$|M|_{\mu\nu} = -\frac{\hbar^2}{2m} \int d\vec{S} \cdot (\psi^*_\mu \nabla \psi_\nu - \psi^*_\nu \nabla \psi_\mu)$$  \hspace{1cm} (1.3)

$\psi_\mu$ are the states of the tip and $\psi_\nu$ those of the sample, respectively. The integral is over any surface in the vacuum barrier and the quantity in parentheses is the current operator.

![Figure 1.2: Geometry of the STM Matrix element calculation by Tersoff and Hamann.](image)

$R$ is the radius of curvature of the STM tip, assumed spherical, $z_\delta$ is the distance of closest approach to the sample (shaded), center of curvature of tip is labeled $\vec{r}_0$. Figure adapted from Tersoff and Hamann[51].

Assuming a spherical tip and a planar surface, the tip wavefunctions are expanded in an asymptotic spherical form and the sample wavefunctions are expanded into
Bloch states in a region of negligible potential. In short, and disregarding normalization prefactors,

$$\psi_\mu \propto e^{\kappa R} e^{\kappa |\vec{r} - \vec{r}_0|}$$  \hspace{1cm} (1.4)$$

Here $\vec{r}_0$ is the center of the spherical apex of the tip and $R$ is the radius of curvature of the tip apex. In Tersoff and Hamann’s geometry, $r_0 = R + z_\delta$, where $z_\delta$ is the tip-sample separation distance.

$$\psi_\nu \propto e^{-\kappa z} e^{i (\vec{k}_\parallel + \vec{G}) \cdot \vec{x}}$$  \hspace{1cm} (1.5)$$

Here $\vec{k}_\parallel$ is the surface Bloch wavevector of the state and $\vec{G}$ is a surface reciprocal lattice vector.

TH take the work functions of tip and sample to be equal, so in both equations, $\kappa = \sqrt{2m\phi/\hbar}$, the inverse decay length for the wavefunctions in vacuum (a more detailed analysis shows that the $\phi$ in the final equation is the average of $\phi_t$ and $\phi_s$ [5, 45]). Plugging 1.4 and 1.5 into 1.3 and carrying out the integral yields

$$|M|_{\mu\nu}^2 \propto e^{2\kappa R} |\psi_\nu(\vec{r}_0)|^2 \propto e^{2\kappa R} e^{-2\kappa(R + z_\delta)} \propto e^{-2\kappa z_\delta}$$  \hspace{1cm} (1.6)$$

$r_0^\parallel$ remains in the equation because it is equal to the tip radius of curvature plus the tip-sample separation distance and is the appropriate length scale to describe the lateral averaging due to finite tip size. This expression is combined with the tunneling equation calculated previously and we arrive at the final expression for tunneling current typically used by STM experimentalists.
Here, $\phi$ is the average of the tip and sample work functions. A few things are worth noting. One is that while the explicit temperature dependence has been removed, the effect of the Fermi function is to “smear” the energy resolution by roughly $4k_B T$, $2k_B T$ each for tip and sample wavefunctions. Second, the work function, $\phi$, is not given explicit spatial dependence in this equation, but as we shall see in Section 1.3.5, $\phi$ does vary by $\pm 10\%$ on an atomic length scale. A dependence on $(x, y)$ comes in three different places, in fact, since in general $z_{\delta}$ also varies with the lateral position. The three different sources of variation with $(x, y)$ present in this expression for tunneling current are extraordinarily difficult to disentangle.

It behooves us to keep careful track of all of the dependencies that are normally swept under the rug with the adoption of Equation 1.7, so a more useful restatement, and one that we shall use throughout the rest of this dissertation, is

$$I(x, y, z_{\delta}, V) \propto \exp \left[ -2z_{\delta}(x, y) \sqrt{2m\phi(x, y)/\hbar} \right] \int_{-eV}^{0} \text{DOS}(x, y, E) \, dE \quad (1.8)$$

### 1.2 Scanning Tunneling Microscope Design

A number of design elements are required for successful Scanning Tunneling Microscopy. The primary difficulty is in bringing together two macroscopic objects, the tip and the sample, and maintaining a near-constant few-Å separation between the two while raster scanning the tip across the sample surface, without ever allowing the
tip and sample to come into contact.

The data presented in this dissertation was partly taken using a Hoffman-Lab custom-built STM with a Pan-style walker in a cryogenic high vacuum cryostat with a \(^4\)He pot. Operating temperatures were \(2K\) to \(15K\) and the STM was fixed in a vertical magnetic field of up to \(9T\). Other data, included in the analysis in Chapter 3, was taken in the lab of Eric Hudson at MIT by a similar STM.

One of the key challenges of STM is shielding the microscope from vibrations and acoustical noise. We achieve this by a combination of extremely high inertia environment and mismatch of resonant frequencies. Our STM is inside of a \(^4\)He dewar which is suspended from a 3400 lb lead-filled wooden table, which is supported by three commercial airsprings with resonant frequency of \(15Hz\). Wood was chosen because it is an inherently lossier (lower Q) substance than metal. The experiment is inside of a insulating-foam-coated room which is built on a 20 ton concrete slab which is suspended on four further airsprings with resonant frequency of \(2Hz\). The STM head was designed to be very compact and rigid and has a resonant frequency of over \(1kHz\), so any vibrations which do reach the STM head do not couple into vibrational modes of the STM body.

Samples can be transferred into the STM without breaking vacuum by means of a sample transfer rod which slides through a differentially-pumped double o-ring sliding seal. Sample are mechanically cleaved at \(\sim 30K\) during insertion, exposing a clean, atomically flat plane for study (in the Bi-based cuprate compounds, the BiO\(_2\) plane is the terminating layer). The tip is then walked up until it comes within tunneling range of the sample surface. Coarse motion is achieved by means of a piezoelectric
Pan-style walker[38]. A sequence of time-staggered voltage pulses are sent to 6 stacks of piezos, which slip one at a time against a central sapphire prism and then relax together to move the beam a single step. A typical step size at base temperature is 50 nm and during a typical coarse approach the walker will walk \( \sim 1 \text{ mm} \) in 2 to 3 hours.

Once the tip has approached the sample surface, the \((x, y)\) and \(z\) motion of the tip is controlled with a piezoelectric scantube with picometer precision by the control electronics, a commercial unit by Nanonis. The tunneling current is amplified by \(10^9\) by a commercial Femto preamplifier at room temperature, \(\sim 5 \text{ ft}\) above the STM head. The bias voltage is supplied by Nanonis, as well as a small modulation to the bias; the DC and AC components are added together just before the vacuum feedthrough, after dividing down the AC component by a factor of 100, to reduce noise.

Mechanically cut PtIr tips were used to collect all data presented in this thesis. Before approaching on a surface, the tip is cleaned by Field Emission on an Au surface. Topographic scans of the Au surface are taken to ensure that the tip has no atomic-scale structure and is atomically sharp, and \(I(V)\) spectra, which should be linear on a metallic surface, are taken to ensure that the tip has a flat DOS in the energy range of interest, typically \(\pm 100 \text{ mV}\) of the Fermi level.

## 1.3 Experimental Data

STM can collect a variety of different kinds of data in different modes. The topographic structure of the sample surface can be imaged, the DOS of the sample
can be probed as a function of the location, \((x, y)\), on the sample surface and as a function of energy, and the local work function can be measured. Additionally, Fourier Transforms of \(dI/dV\) maps allow the extraction of momentum-space information.

### 1.3.1 Constant-Current Topography

![Figure 1.3](image)

Figure 1.3: The key elements of STM. A voltage \(V_s\) is applied between the sample surface and a sharp metallic tip and electrons tunnel through the vacuum barrier between with some current \(I\). In constant-current imaging mode, \(I\) is compared to some setpoint \(I_s\) and the feedback loop adjusts the voltage to the piezoelectric scantube to change \(z\) to keep \(I = I_s\).

In topographic imaging mode, the tip is scanned in a raster pattern over the sample surface at a speed of typically \(5 - 50 \text{ nm/s}\). The bias voltage is held constant.
at $V_s$ and the tunneling current feedback loop is enabled to keep $I = I_s$. The control electronics continuously adjust the $z$ of the tip to keep the tunneling current at the current setpoint, and an image is created by recording $z$ as a function of $x$ and $y$. This $z(x, y, V_s)$ is defined to be a topograph: an image which shows how much $z$ must vary to keep $I = I_s$ as $x$ and $y$ are scanned across the sample surface. The scan speed is limited by the bandwidth of the feedback loop.

An STM topograph is not strictly speaking a purely topographic image. As can be seen in Equation 1.8, the tunneling current depends on both the tip-sample separation distance and the DOS of the sample, so for a material with spatially inhomogeneous DOS a topographic image will have information about both physical and electronic structure. In general, $z$ will depend on $(x, y), V_s$, and the DOS at $(x, y)$.

$$z_{\text{topo}}(x, y, V_s) = -\frac{1}{2\kappa(x, y)} \ln \left[ \int_{-eV_s}^{0} I_s \frac{DOS(x, y, E)}{dE} dE \right]$$ (1.9)

In practice, it is possible to adjust the tunneling parameters to ensure that the geometrical information dominates in the image. Typically we use a bias setpoint of $-100\, mV$, which is far from the superconducting gap structure of cuprates at $20 - 50\, meV$. Since the tunneling current depends on the integral of the DOS from the Fermi level to the bias setpoint, the DOS contribution to the image is much smaller than if the bias voltage were to be set to a value where there is a lot of spatial variation in the DOS. The surface of the Bi-based cuprate superconductors discussed in this dissertation is fragile since the inter-plane coupling of this quasi-2d material is weak, so it is difficult to use bias voltages much greater in magnitude than $\pm150\, mV$ without destroying the surface and dirtying the tip.
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Figure 1.4: Constant-current topographic images of the BiO₂ surface of overdoped Bi₂₋ₓPbₓSr₂CuO₆₊δ (Tₐ = 16 K). The Bi atoms are seen as regular corrugations and isolated bright atoms are Pb impurities. O atoms are not visible to STM. The Bi-Bi separation distance is 3.83 Å. Both images were taken with a sample bias voltage of −100 mV and a tunneling resistance of 2.86 GΩ at 4.3 K. a) A 50 × 50 nm² area of 512 × 512 pixels². b) A 20 × 20 nm², 512 × 512 pixels² image of the same surface.

Typical topographic images of Bi₂₋ₓPbₓSr₂CuO₆₊δ are shown in Figure 1.4. Both were taken with a bias voltage of −100 mV and a tunneling resistance of 2.86 GΩ = −100 mV/35 pA. After subtracting an overall planar tilt, the atomic lattice is clearly visible as a regular corrugation. Structure of ∼ nm length scales is due to spatial inhomogeneity of the DOS. Isolated brighter atoms are Pb impurities. The Pb impurities suppress the well-known incommensurate lattice distortion known as the supermodulation. The Pb atoms do not have a prominent electronic presence at the energy ranges of interest, and are only relevant structurally. They are physically larger than the Bi atoms and push neighboring Bi atoms out of their lattice.
positions by $\sim 1\%$ of a lattice spacing.

1.3.2 I(V) Spectroscopy

Another type of data that STM can collect is information about the current as a function of energy. At a set $(x, y)$ location on the sample surface, after both the lateral and vertical position of the tip have stabilized, the tunneling current feedback loop is disabled. The current is recorded as a function of changing bias voltage, which can be thought of as a function of energy, since $E = eV$. Since the feedback condition sets $z_{\delta}$, the $I(V)$ spectrum can be written as either

$$I(x, y, V, z_{\delta}) \propto \exp \left[-2\kappa(x, y)z_{\delta}(x, y)\right] \int_{eV}^{0} DOS(x, y, eV)$$

or equivalently,

$$I(x, y, V, I_{s}, V_{s}) \propto \frac{I_{s}}{\int_{-eV_{s}}^{0} DOS(x, y, E)dE} \int_{eV}^{0} DOS(x, y, eV)$$

1.3.3 Differential Conductance Spectroscopy

STM can also collect information about the local differential conductance, $g(x, y, E)$, through a similar, or simultaneous, process to an $I(V)$ measurement. In theory one could record an $I(V)$ spectrum and numerically differentiate in order to obtain the $g(x, y, E)$ of interest, but in practice better signal-to-noise is obtained with a lock-in amplifier. A small AC modulation, $V_{AC}$, is added to the DC bias voltage. The DC bias voltage is ramped through a range of voltages, pausing at evenly spaced voltages while the current is demodulated and recorded for 10-20 modulation periods.
The energy resolution of such a spectrum is fundamentally limited by thermal broadening, which is $4k_B T \sim 1.4 \text{meV}$ at $4.2 \text{K}$. The adjustable parameters which determine energy resolution are the $V_{AC}$ and the spacing between adjacent bias voltage points, $\Delta V$. The signal-to-noise ratio can be increased by increasing the integration time at each step in the bias voltage ramp sequence or by increasing $V_{AC}$. $V_{AC}$ and $\Delta V$ are chosen to be roughly the same, since if $V_{AC} \ll \Delta V$ signal-to-noise is lower than it could be and some information is lost and if $V_{AC} \gg \Delta V$ information is duplicated over multiple points in the spectrum. We typically choose $V_{AC} \approx \Delta V = 0.5\text{–}3 \text{mV0–peak}$. We use a modulation frequency of 1115 kHz because we have found it to be a very quiet location in the noise profile of our experimental setup, avoiding vibrational modes and 60 Hz harmonics.

The demodulated current as a function of bias voltage is known as a $dI/dV$ spectrum, and is given by

$$\frac{dI(x,y,V,z_\delta)}{dV} \propto \exp\left[-2\kappa(x,y)z_\delta(x,y)\right] e\text{DOS}(x,y,eV) \quad (1.12)$$

Because $z_\delta$ is set by the current feedback loop before the spectrum is taken, an equivalent expression for $dI/dV$ spectra is

$$\frac{dI(x,y,V,V_s,I_s)}{dV} \propto \frac{eI_s}{\int_{-eV_s}^{0} \text{DOS}(x,y,E)dE} \text{DOS}(x,y,eV) \quad (1.13)$$

At a given location, $z_\delta$ will vary with varying $V_s$ and $I_s$. The relationship between these three quantities is given in Equation 1.8. The setup condition dependence in the expression for $dI/dV$ can be given in terms of either $z_\delta$ or $V_s$ and $I_s$. $V_s$ and $I_s$ are the user-adjustable parameters, and $z_\delta$ is the physical manifestation of those
parameters. The two ways of expressing the equation for $dI/dV$ contain the same information, and either may be used, depending on which is most convenient in a given situation.

A $dI/dV$ spectrum at a particular location on the sample surface is known as a point spectrum. A typical example, taken on an overdoped Bi$_{2−y}$Pb$_y$Sr$_2$CuO$_{6+δ}$ ($T_c = 16$ K) surface, is seen in Figure 1.5. The x axis is sample bias in $mV$ and can also be thought of as the energy in $meV$.

Many STM studies take $dI/dV$ spectra to be proportional to the bare DOS of the sample, ignoring the prefactor. If the variation in $e^{−2z(x,y)\sqrt{2m\phi(x,y)/\hbar}}$ is sufficiently small, then this is a reasonable approximation. However, in a material like the cuprates with complex, spatially inhomogeneous electronic structure over variable energy ranges within $[−eV, 0]$ span, this may not be a good approximation. This will be discussed further in Chapter 2.

In the following chapters, we will use $dI/dV$ and $g$ interchangeably.

1.3.4 Differential Conductance Mapping

The topographic imaging and spectroscopic modes of data acquisition can be combined to create a spatial map of $g(x, y, E)$. A differential conductance map consists of a series of $dI/dV$ spectra taken at a finely spaced grid of points in $(x, y)$. A grid is defined and throughout the course of the map the sequence of events is as follows:

1. Move tip to a new location with the current feedback enabled.
2. Hold $(x, y)$ location constant while the current feedback loop stabilizes $z$. 


Figure 1.5: A typical $dI/dV$ spectrum of overdoped Bi$_{2-y}$Pb$_y$Sr$_2$CuO$_{6+\delta}$ ($T_c = 16$ K). The spectrum is taken with an applied sample bias of $V = -100$ meV and $I_{set} = 250$ pA at $T = 6$ K. The sample bias is modulated with an AC voltage of zero-to-peak amplitude 2.5 mV and frequency 1.115 kHz.

3. Record $z(x, y)$ as a pixel in the simultaneous topographic image.

4. Disable feedback loop.

5. Measure a single $dI/dV$ spectrum.

6. Enable feedback loop.

Typical timing parameters are given in Table C.1.

The end result is a topographic image of $z(x, y)$, and at each pixel in that image, a full $dI/dV$ spectrum.
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This three-dimensional dataset can be visualized in a variety of ways. At a single spatial location, we can look at the local \( g(x_0, y_0, E) \), the point spectra discussed in the previous section. At a single energy, we can look at \( g(x, y, E_0) \), a map of the spatial variation of the differential conductance.

We have developed the capability to take simultaneous maps of multiple different kinds of spectra. This has been accomplished by a small modification to the sequence of events given above: steps 2-6 are repeated \( n \) times. This capability has been used to take simultaneous maps with different bias setpoints and to take simultaneous maps of the differential conductance and the work function. Details are discussed in Chapter 2 and in Appendix A.

1.3.5 Work Function Measurements

If we turn again to Equation 1.8, we can see that it is also possible to measure the tunneling current as a function of the tip-sample separation distance, \( z_\delta \). If the \((x, y)\) position of the tip is held fixed while \( z \) is smoothly ramped, an exponential decay in current is measured. If we take the natural logarithm of both sides of 1.8, we arrive at a suggestive equation.

\[
\ln[I(x, y, z, V)] \propto -2\kappa z + \ln \left[ \int_{-eV}^{0} DOS(x, y, E) dE \right] \tag{1.14}
\]

The natural logarithm of \( I(z) \) is a line of the form \( y = ax + b \) and the slope of that line can be seen to be \(-2\kappa\). If the slope, \( s \), is calculated in \( nm^{-1} \), then the work function can be computed by
Figure 1.6: Map of the work function. (a) A typical $\phi$ map of $9 \times 9 \text{nm}^2$ area of $128 \times 128$ pixels$^2$ of overdoped Bi$_{2-y}$Pb$_y$Sr$_2$CuO$_{6+\delta}$ ($T_c = 16$ K). Atomic-scale corrugations are clearly seen. (b) The topographic image taken at the same location.

In exactly the same way that $g(x, y, E)$ can be mapped, the work function can also be mapped. A typical work function map is shown in Figure 1.6a. Work function maps are discussed further in Chapter 2.

$$\phi = \frac{(\hbar s)^2}{8m} = 0.00952 s^2 \text{eV} \quad (1.15)$$

1.4 Drift Correction

Over the course of a full spectral map, which is typically of a duration of 12 hours to 4 days, $mK$ changes in temperature and small imperfections or creep in the piezoelectric scantube lead to a slow drift over the course of the map which subtly distorts the data from a true lattice. An algorithm introduced by Lawler et al. removes this slow drift and aligns the data onto a perfect atomic lattice [28]. The procedure is applied to the simultaneous topographic image in order to find the drift
fields, or the local amount by which the raw data must be displaced in order to bring it onto the un-distorted lattice, and then those same drift fields are applied to the spectroscopic map.

Once the map is recast onto a perfect lattice, a variety of new analysis techniques become available. An entire map can be averaged to examine average intra-atomic cell structure. Fourier Transforms of either the topographic or spectroscopic data have single-pixel peaks at points which are multiples of lattice vectors. This allows for much more careful characterization of periodicities and spatial phases of those modulations in the data. This capability will be made use of extensively in Chapter 3.
Chapter 2

Normalization of STM Spectroscopy

While Scanning Tunneling Microscopy has contributed greatly to our current understanding of the high-temperature superconductors, every study to date has been plagued by a tricky normalization problem. Recall from Section 1.3.3 that the conductance, $g(x, y)$, is not simply proportional to the Local Density of States (LDOS), but rather to the product of that physically meaningful quantity and a prefactor, which can be viewed as either the tunneling matrix element or equivalently (due to the feedback setup condition) the integral of the LDOS from the Fermi level to the bias setpoint. Either view of the prefactor contains complex dependence on spatial location and feedback setup condition.

A host of issues could be addressed definitively if STM could measure the LDOS of the cuprates (or any material) free of any confounding prefactors. For example, much has been made of the spatial inhomogeneity of the LDOS as measured by STM [27, 40,
but since the prefactor also varies spatially, we are unable to distinguish between real inhomogeneity in a given energy range and artifact folded in from a different energy range. Without access to the true LDOS, we cannot understand fundamentally local phenomena like the proximity effect or the role of randomly dispersed charge dopants in a superconductor. STM seems well-suited to measure local charge density, but due to the normalization condition we cannot say with confidence what the spatial variation of charge density actually is and judge whether or not it is important to superconductivity.

In this chapter I describe a promising but not-yet-entirely-functional method to remove that confounding prefactor by dividing it out. This requires direct measurement of the work function and a method for extracting the tip-sample separation from measurable quantities.

### 2.1 Problematizing the STM Tunneling Equation

The STM Tunneling Equation was derived in Section 1.1. Since the nuances of that equation are the focus of this chapter, in this section we will more carefully explicate sources of spatial variation and the relationships between $z_{\text{topo}}$, $z_{\text{surface}}$, and $z_\delta$. Figure 2.1 defines the three different heights of interest.

First is the purely structural (topographic in the more traditional sense of the word) height of the surface: $z_{\text{surface}}$. This $z_{\text{surface}}$ contains only information about the size and location of the atoms on the surface plane. STM is not able to directly measure $z_{\text{surface}}$. There are several sources of ambiguity in this conception of $z_{\text{surface}}$. One is that $z_{\text{surface}}$ is measured from some arbitrary constant height and is therefore
Figure 2.1: A graphical representation of the constant-current tunneling condition. The round blue array represents the atomic lattice. The overall blue gradient represents a long-length-scale modulation of the LDOS. \( z_{\text{surface}} \) is the contour of the atoms and contains only structural information about atom size and location. \( z_{\text{topo}} \) is the path that the STM tip takes as it scans across the surface, enforcing a constant-current feedback condition. \( z_{\delta} \) is the tip-sample separation distance, defined as \( z_{\text{topo}} - z_{\text{surface}} \). Even though structurally the atoms form a perfect lattice, the \( z \)-controller will modulate the tip-sample separation distance, \( z_{\text{surface}} \), because at the edges the integrated LDOS contribution is larger, forcing \( z_{\delta} \) to grow to keep the tunneling current constant.

only well-defined up to a constant. Another is that the size of an atom is not a well-defined quantity because the probability cloud of its electrons has no sharp edge. The best that we can do is to say that \( z_{\text{surface}} \) is some contour of constant charge density. \( z_{\text{surface}} \) will, of course, vary with \( I_s \) and \( V_s \), since the STM probe is sensitive to electronic states, which have complex relationships between spatial extent and energy.
In any case, the intent of $z_{\text{surface}}$ is to capture the size and regular arrangement of
the atoms that comprise the surface plane.

Structurally, as far as can be determined from other experimental techniques,
such as x-ray or neutron scattering, or low energy electron diffraction, the Bi atoms
of the surface form a regular lattice. Although nearly tetragonal, a 0.5% differ-
ence between $a$ and $b$ axes make the primitive 2-dimensional unit cell orthorhombic,
with two Cu atoms per cell in the critical CuO$_2$ layer [49]. In addition, there is an
inversion-symmetry breaking orthorhombic distortion of one Bi sublattice relative to
the other [49, 63]. Additionally, non-Pb doped BSCCO has an incommensurate bulk
structural distortion of wavevector $\frac{1}{7} \frac{2\pi}{a_0}$, the ‘supermodulation.’ Note that all of these
lattice effects have wavevectors of $\sim \frac{1}{7} \frac{2\pi}{a_0}$ or larger.

Additional short-wavevector structural information may be present in the form
of randomly arranged dopants or localized lattice defects such as vacancies. In the
Pb-doped compounds studied here, there is structural information due to the random
distribution of Pb-dopants, which are physically larger in size than the Bi atoms but
are similar spectroscopically. STM is sensitive only to the Bi atoms in the surface
layer, due to destructive interference through neighboring Cu orbitals when the tip is
directly above O sites [37].

The feedback condition enforced in constant-current tunneling mode varies $z$
to keep $I = I_s$, at a fixed $V = V_s$.

$$I_s(x, y, z_{\text{topo}}, V_s) \propto e^{\exp \left[ -2\kappa(x, y)z_{\text{topo}}(x, y) \right]} \int_{-eV_s}^{0} DOS(x, y, E) \, dE \quad (2.1)$$

We record the $z$-voltage sent to the scantube, which is controlled by the feedback
condition. This by definition is the \( z_{\text{topo}} \) map that satisfies Equation 2.1 at every \((x,y)\) location. It is registered from \( z = 0 \), which is a constant height at an arbitrary distance from the surface, so like \( z_{\text{surface}} \), \( z_{\text{topo}} \) is only defined up to an arbitrary constant. This \( z_{\text{topo}} \) contains both the structural information of \( z_{\text{surface}} \) and the integrated LDOS. The LDOS varies on the length scale of \( \xi \), the superconducting coherence length, which is 2.2 \( nm \) in Bi-based cuprates [39]. Atomic scale structure is present at length scales of 0.383 \( nm \), the Bi-Bi spacing.

As shown in Figure 2.1, \( z_\delta \) is defined as \( z_{\text{topo}} - z_{\text{surface}} \). Unlike the other two heights, \( z_\delta \) is an absolute quantity, although not a quantity that STM experiments are able to absolutely extract. \( z_\delta \) depends sensitively on the definition that is adopted for \( z_{\text{surface}} \). If the structural topographic information varies only on atomic-spacing length scales and the integrated LDOS varies only on \( \xi \) length scales, then \( z_\delta \) could be approximated by low-pass Fourier filtering \( z_{\text{topo}} \). However, any localized topographic information makes the extraction of \( z_\delta \) a far more complicated task.

When we take a measurement of \( I(V) \) or the local differential conductance \( g(V) \), we first fix the tip height at \( z_{\text{topo}} \) by enforcing the feedback condition, and then we sweep \( V \) to measure \( I(V) \) or \( g(V) \) at that fixed \( z_{\text{topo}} \). If \( z_\delta \) varies spatially, then \( I(V) \) or \( g(V) \) will vary spatially in a related fashion, and assumption of \( g(V) \propto LDOS(eV) \) will lead to the erroneous conclusion that \( LDOS(eV) \) varies spatially. In particular, spatially varying order at a one energy could appear to be present in other energies where in fact it is not, through the influence of \( z_\delta \).

As a simple example, take a spatially homogeneous, d-wave superconducting DOS and couple in a checkerboard modulation of \( Q = \frac{2\pi}{3a_0} \) with a Gaussian amplitude cen-
Chapter 2: Normalization of STM Spectroscopy

Figure 2.2: The spectra from the toy model calculation described in the text. We take a spatially homogenous d-wave superconducting DOS and couple in a checkerboard modulation of $Q = \frac{2\pi}{a_0}$ inside a Gaussian window centered at the Fermi level of half-width 10 mV. The amplitude of the modulation is shown in the inset. The green spectrum is a simple d-wave superconducting $DOS(E)$. The red spectrum is a simulated STM $dI/dV$ curve, taken at the spatial location of a peak of the modulation, and the blue curve is the equivalent spectrum at the spatial location of a trough of the modulation. The constant-current normalization condition is computed assuming $V_s = -100 \text{ mV}$.

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tered at the Fermi level with half-width of 10 mV. When the typical STM tunneling condition normalization is applied, the spectra are affected throughout the measured $[-100 \text{ mV}, +100 \text{ mV}]$ energy range, even though the LDOS modulation exists only in a very small range about the Fermi level. Figure 2.2 shows the output of such a calculation. The green spectrum is the unaltered d-wave spectrum, our LDOS. The red spectrum is a simulated STM $dI/dV$ curve, taken at the spatial location of a peak of the modulation, and the blue curve is the equivalent spectrum at the spatial location of a trough of the modulation. The spatial modulation can be seen in every
energy layer through the measured range, with an apparent phase-flip at ±20\,meV.

2.2 Normalization in Prior STM Studies

In this section I will briefly discuss a few seminal STM-on-cuprates papers and how the authors attempted to deal with normalization-dependence.

Pan et al. made one of the first attempts to directly address the prefactor [40], in a study of optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. Pan Fourier filters the topograph with a low-pass filter and calls the resulting map the “integrated Density of States.” Contrary to Pan’s claim, this map is proportional to the natural logarithm of the integrated DOS. Additionally, Pan explicitly assumes no spatial variation in the tunneling matrix element (and therefore no spatial variation in $\phi$), which as we have mentioned in Section 1.3.5 and will discuss further in later sections, is inaccurate. Pan finds a correlation between the so-defined integrated DOS and the gap size, $\Delta$, unsurprisingly, since both are features of the underlying spectral shape.

Lang et al., in a ground-breaking study of spatial inhomogeneity in underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [27], makes a number of assertions that are normalization-dependent. Like most STM studies, Lang takes $g \propto DOS(E)$. Specifically, Lang claims that the LDOS is spatially homogeneous inside 30\,meV, and then diverges. McElroy et al. make a similar claim, pointing out that spectra that have been binned by apparent gap size and averaged appear to show a remarkably homogeneity up to $\sim 25\,meV$ [33]. Since both use constant-current normalized $g$ spectra, it is possible that apparent spatial (in)homogeneity is folded in from other energy ranges.

Several attempts have been made to glean physical insight from fits of $g(V)$ spectra
to various models, most notably in studies by Alldredge et al. [2] and Pushp et al. [46].

Alldredge fits each individual \( g(x, y, V) \) in several spectral surveys to a modified d-wave superconducting \( N(E) \), with a particle-hole asymmetric energy gap, \( \Delta(k) = \Delta_1(\cos(k_x) - \cos(k_y))/2 \), and an inelastic scattering rate that varies linearly with energy, \( \Gamma_2 = \alpha E \).

\[
N(E, \Gamma_2) = A \times \Re \left( \left\langle \frac{E + i\Gamma_2(E)}{\sqrt{(E + i\Gamma_2(E))^2 - \Delta(k)^2}} \right\rangle_{fs} \right) + B \times E \tag{2.2}
\]

A constant scaling factor in the fit, \( A \), will absorb to some degree the \( \exp(\kappa z) \) pre-factor. However, a key factor in the fit is the broadening, \( \alpha \), which determines how rounded or \( \bigtriangledown \)-shaped the spectra appear, and which is a parameter that is sensitively dependent on features at higher energies due to the STM tunneling condition.

Pushp also fits \( g(V) \) spectra, grouped by apparent gap size and averaged, to a sum of s-wave gaps. The nodal slope, or the slope of the spectra at low energy, is extracted to argue that underdoped compounds have a universal nodal gap behavior, which extends across smaller and smaller portions of the Fermis surface as doping is further reduced, and overdoped materials display a pairing strength that decreases with increasing doping.

These instances of use of the slope at small energies are highly questionable because the low-energy slope contains an arbitrary multiplicative factor which likely contains information coupled in from other energy scales. Pushp normalizes with both \( V_s = -100 \, \text{mV} \) and \( V_s = -150 \, \text{mV} \) and concludes that since the two produce similar results, normalization is not a problem. However, all that proves is that there is not significant LDOS variation in the range of \([-150 \, \text{meV}, -100 \, \text{meV}] \). It may still
be a problem that inhomogeneous feature at higher energies are altering the apparent shape of features at the gap node.

For exactly the reasons outlined in Section 2.1 above, Kohsaka et al. introduced the ratio maps $Z(V)$ and $R(V)$, which remove the setup condition, in a 2007 study of highly underdoped Ca$_{1.88}$Na$_{0.12}$CuO$_2$Cl$_2$ and Bi$_2$Sr$_2$Dy$_{0.2}$Ca$_{0.8}$Cu$_2$O$_{8+\delta}$ [24]. Motivated by the calculations of electronic correlations of Anderson et al. [3], they define $Z(V)$ as the ratio of the average differential conductance for empty states to that of filled states. Since the differential conductance of each layer has an exactly identical prefactor, the prefactors cancel, and $Z(V)$ is simply [3]

$$Z(V) = \frac{\text{DOS}(E = +eV)}{\text{DOS}(E = -eV)} \approx \frac{2n}{1 + n} \quad (2.3)$$

Experimentally, this is realized as

$$Z(x, y, V) = \frac{g(x, y, z, +V)}{g(x, y, z, -V)} \quad (2.4)$$

Additionally, motivated by spectral-weight sum rules calculations that relate the current ratio to local charge density, $n(x, y)$ [47], Randeria defines $R(V)$ as

$$R(V) = \frac{\int_0^{\infty} \text{DOS}(x, y, E) dE}{\int_{-\infty}^0 \text{DOS}(x, y, E) dE} \approx \frac{2n(r)}{1 - n(r)} \quad (2.5)$$

Experimentally, this is realized as [24]

$$R(x, y, V) = \frac{I(x, y, z, +V)}{I(x, y, z, -V)} \quad (2.6)$$

$Z(V)$ maps and $R(V)$ maps have a number of advantages and disadvantages. They do exactly cancel out any spatially varying prefactor in a very straight-forward and
unambiguous way. By design, they cancel out any signals which are constant in energy or symmetric about the Fermi level and enhance signals that are anti-symmetric about the Fermi level. $Z(V)$ maps are particularly well-suited to the extraction of quasiparticle interferences (QPI), and have been used effectively to do so in a number of STM studies [24, 29, 33, 25, 11]. $R(V)$ maps, since they integrate over all energies, can enhance a very small signal and proved crucial in the exposure of static checkerboard order in highly underdoped cuprates [24]. However, there are some limitations. The theory behind both $R(V)$ maps assumes an integration up to very high energy ($\sim 1\, \text{V}$), higher than any other energy scale in the system. STM tunneling setpoints are typically not greater than $-150\, \text{mV}$, which may not be large enough to satisfy that assumption. Additionally, an $R(V)$ map is completely blind to any signal that is symmetric about the Fermi level and may enhance or destroy in a confusing manner any signal which is not exactly symmetric or antisymmetric, such as, potentially, a charge density wave order.

Many recent STM studies begin by asserting that $g(x, y, V) \propto DOS(x, y, eV)$ [41, 42, 60, 62]. Some take advantage of the setpoint removal in $Z(V)$ maps, accepting the loss of symmetric-about-the-Fermi-level information. For some observations, in some materials, this may be a reasonable approximation. For a highly spatially inhomogeneous material with complex orders at multiple different energy scales like the cuprates, it would be better to have a way to reliably extract the unadulterated $LDOS(x, y, E)$ without losing energy resolution. That is the goal of the normalization method described in this chapter.
2.3 Introduction to the Case Study Dataset

The case study dataset that we use in this chapter is introduced in Appendix A.1 and discussed extensively in various sections of Appendix B. It consists of three interleaved spectral surveys, where each of the three spectra were taken in sequence at the same location before moving onto the next point on the grid, in the process described in Section 1.3.4. The three data sets are: a $g(x, y, V)$ map taken with $V_s = -100mV$ (which we will refer to as $g_1$), a $g(x, y, V)$ map taken with $V_s = +100mV$ (which we will refer to as $g_2$), and an $I(z)$ map taken with $V_s = -100mV$. All three were taken with $I_s = 100pA$. The map is nominally $9 \times 9 \, nm^2$ and $128 \times 128$ pixels$^2$, with 5pixels/atom resolution. For each spectral survey there is an associated simultaneous topograph. For the $dI/dV$ maps, the height that the tip was fixed at during the spectrum is recorded as a pixel in the simultaneous topograph. For $I(z)$, the height that the tip is stabilized to before beginning the $I(z)$ sweep is recorded as a pixel in the simultaneous topograph. At each location in space, then, we have the $dI/dV$ recorded with two different setup conditions and a measure of the local work function, $\phi(x, y)$.

Figure 2.3 shows the drift-corrected simultaneous topographs and associated Fourier transforms. The atomic scale information is clearly congruent between the two topographs, but $\xi$-length scale information of dappled light and dark patches differs. The lattice periodicity has been collapsed onto single real, positive Bragg pixels. The streaks of negative value that cross the Bragg pixels are an artifact of the drift-correction algorithm. The topographs show the variation in $z_{\text{topo}}$ with $V_s$ and contain spatially varying information about the integral of the LDOS. These particular to-
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Figure 2.3: Simultaneous topograph from the \textit{g}_1 map, taken with $V_s = -100 \text{ mV}$, (a) and \textit{g}_2 map, taken with $V_s = +100 \text{ mV}$, (d). The topographs are $9 \times 9 \text{ nm}^2$ and $128 \times 128$ pixels$^2$ and have been drift-corrected. The flat gray stripe on the edge is an artifact of drift-correction. b) and c) are Real and Imaginary parts, respectively, of the Fourier Transform of a) and e) and f) are Real and Imaginary parts, respectively, of the Fourier Transform of d). The Bragg pixels are at the corners of the “box.” The erased white vertical stripe is the byproduct of row-wise background subtraction.
Figure 2.4: Constant-energy layers extracted from the two $g$ maps. a), b), and c) are the $-100\, mV$, $0\, mV$, and $+100\, mV$ layers of the $g_1$ map, taken with $V_s = -100\, mV$. d), e), and f) are the $-100\, mV$, $0\, mV$, and $+100\, mV$ layers of the $g_2$ map, taken with $V_s = +100\, mV$. Note that a) and f) are the layers of the respective setpoint for the two maps. The $g$ layers are $9\times9\, nm^2$ and $128\times128\, pixels^2$ and have been drift-corrected.
pographs provide an interesting way to visualize spatial variation in tunneling asymmetry; this is explored further in Appendix B.10.

In Figure 2.4 are three slices from the $g(x, y, V)$ maps. The $\xi$-length scale spatial variation is clearly not the same between maps taken at the same energy and exactly the same location with different $V_s$. The strongest periodicity may appear to be atomic-scale periodicity but it is in fact a wavevector that is $\sim \frac{3}{4} \frac{2\pi}{a_0}$.

2.4 Work Function Normalization: The Process

The goal of this normalization procedure is to use a measured $\kappa$ and a $z_\delta$ that we extract from measured quantities to explicitly divide out the prefactor, leaving only the LDOS behind. The reason this is difficult is that our map of $\kappa(x, y)$ may have geometric effects and, as discussed above, $z_\delta$ is an ill-defined and difficult-to-extract quantity. This section contains a discussion of several attempts to apply this normalization scheme.

More explicitly, the goal is to take the measured quantity

$$g(x, y, V, z_\delta) \propto \exp(-2\kappa z_\delta) DOS(x, y, eV)$$

and multiply it by $\exp(2\kappa z_\delta)$, where here $\kappa$ is directly measured with an $I(z)$ map and $z_\delta$ is extracted from the topograph. If the appropriate $\kappa$ and $z_\delta$ are used, this should expose the true $DOS(x, y, eV)$ for study. We will call this map of $\exp(2\kappa z_\delta) \ast g$ a $P$ map. The same argument exactly applies to the current, which as measured is
\[ I(x, y, V) \propto e^{\exp(-2\kappa z_\delta)} \int_{-eV}^{0} DOS(x, y, E) dE \]  

(2.8)

and the same normalization factor would expose the true integral of \( DOS(x, y, eV) \) for study. We will call this map of \( e^{\exp(2\kappa z_\delta)} \times I \) a Q map.

In the next few sections you will see many figures that use the same four-paneled arrangement, which I call “Quad” comparisons. For all of these figures, raw data from the first map, with \( V_s = -100 \) mV, is in the top left. Raw data from the second map, with \( V_s = +100 \) mV, is in the bottom left. Normalization by multiplication of \( e^{\exp(2\kappa z_\delta)} \), where the \( \kappa \) and \( z_\delta \) in question will vary, is applied to the objects in the left column. The corresponding \( P \) or \( Q \) maps are displayed to the right. There are three interesting points of comparison. In the left column, comparing top to bottom: in the raw data, how does a different \( V_s \) cause the data to vary? Since these are taken at the same location and energy, any differences are due to the setpoint effect. In the right column, comparing top to bottom: in the normalized data, is there agreement between data taken with different \( V_s \)? This is a necessary but not sufficient condition for successful normalization. Comparing left to right: how has the normalization factor changed the data? Note which features and periodicities are introduced or eliminated.

### 2.4.1 Work Function of Cuprates Measured by STM

We take a brief digression here into a discussion of how the work function, \( \phi \), and therefore the \( \kappa \), can be measured by STM. The work function of a cuprate superconductor, \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \), was first measured with an STM by Jia et al. in
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1998 [20]. Jia measures local work function with a lock-in technique, modulating \( z \) and demodulating \( I \), and reports the observation of supermodulation-scale structure in a map of work function.

This spatial variation of work function, correlated with structural features, was observed as well by Sugimoto et al. in a 2008 study of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) [50]. Sugimoto maps the local work function by fitting an exponential decay to \( I(z) \) and shows atomic-scale variation in \( \phi \) as well as strong anti-correlation of \( \phi \) with supermodulation height. They speculate that the supermodulation changes the local density of Bi atoms and areas of high Bi density have higher \( \phi \). Motivated by the model of Tersoff and Hamann [51] discussed in Section 1.1, they create a “real” LDOS map by multiplying \( g(x,y,V) \) by \( L(\vec{r}) \equiv \exp(-2\sqrt{2m_e\phi(\vec{r})R/\hbar}) \). \( R \), the effective radius of the STM tip, is estimated to be \( \sim 1 \text{ Å} \) from spatial resolution. They conclude that since the LBH varies so much less than \( g(x,y) \), the correction is negligible. This is an interesting interpretation of Tersoff and Hamann’s theory, and assumes that the constant tip radius will play a larger role than the variation in tip-sample separation distance. As we shall show in later sections, the inclusion of the spatially varying tip-sample separation information is a crucial element to the work-function normalization process that we adopt.

We measure work function by fitting a full \( I(z) \) spectrum to an exponential decay. A map of \( \kappa \), from our case study dataset, can be seen in Figure 2.8g. We find that in this dataset, \( \phi = 4.7 \pm 1.1 \text{ eV} \) (standard deviation from spatial variation), which is roughly commensurate with Sugimoto’s finding of \( 5.3 \pm 0.4 \text{ eV} \). It is unclear why we measure such a larger standard deviation, but it is possible that tip effects are
the culprit, since we have found that the standard deviation from spatial variation of \( \phi \) as measured over 5 different maps, with different tips, on the same surface varies from 5\% to 22\% of the mean. The samples we study are Pb-doped and do not display supermodulation, so the features that we observe in a map of \( \phi \) are atomic-scale variation and some signature of the randomly distributed Pb atoms, either due to larger geometric size or to the very slightly different work function of Pb as compared to Bi. \( \phi_{Pb} = 4.25 \text{eV} \), and \( \phi_{Bi} = 4.34 \text{eV} \), so the difference in \( \kappa \propto \sqrt{\phi} \) should be only 1.1\% [54].

Several factors may contribute to the observed atomic-scale variations in the measured work function. Supermodulation scale variations have been posited to be the result of varying local density of Bi atoms leading to varying local charge density. In theory, the work function we measure should be a mixture of \( \phi_{\text{surface atoms}} \) and \( \phi_{\text{tip}} \). Without supermodulation, the local density of Bi does not vary regularly, although the Bi are slightly displaced by physically larger Pb neighbors. It’s possible that there are subtle geometric effects at work: the local environment of a tip in a valley between atoms will be different from the environment of a tip at the very apex of the atom.

### 2.4.2 Take \( z_{\text{topo}} = z_\delta \)

An interesting, and quite tractable, first step is to take \( z_{\text{topo}} \) in our exponential correction factor. Then we can plug Equation 2.1 into Equation 2.7 and get

\[
P(x, y, V) \propto \exp(2\kappa z_{\text{topo}}) \ast g(x, y, V)
\]
\[
\propto \exp(2\kappa z_{\text{topo}})\exp(-2\kappa z_{\delta})\text{DOS}(x, y, eV) \\
\propto \exp(2\kappa(z_{\text{topo}} - z_{\delta}))\text{DOS}(x, y, V) \\
\propto \exp(2\kappa z_{\text{surface}})\text{DOS}(x, y, V)
\]

The \(P\) map produced is not the unadulterated LDOS, but a multiplicative mixture of topographic and LDOS information. However, and this is the key point, the prefactor has no energy dependence or LDOS dependence. The exponential of this \(P\) map contains just the purely structural information about the size and location of atoms in the surface plane. The only energy dependence in the map comes from a linear proportionality to the LDOS. This \(P\) map eliminates the possibility of electronic modulations in the LDOS appearing in energy ranges where they are not actually present.

Figure 2.5 shows a comparison between \(g\) maps and \(P\) maps calculated using the \(\kappa(x, y)\) as measured and \(z_{\text{topo}}\) as the \(z\). \(P_1\) and \(P_2\) are strikingly similar to each other, especially as compared to \(g_1\) versus \(g_2\), which for some layers appear to have very little in common. While the \(P\) maps contain a great deal of structural, topographic information, including the irregularly distributed Pb-dopants, it is clear that the \(\xi\) length scale structure, or the light and dark patches of \(\sim nm\) size, agree exactly between the two maps. In short, because the two maps taken with different \(V_s\) have been made identical, the setpoint effect has been removed. The utility of this particular \(P\) map, since it is a mixture of topographic and spectroscopic information, is that the energy dependence of non-atomic scale orders can be trusted to be reliable. Many effects, such as static charge ordering or nematic order, appear to have different
energy dependences if calculated from differently normalized maps. A comparison to this kind of $P$ map can verify the accuracy of the energy dependence.

While the $P$ and $Q$ maps certainly look more similar to each other than the $g$ and $I$ maps to the naked eye, a better way to qualify the degree of similarity is by computing the correlation coefficient between the two maps. Most generically, the correlation coefficient between two sets of data, $x$ and $y$, is given by

$$\sum_{i} \frac{(x_i - \bar{x})(y_i - \bar{y})}{(N-1)\sigma_x\sigma_y}$$

where $N$ is the number of points in each dataset, $\bar{x}$ and $\bar{y}$ are the means, and $\sigma_x$ and $\sigma_y$ are the standard deviations of $x$ and $y$, respectively. The correlation between each energy layer of the two $g$ maps is shown in the upper left panel of Figure 2.7. The correlation of the raw $g$ peaks around $0\,mV$ at 0.8, and falls all the way to 0.0 at high positive energies. The upper right panel of Figure 2.7 shows the correlation between the two $P$ maps as a function of energy. These correlation coefficients are near-constant in energy and all above 0.95. In the lower panels of Figure 2.7 are angularly averaged correlations, as a function of distance, for each energy layer. The color of each curve in the lower panel corresponds to the color of a single point in the upper panel. The single point in the upper panel is the value of the $y$-intercept of the curve in the lower panel. The correlation length of the $g$ maps seems to be dominated by $\xi$ scale structure, on order $2\,nm$. The atomic-size correlation length and clear atomic resolution makes it clear the structural congruence is a significant part of the high degree of correlation between $P$ maps. The correlations between $Q$ maps, not shown, is almost exactly similar to the corresponding correlations in Figure 2.7.
Figure 2.5: (next page) Comparison of $g$ and $P$ maps. These $P$ maps were made with the $\kappa$ as measured and the unaltered $z_{\text{topo}}$ and the exponential factor was multiplied by the raw, as-measured $g$. Three representative energy layers are shown. The schematic on the left shows the arrangement of data in the Quad format described in the text. In the upper left of each panel is $g_1(x, y, V, V_s = -100 \text{ mV})$. In the lower left of each panel is $g_2(x, y, V, V_s = +100 \text{ mV})$. In the upper right is $P_1 = \exp(2\kappa(x, y)z_{\text{topo}}(x, y, V_s = -100 \text{ mV}))g_1(x, y, V, V_s = -100 \text{ mV})$. In the lower right is $P_2 = \exp(2\kappa(x, y)z_{\text{topo}}(x, y, V_s = +100 \text{ mV}))g_2(x, y, V, V_s = +100 \text{ mV})$. 
Schematic of the Quad figure arrangement: the four sections in each of the three panels to the right are as labeled below.

<table>
<thead>
<tr>
<th>$g_1$</th>
<th>$P_1 \equiv \exp(2\kappa z_{\text{topo},1}) \ast g_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_2$</td>
<td>$P_2 \equiv \exp(2\kappa z_{\text{topo},2}) \ast g_2$</td>
</tr>
</tbody>
</table>

![Images of Quad figure arrangement with voltages V=+100mV, V=0mV, V=-100mV]
Figure 2.6: (next page) Comparison of $I$ and $Q$ maps. These $Q$ maps, like the $P$ maps in the previous figure, were made with the $\kappa$ as measured and the unaltered $z_{\text{topo}}$ and the exponential factor was multiplied by the raw, as-measured $I$. Three representative energy layers are shown. Note that $-100 \text{mV}$ is $V_s$ of $I_1$ and $+100 \text{mV}$ is $V_s$ of $I_2$ and the current at that energy level is therefore constant. The schematic on the left shows the arrangement of data in the Quad format described in the text. In the upper left of each panel is $I_1(x, y, V, V_s = -100 \text{mV})$. In the lower left of each panel is $I_2(x, y, V, V_s = +100 \text{mV})$ In the upper right is $Q_1 = \exp(2\kappa(x, y)z_{\text{topo}}(x, y, V_s = -100 \text{mV}))I_1(x, y, V, V_s = -100 \text{mV})$. In the lower right is $Q_2 = \exp(2\kappa(x, y)z_{\text{topo}}(x, y, V_s = +100 \text{mV}))I_2(x, y, V, V_s = +100 \text{mV})$. 
Schematic of the Quad figure arrangement: the four sections in each of the three panels to the right are as labeled below.

<table>
<thead>
<tr>
<th>$I_1$</th>
<th>$Q_1 \equiv \exp(2\kappa z_{\text{topo},1}) * I_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2$</td>
<td>$Q_2 \equiv \exp(2\kappa z_{\text{topo},2}) * I_2$</td>
</tr>
</tbody>
</table>

$V = -100 \text{mV}$

$V = 0 \text{mV}$

$V = +100 \text{mV}$
Figure 2.7: Correlation between $g$ maps and $P$ maps. The upper left panel is the correlation between each energy layer of the two $g$ maps. The upper right panel is the correlation between the two $P$ maps as a function of energy. The lower panels are angularly averaged correlations, as a function of distance, for each energy layer. The color of each curve in the lower panel corresponds to the color of a single point in the upper panel. The single point in the upper panel is the value of the y-intercept of the curve in the lower panel.
2.4.3 Failed Attempts to Capture $z_\delta$

The proper procedure for extracting $z_\delta$ from $z_{\text{topo}}$ is not obvious. As mentioned above, if the topographic information consisted of a regular atomic lattice and the LDOS modulations happened on a $\xi$ length scale, then a Fourier filter would cleanly separate the two. We attempted to Fourier the filter the topographs in multiple ways to expose $z_\delta$ and did not succeed. In this section we will explain why a simple Fourier filter will not suffice for this material.

In Figure 2.8 we show the effect of Fourier filters on the inputs to the $P$ map: the $z_{\text{topo}}$, $\kappa$, and $g$. We Fourier filter all inputs in the same fashion so that we don’t have un-normalized long-wavevector information in the $P$ map. The top row contains Fourier filtered topographs. The leftmost is the raw topograph and shows a regular atomic lattice, randomly dispersed Pb atoms, and $\xi$ scale variations. It is straightforward to identify the different sources of spatial variation. Unfortunately, it is not straightforward to separate them. Figure 2.8b shows a topograph filtered by a Fourier filter which sets to zero all wavevectors that are not inside the box defined by the Bragg pixels. This filter shall be referred to with a box subscript, eg. $g_\Box$. The Pb atoms are clearly still present in the filtered topograph. Even in a far more aggressive Fourier filter, a circle which sets to zero all wavevectors larger than $\frac{1}{3}a_0$, the Pb atoms are still present (Figure 2.8c). This filter shall be referred to with a circle subscript, eg. $g_\circ$.

The red circle identifies two Pb atoms that at adjacent lattice sites in the unfiltered topograph. The local LDOS environment around them is relatively depressed, and clearly $z_\delta$ at that location should be lower than average. In the Fourier filtered
Figure 2.8: (next page) The effects of Fourier filters on the $V_s = -100 \text{ mV}$ simultaneous topograph, a), b), c). Effects of Fourier filters on $\kappa(x,y)$, g), h), i). Effects of Fourier filters on $g_1(x,y, V = 0 \text{ mV})$, m), n), o). The Real parts of the Fourier transforms of each object are displayed directly below. The leftmost column is raw data. The middle column shows the effect of a filter which sets to zero every wavevector that is not inside the box defined by the Bragg pixels. The rightmost column shows the effect of a filter which sets to zero every wavevector that is larger than $\frac{1}{3} a_0$. 
topographs, we see that the area is locally still quite bright, reflecting still-present topographic information.

Fourier filtering will never remove the Pb atoms entirely because the random dispersal of the Pb atoms means that information about their location is present in the Fourier transform at extremely small wavevectors. \( P \) maps made with these Fourier filters applied to the inputs are tantalizing. The box-filtered \( P^\square \) map can be seen in Figure 2.9 and the small circle-filtered \( P^\circ \) map can be seen in Figure 2.10. Clearly, the \( P \) maps are identical and the setpoint effect has been removed. However, topographic information is still present in these \( P \) maps, and we have yet to achieve our goal of clean separation of the unadulterated LDOS.

This section shows that it is easier than one might think to make two different \( g \) maps taken with two different \( V_{set} \) look the same. The key thing is that the topographic information that is included in the normalization is \textit{in common} and the spectroscopic information that is included in the normalization is \textit{different, and correct}. By “correct,” I mean that it properly normalizes away the prefactor. The fact that the two \( P \) maps agree, then, is a necessary but not sufficient condition for declaring them properly normalized.

2.4.4 Ideas, not yet implemented, for how to capture \( z_\delta \)

There are several promising directions that we could go with this normalization method.

While the Pb-doped material that lacks supermodulation is not conducive to Fourier filtering, it is possible that a material with only long-range order, and no
Figure 2.9: (next page) Comparison of $g$ and $P$ maps. These $P$ maps were made with low-pass Fourier filtered $\kappa$ (which can be seen in Figure 2.8h) and low-pass Fourier filtered $z$ (one of which can be seen in Figure 2.8b). The exponential factor was multiplied by low-pass Fourier filtered $g$ (the $-100 \, mV$ slice of $g_{\square,1}$ can be seen in 2.8n). The low-pass filter in all cases consists of a box, centered at the origin, with the edges just inside the box defined by the Bragg pixels. Three representative energy layers are shown. The schematic on the left shows the arrangement of data in the Quad format described in the text. In the upper left of each panel is $g_{\square,1}(x, y, V, V_s = -100 \, mV)$. In the lower left of each panel is $g_{\square,2}(x, y, V, V_s = +100 \, mV)$ In the upper right is $P_{\square,1} = \exp(2\kappa(x, y)z(x, y, V_s = -100 \, mV))g_{\square,1}(x, y, V, V_s = -100 \, mV)$. In the lower right is $P_{\square,2} = \exp(2\kappa(x, y)z(x, y, V_s = +100 \, mV))g_{\square,2}(x, y, V, V_s = +100 \, mV)$. 

Schematic of the Quad figure arrangement: the four sections in each of the three panels to the right are as labeled below.

\[
\begin{array}{|c|c|}
\hline
\text{\(g_1\)} & \mathcal{P}_{c,1} \equiv \exp(2\kappa z_{c,1})g_1 \\
\hline
\text{\(g_2\)} & \mathcal{P}_{c,2} \equiv \exp(2\kappa z_{c,2})g_2 \\
\hline
\end{array}
\]
Figure 2.10: (next page) Comparison of $g$ and $P_\circ$ maps. These $P_\circ$ maps were made with low-pass Fourier filtered $\kappa_\circ$ (which can be seen in Figure 2.8h) and low-pass Fourier filtered $z_\circ$ (one of which can be seen in Figure 2.8c). The exponential factor was multiplied by low-pass Fourier filtered $g_\circ$ (the $-100\,mV$ slice of $g_{\circ,1}$ can be seen in 2.8o). The low-pass filter in all cases consists of circle, centered at the origin, of radius $\frac{1}{3}a_0$. Three representative energy layers are shown. The schematic on the left shows the arrangement of data in the Quad format described in the text. In the upper left of each panel is $g_{\circ,1}(x,y,V,V_s = -100\,mV)$. In the lower left of each panel is $g_{\circ,2}(x,y,V,V_s = +100\,mV)$. In the upper right is $P_{\circ,1} = exp(2\kappa_\circ(x,y)z_\circ(x,y,V,V_s = -100\,mV))g_{\circ,1}(x,y,V,V_s = -100\,mV)$. In the lower right is $P_{\circ,2} = exp(2\kappa_\circ(x,y)z_\circ(x,y,V,V_s = +100\,mV))g_{\circ,2}(x,y,V,V_s = +100\,mV)$. 
Chapter 2: Normalization of STM Spectroscopy

Schematic of the Quad figure arrangement: the four sections in each of the three panels to the right are as labeled below.

\[
\begin{array}{c|c}
\text{g}_1 & \rho_{0,1} \equiv \exp(2 \kappa z_{0,1}) g_1 \\
\hline
\text{g}_2 & \rho_{0,2} \equiv \exp(2 \kappa z_{0,2}) g_2 \\
\end{array}
\]
localized, point-like topographic information, could be effectively Fourier filtered. An atomic lattice and supermodulation could be filtered out and the real DOS of the sample revealed. Open questions about spectral inhomogeneity could be addressed. However, Fourier filtering requires giving up some information, so questions about the energy dependence of, for example, lattice-matched electronic structure or the \( \vec{q}_\frac{3}{4} \) feature could not be answered, and removal of the supermodulation through Fourier filtering requires a very aggressive filter, since the wavevector is only \( \frac{1}{7} \frac{2\pi}{a_0} \).

The make-average-unit cell algorithm, described in Appendix B, can be used to build up a composite unit cell which accurately describes the average atom shape and eliminates by averaging out all of the \( \xi \) length scale electronic structure. A composite topograph, made up of average unit cells arranged to form a regular lattice, can be subtracted from the measured \( z_{\text{topo}} \), giving a good approximation to \( z_\delta \). If Pb atoms are identified and averaged into a separate average unit cell, then a composite topograph of appropriately arranged Bi and Pb can be built up and subtracted from the topograph. In practice, this is quite difficult, and does not work well yet. It may at some point in the future.

### 2.5 Charge Checkerboard Dependence on Normalization

A great deal of recent attention has fallen on the charge modulation that STM observes at \( q \sim \frac{3}{4} \frac{2\pi}{a_0} \) [28, 34, 32], which some call the “smectic” order. This translational and rotational-symmetry breaking order may be coupled to the nematic order [28, 34]
Figure 2.11: The relative amplitude and wavevector of the \( \vec{q}_3 \) modulation for a variety of different normalizations. The first is the raw \( g \) maps. The last is the \( P \) maps described in earlier sections. The others are \( Z^- \) and \( Z^+ \) normalizations, or division by the lowest and highest energy layer, respectively. The subscript 1 refers to the dataset taken with \( V_s = -100 \text{ mV} \), and the subscript 2 refers to the dataset taken over the same area with \( V_s = +100 \text{ mV} \). The approximate range of the the superconducting gap, \( \pm 8 \text{ meV} \) in this overdoped material, is marked by a gray band about the Fermi level.
and may be related to the static charge order that STM observes at $q \sim \frac{1}{4} \frac{2\pi}{a_0}$ [32]. If the relationship between these different orders is to be disentangled, then it is crucial that the true energy dependence of each is known.

The energy dependence of the $\vec{q}_4$ peak is an issue that can be addressed by the $P$ map which is made by taking $z_\delta = z_{topo}$, since the extra topographic information present in the $P$ map is concentrated at the Bragg pixels (atomic lattice information) and at very low wavevectors (Pb dopant location information). Since this $P$ map does properly normalize the LDOS information, a reliable extraction of the $\vec{q}_4$ energy dependence is possible.

Figure 2.11 shows the relative amplitude (normalized to the average at each energy) of the $\vec{q}_4$ wavevector as well as the actual size of the wavevector. While we refer to it as $\vec{q}_4$, it actually varies from 0.79 to 0.85, varying both with doping and on a local level [32]. We plot here the full field-of-view average of the wavevector. The peak finding method is described in detail in Elizabeth Main’s PhD thesis [32]. In short, we take a spatial lock-in at a range of possible $q$ and take a weighted average. We look at the apparent behavior of this order in four different normalization schemes. The first is the raw $g$, as in Parker et al. Figure S5 [41]. We see a peak at low positive energies for the $V_s = -100\,mV$ map, and very different behavior for the $V_s = +100\,mV$ map, which shows a strong peak at low negative energies. This should give serious pause to any efforts to study this feature in the raw $g$ maps.

We compare the $P$ map to two other normalization schemes: division by the lowest ($Z-$) or highest ($Z+$) energy layers. The motivation behind these normalizations is that the division by any layer removes the exponential pre-factor, as in the $Z(V)$
maps pioneered by the Davis group, but information about energy-dependence over nearly the full spectral range is retained. If one can divide by an energy layer where no interesting features are present (i.e., outside the superconducting gap, the pseudogap, and any other charge order), then no artifacts are introduced. The two obvious candidates for boring energy layers are the layers farthest away from the Fermi level. This normalization method has the advantage over $P$ map normalization that no extra data is required and it can be made from a simple raw $g$ map.

As we can see in Figure 2.11, the $P$ maps do show exactly the same behavior for maps taken with different setpoints, showing that the setpoint effect has been successfully removed. Interestingly, it shows the best agreement with $Z^-$ at positive energies and $Z^+$ at negative energies, suggesting that a piece-wise normalization scheme may be the best way to extract reliable information from datasets that do not have an accompanying $I(z)$ map.

The plot of wavevector versus energy suggests that $P$, $Z^-$, and $Z^+$ all give trends that agree with each other and seem impervious to setpoint effect, so any of these normalization schemes would be preferable to using raw $g$. Slight dispersion of the $\vec{q}_3$ wavevector can be seen at low negative energies. The signal-to-noise of the $\vec{q}_3$ peak in this dataset is low, and the algorithm that I used to find this peak is susceptible to under-estimating dispersion (that is, skewing $q$ more towards the average value) with low signal-to-noise. The true dispersion of the $\vec{q}_3$ peak will have to be calculated from a $P$ map computed from a dataset with better signal-to-noise.
2.6 Conclusions

In conclusion, I have shown that it is possible to remove the setpoint effect inherent in $dI/dV$ maps taken with a constant-current setup condition. This can be accomplished by creating a map of $P(x, y, V) \equiv exp[2\kappa(x, y)z(x, y)]\frac{dI}{dV}((x, y, V, V_s)$, where $\kappa(x, y)$ is extracted from the slope of a linear fit to $\ln[I(z)]$ versus $\ln(z)$ and $z$ is an approximation to $\Delta_z$. Since $dI/dV \propto exp(-2\kappa z_\delta)LDOS(x, y, eV)$, a $P$ map should in theory expose the true LDOS.

While we have yet to cleanly separate $\Delta_z$ from $z_{topo}$, and cannot therefore yet create a $P$ map which is the true LDOS alone, we have shown that a $P$ map computed with $z_{topo}$, which is a mixture of topographic information and properly normalized LDOS information, can be a useful object in exposing true energy dependence. We have studied the incommensurate charge modulation at $\vec{q} \sim \frac{3\pi}{4a_0}$ in this $P$ map, and have found that the energy dependence, which appears dramatically different in raw $dI/dV$ maps taken with different $V_s$, can be cleanly extracted and is identical in $P$ maps taken with different $V_s$. Figure 2.11 shows unambiguously that, in the case of the incommensurate charge modulations in the cuprate superconductors, the typical STM experimentalist approximation of $\frac{dI}{dV} \propto LDOS$ is not acceptable and may lead to significant confusion.

This method of normalization via multiplication by $exp[2\kappa(x, y)z_{topo}(x, y)]$ may prove useful in the study of the incommensurate charge modulations at $\vec{q} \sim \frac{12\pi}{4a_0}$ and $\vec{q} \sim \frac{3\pi}{4a_0}$, and in finally determining whether they are related orders. Indeed, this general method may prove useful in exposing the true energy dependence of any order in a wide variety of materials, and should be a standard tool in any scanning
tunneling microscopist’s arsenal.
Chapter 3

Broken Symmetry in the Electronic Structure of Bi-based Cuprates

The pseudogap is a region of phase space characterized by depressed Fermi level Density of States at low hole doping (from highly underdoped through optimally and even slightly overdoped), bounded by a crossover temperature $T^*$ [8, 53]. Angle resolved photoemission (ARPES) [14, 12] and c-axis tunneling [26] see a gap open with falling temperature that is highly reminiscent, in scale and momentum dependence, of the d-wave superconducting gap that is the signature of superconductivity, but there is a growing consensus among STM experimentalists that there are two energy scales in the single particle excitation spectrum, one that turns on at $T_c$ and is due to superconductivity, and one that can be attributed to the as-yet unidentified order that comprises the pseudogap state.

In the past few years there have been puzzling hints of a pseudogap-phase symmetry-breaking order from a wide variety of experimental techniques, including STM, ARPES,
neutron scattering, nuclear magnetic resonance (NMR), nuclear quadropole resonance (NQR), and electronic and thermal transport. The existence of rotational and lattice-translational symmetry breaking charge and spin order on a few-CuO$_2$-unit cell length scale (referred to as “stripe” ordering, “checkerboard,” or “smectic,” in analogy to liquid crystals) has been well-established but not well understood. In addition there may be some kind of intra-unit-cell symmetry-breaking order (such as “nematic” ordering [28] or inversion symmetry breaking [30, 31]).

STM has shown evidence for electronic checkerboard states breaking translational symmetry [59, 17, 18, 57, 33] and, more recently, nematic states breaking rotational symmetry [28, 34]. These checkerboard states take the form of incommensurate charge modulations with $\vec{q}_1 \sim \frac{1}{4} \vec{Q}$, where $Q_x = (1, 0) \frac{2\pi}{a_0}$ and $Q_y = (0, 1) \frac{2\pi}{a_0}$. A charge ordering signature is also seen at $\vec{q}_2 \sim \frac{3}{4} \vec{Q}$. Furthermore, STM has found nanoscale variations in these symmetry breaking states [17, 18, 57, 33, 60, 41, 32].

ARPES has observed electronic states that break time-reversal symmetry [21] and both particle-hole symmetry and translational symmetry in the pseudogap region of Bi-compounds [61, 15].

Scattering experiments have shown a variety of different symmetry-breaking orders in different cuprate compounds. Static charge and spin ordering near x~0.125 compatible with the theorized stripes has been observed via neutron scattering in the LBCO and LSCO compounds [55, 56] and via resonant x-ray scattering in LBCO [1, 22]. In the pseudogap region of YBCO, neutron scattering experiments have exposed a subtle staggered magnetic order that breaks time-reversal symmetry while preserving the translational symmetry of the crystal [13]. Other neutron scattering results
on YBCO [16] also point towards an electronic nematic state. Similar states have been observed in the pseudogap phase of Hg-compounds [30, 31].

Both electronic and thermal transport studies have shown evidence of broken symmetries in the pseudogap phase. Nernst effect studies in YBCO [10] and LSCO [9] are compatible with an electronic nematic state. NMR and NQR have observed freezing of anti-ferromagnetic fluctuations into a static stripe phase that breaks four-fold symmetry [19, 35].

The theoretical efforts to describe the pseudogap phase and its relationship, along with superconductivity, to a quantum critical point are well summarized in Kivelson [23] and Vojta [58].

This is an exciting time to be exploring the pseudogap phase. New pieces of the puzzle, from different experimental techniques, applied to different members of the cuprate family, are being brought into play at a rapid pace. This chapter details the use of STM to explore electronic nematic order in the overdoped Bi-based cuprates.

3.1 Lattice Geometry and Notation

The cuprate superconductors are a family of quasi-2 dimensional compounds that have in common one or more CuO$_2$ planes. The structure is a perovskite-type, with each Cu atom surrounded by a tetrahedron of 5 O atoms (shown in Figure 3.1a). In the parent compounds, each Cu atom has one electron in a $d_{x^2-y^2}$ orbital which hybridizes with the O $p_x/p_y$ orbital, resulting in a half-filled band. Due to strong Coulomb repulsion, the electrons are localized and the material behaves as a Mott insulator. As holes dopants are added, the pseudogap phase, with steadily decreasing
Figure 3.1: a) The crystal structure of Bi$_2$Sr$_2$Cu$_{1+\delta}$O$_{6+\delta}$, or Bi2201. Room temperature lattice constants are $a = b = 5.4\text{Å}$ and $c = 24.6\text{Å}$. (Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, or Bi2212, has an additional Ca plane.) Cleavage planes are identified with arrows. The average Cu-Cu distance, and the average Bi-Bi distance imaged by STM, is 3.8Å. b) Schematic of a single CuO$_2$ plane. Black arrows represent the spin of each Cu ion in the antiferromagnetic state. c) A generic hole-doped cuprate superconductor phase diagram. The parent state is an antiferromagnetic Mott insulator. As hole dopants are added, charge carriers becomes mobile. There is a characteristic dome-shaped superconducting phase bounded by the critical temperature $T_c$. At low doping the mysterious pseudogap phase exists up to a temperature scale $T^*$. $T^*$, and the superconducting phase, with characteristic dome-shaped $T_c$, are traversed.

STM and ARPES access the BiO plane, which is exposed after mechanical cleav-
Figure 3.2: The CuO$_2$ plane as seen from above, as in Figure 3.1b: Cu $d_{x^2-y^2}$ orbitals are in blue and O $2p_{\sigma}$ orbitals are in yellow. The Real part of the FT at $Q_x$ and $Q_y$ give the Bi lattice modulation, a cosine since we place the center of a Bi atom at (0,0). Adapted from Lawler et al. [28].

The regular atomic lattice seen in STM images is the Bi atoms; O atoms are not visible to STM [37]. Each Bi atom is directly above a Cu atom. Both the BiO and SrO planes are semiconducting with a large gap, so in the energy ranges of typical experiments, they act as extensions to the vacuum tunneling barrier [48, 36]. Therefore the LDOS that we measure is of the electrons in the CuO$_2$ plane, and the Bi atoms can be thought of as spatial markers for the Cu atom locations. Figure 3.2 shows the CuO$_2$ plane and identifies the geometry of interest. The Bi atoms form a regular tetragonal lattice with a small ($\sim 2\%$ of the the tetragonal lattice vector) orthorhombic distortion [63] which is not relevant to this discussion.

The drift correction procedure is of crucial importance for the analysis presented...
in this chapter. I will not repeat here a mathematical description of the algorithm (see Lawler et al. Supporting Online Material for a full treatment [28] and Appendix B for a full consideration of systematic effects). Suffice to say that the purpose of the algorithm is to take the data in a full spectral map, which is typically taken over the course of 0.5 to 4 days, and subject to a number of temperature-drift and piezo-imperfection caused distortions, and to align it onto a perfect atomic lattice, with the center of a Bi atom placed exactly at the (0,0) pixel. The Bragg peaks, \( Q_x = (1,0) \frac{2\pi}{a_0} \) and \( Q_y = (0,1) \frac{2\pi}{a_0} \), which are typically a few pixels wide in raw topographic data, are collapsed onto a single pixel. This drift-correction procedure makes possible algorithms that use all of the information in the full field of view to study intra-atomic electronic structure or lattice-vector periodicities.

We follow Lawler in defining the displacement fields \( \vec{u}(\vec{r}) \) such that the positions \( \vec{r} - \vec{u}(\vec{r}) \) form a perfect square lattice with a Bi atom (or equivalently, Cu atom) at the origin. The drift fields are found by convolving the raw topographic image with a pure lattice over some length scale much larger than the lattice periodicity, computing the phase between the raw lattice and the pure lattice, and then turning that phase into two drift field image objects. The drift fields \( u_x(\vec{r}) \) and \( u_y(\vec{r}) \) are the amount (measured in pixels) that the data needs to be shifted in \( x \) and \( y \), respectively, to fall on a perfect lattice. The drift fields are then applied to the raw data to recast it onto the perfect atomic lattice. Since the drift correction algorithm places a Bi atom at the (0,0) pixel, the topograph \( z(\vec{R}) \) can be written as \( z(\vec{R}) = z_0[\cos(Q_xx) + \cos(Q_yy)] + ..., \) where ... refers to impurities, \( \xi \)-length scale DOS variations, etc. The Real part of any electronic structure at the Bragg wavevectors is therefore in phase with and even
Figure 3.3: Method for mapping local Fourier properties in real space. a) is a topog-raph, or $z_{topo}(x,y)$, $14 \times 14 \text{nm}^2$. The atomic lattice coordinate system is indicated with arrows. b) shows the Real part of the global FT of the topograph, $\mathcal{R}[z_{topo}(\vec{Q})]$, calculated from the entire field of view in a). The Bragg pixels, $Q_x$ and $Q_y$, are the strong positive pixels at the corners of the “box,” indicated by green arrows. In panels c) and d) are the plotted the local value of the Real part of the FT at $Q_x$, or $\mathcal{R}[z_{topo}(\vec{Q}_x)](x,y)$, and the local value of the Real part of the FT at $Q_y$, or $\mathcal{R}[z_{topo}(\vec{Q}_y)](x,y)$, respectively. The images in c) and d) are the same field of view as the topograph in a). At each pixel in c) and d), the FT inside of a Gaussian window of half-width $L$ (radius of the dashed circle, $L = 5\text{atoms}$), centered at that pixel, is calculated, and the Real part of the values at $Q_x$ and $Q_y$, respectively, are extracted and plotted.
about the Bi/Cu lattice and the Imaginary part is even about the Cu-O bond center.

All of the analysis in this chapter is carried out on drift-corrected data, and all of the physics in this section is derived from four pixels of the Fourier Transform (FT) of various objects, the Real and Imaginary parts at the Bragg pixels $Q_x$ and $Q_y$. The Real part of the FT at $Q_x$ of any quantity $A$ will be referred to as $\Re[\tilde{A}(\vec{Q}_x)]$, the Real part at $Q_y$ as $\Re[\tilde{A}(\vec{Q}_y)]$, the Imaginary part at $Q_x$ as $\Im[\tilde{A}(\vec{Q}_x)]$, and the Imaginary part at $Q_y$ as $\Im[\tilde{A}(\vec{Q}_y)]$. These quantities can be computed globally, by taking the FT of the entire field of view. They then are a single value per field of view, or a single value per energy if calculated from a full 3d $g(x,y,V)$ map, and can be plotted as a function of energy. They can also be computed locally, by taking the FT inside of a moving Gaussian window of half-width $L$. An image can be built up by calculating at every point the quantity of interest within that window, centered at that point. These will be referred to as $\Re[\tilde{A}(\vec{Q}_x)](x,y)$, etc. These maps then form a 3d dataset if energy dependence is taken into account. In this chapter, typically a few representative energies are shown from the full 3d dataset.

An example calculation is given in Figure 3.3. In panel a) is shown a topograph. The atomic lattice coordinate system is indicated with arrows. In panel b) is shown the Real part of the FT of the topograph, $\Re[z_{\text{topo}}(\vec{Q})]$. The Bragg pixels are the strong positive pixels at the corners of the “box,” indicated by arrows. In panels c) and d) are the plotted the local value of the Real part of the FT at $Q_x$, or $\Re[z_{\text{topo}}(\vec{Q}_x)](x,y)$, and the local value of the Real part of the FT at $Q_y$, or $\Re[z_{\text{topo}}(\vec{Q}_y)](x,y)$, respectively. As expected, the Real part of the FT of a topograph at the Bragg pixels is everywhere strongly positive, because the dominant features are the Bi lattice described
by \cos(Q_x) and \cos(Q_y), although some subtle local variations can be seen.

### 3.2 Electronic Nematic Order

The focus of this chapter is the electronic nematic state, which breaks rotational symmetry, reducing \( C_4 \) to \( C_2 \) symmetry, but does not break lattice translational symmetry. We focus on the Bragg pixels to lock into electronic structure with the same periodicity as the crystal and compare strength at \( Q_y \) to that at \( Q_x \) to quantify \( C_4 \) symmetry breaking.

Lawler [28] defines a general measure of electronic nematic order as

\[
O_n[A] = \frac{1}{2} [ \tilde{A}(\vec{Q}_y) - \tilde{A}(\vec{Q}_x) + \tilde{A}(-\vec{Q}_y) - \tilde{A}(-\vec{Q}_x) ] = \Re[\tilde{A}(\vec{Q}_y)] - \Re[\tilde{A}(\vec{Q}_x)] \tag{3.1}
\]

where \( \tilde{A}(\vec{Q}) = \Re[\tilde{A}(\vec{Q})] + i\Im[\tilde{A}(\vec{Q})] \).

Since this particular electronic nematic order parameter relies only on the Real parts, we will refer to it as \( \Re O_n \). The order parameter computed at a specific energy \( eV \) is normalized with the average at that energy level, \( \overline{A(eV)} \).

An analogous order parameter, in phase with the Imaginary part of the lattice-periodic electronic structure, quantifies the rotational symmetry breaking, but centered at the Cu-O bond centers rather than at the atomic sites.

\[
O_n[A(eV)] = \frac{\Im[\tilde{A}(\vec{Q}_y, eV)] - \Im[\tilde{A}(\vec{Q}_x, eV)]}{\overline{A(eV)}} \tag{3.2}
\]

Because this order parameter relies on the Imaginary components, we will refer to it as \( \Im O_n \). The \( \Re O_n \) order parameter quantifies, in effect, how dis-similar the two
Oxygen sites are, since it is symmetric about the Cu site. The $^3O_n$, by contrast, quantifies how dis-similar the Cu-O bonds are along $x$ versus along $y$.

Additionally, motivated by the calculations of Carlson et al. [44], we define an amplitude nematic order parameter as

$$O_n[A(eV)] = \frac{\mathfrak{A}[A(Q_y,eV)] - \mathfrak{A}[A(Q_x,eV)]}{\mathfrak{A}(eV)}$$  \hspace{1cm} (3.3)

where $\mathfrak{A}$ is the Amplitude FT, defined as $\mathfrak{A} = \sqrt{\Re^2 + \Im^2}$. We will refer to this order parameter as $^3O_n$. If there are both Real and Imaginary components to lattice-periodic electronic structure, then the apparent peak may be at any arbitrary phase. The $^3O_n$ order parameter quantifies the rotational symmetry breaking in the DOS with no sensitivity to the phase between the electronic order and the crystal lattice. The $^3O_n$ order parameter has the advantage of simplicity, but due to the square in the definition, loses phase information. A peak over a Cu site is physically a very different structure than a peak over an O site, but the $^3O_n$ order parameter would treat them as identical.

In this section, I calculate, both globally and locally, several different order parameters related to electronic nematicity. I demonstrate the robustness or lack thereof of these order parameters by showing correlation between two complementary datasets, taken over the same area at different scan angles.
3.3 Check of Robustness to Rotation

3.3.1 Case Study Datasets

The datasets studied in this section are both $18 \times 18 \text{nm}^2$ and $256 \times 256 \text{pixels}^2$ (prior to drift-correction) and taken over the same field of view, with the same tip, with identical energy resolution and timing parameters. The key difference is that the scan angle is rotated $90^\circ$ from one map to the next. This characteristic enables us to check that subtle calculated order parameters are a robust property of the material itself rather than an artifact of the scan direction. Both maps are aligned such that the scan angle is $45^\circ$ to the Bi lattice, so the maps are referred to throughout this chapter as the “+45” map and the “-45” map. They are introduced thoroughly in Appendix A.2. In particular, the full list of experimental parameters is given in Table A.2 and the simultaneous topographs to each dataset are shown in Figure A.4.

The drift correction algorithm described above requires several decisions, including a choice of background subtraction, a choice of edge crop, and a choice of which orthonormal $\vec{Q}$ to correct the lattice onto (discussed more thoroughly in Appendix B). Both datasets were drift corrected two entirely separate times, with different edge crops and $\vec{Q}$. The first time they were separately drift corrected onto independently ideal lattices, and the second time the were rotated to match, cropped to match, and drift corrected onto an atomically-registered identical lattice. All of the analysis described in this chapter was carried out on both sets of drift corrected data, with consistent results, ensuring that the findings are not the result of drift correction artifacts. The figures presented in this chapter were all produced from the maps
drift-corrected onto the matched lattice, which after aggressive cropping at three edges are $14 \times 14 \text{nm}^2$.

### 3.3.2 Electronic Nematic Computed from Differential Conductance Maps

For all of the reasons described in Chapter 2, energy dependence of order parameters computed from the as-measured differential conductance, $g$, is suspect. We will return to this issue in the next section. In this section, I’ll stick to a straight-forward description of the data at hand and focus on the effect of scan angle.

Figure 3.4 shows local FT of $g$ at the Bragg pixels for a few representative energies. Figure 3.5 shows the three local nematic order parameters defined above, calculated from $g$, at the same few representative energies. The first thing to notice, obviously, is the high degree of correlation between the maps of the electronic structure calculated from the datasets taken at different scan angle. The electronic structure is robust to scan angle, for these particular timing parameters. Figure 3.6 shows the full field of view averages of the FT at the Bragg pixels and the electronic nematic order parameters, as well as the correlations between the two datasets.

The electronic structure exhibits longer range order at high energies than at energies near the Fermi level, but even at $\pm 100 \text{mV}$, the correlation length has not increased to the size of the field of view ($14 \text{nm}$). Curiously, the Real part of the electronic structure, the part that is even about the Cu lattice, is negative, which means that the electronic structure is centered about the O sites. The Imaginary part of the electronic structure, which would be zero if the electronic structure were
Figure 3.4: (next page) Maps of the local FT of $g$ at the Bragg pixels. Each of the three panels has eight sections. Each section is a map, $14 \times 14 \text{nm}^2$, of the FT at a Bragg pixel, where the local value is calculated by taking a FT inside of a Gaussian window of half-width $L = 5 \text{atoms} = 25 \text{pixels}$, indicated by the dashed circle. The columns are as labeled, $\Re[\hat{g}(Q_x)](x,y)$, $\Re[\hat{g}(Q_y)](x,y)$, $\Im[\hat{g}(Q_x)](x,y)$, and $\Im[\hat{g}(Q_y)](x,y)$. The top row of each panel is calculated from the $+45$ map, and the bottom row of each panel is calculated from the $-45$ map. Three representative layers are shown: $100 \text{mV}$, $0 \text{mV}$, and $+100 \text{mV}$. Note that $V_s = -100 \text{mV}$.
Figure 3.5: (next page) Maps of the local nematic order parameters computed from $g$. Each of the three panels has six sections. Each section is a map, $14 \times 14 \text{nm}^2$, of the order parameter labeled at the top of the column, where the local value is calculated by taking a FT inside of a Gaussian window of half-width $L = 5\text{atoms} = 25\text{pixels}$, indicated by the dashed circle. The top row of each panel is calculated from the $+45$ map, and the bottom row of each panel is calculated from the $-45$ map. Three representative layers are shown: $100 \text{mV}$, $0 \text{mV}$, and $+100 \text{mV}$. Note that $V_s = -100 \text{mV}$. 
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\[ \alpha_n[g](x, y) \quad \beta_n[g](x, y) \quad \gamma_n[g](x, y) \]

V = -100 mV

V = 0 mV

V = +100 mV
Figure 3.6: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between +45 map and -45 map, computed from the $g(x, y, V)$ maps.
registered exactly to the atomic sites, is smaller than the Real part, in general, but not zero, indicating a shift of the maxima in the electronic structure in an inversion symmetry-breaking fashion.

Correlations between the quantities calculated from rotated maps show that the strongest correlations are in the Real component, both in the FT at the Bragg pixel itself and in the nematic. This is unlikely to be a signal-to-noise issue because the Real component is not significantly larger than the Imaginary and at many energies is smaller. The Imaginary component may be more susceptible to distortion from scan angle effects. The correlations of the Amplitude FT at the Bragg pixels and $\alpha O_n$ are significantly lower than either piece separately. This implies that the phase information that the Amplitude loses is actually important, and that the $\alpha O_n$ is a less robust order parameter.

### 3.3.3 Electronic Nematic Computed from Ratio Maps

The electronic nematic order parameters can also be calculated for the ratio maps $Z(V)$ and $R(V)$, defined in 2.2. Figure 3.7 shows local FT of $Z$ at the Bragg pixels and the local nematic order parameters, at 100 mV, the highest energy layer. Figure 3.8 shows the full field of view averages and the correlations between the rotated datasets. Figure 3.9 and Figure 3.10 show the equivalent information for the $R$ map. Like the $g$-map calculated values, the FT at the Bragg pixels displays short-range order at low energies that grows as a function of energy. The full field of view averages are close to 0 at the Fermi level and then grow steadily as a function of energy. Like the $g$-map calculated values, the correlations are highest for Real components, slightly lower for
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Figure 3.7: Maps of the local FT of $Z(V)$ at the Bragg pixels and local nematic order parameters calculated from $Z(V)$. Each section is $14 \times 14 \text{nm}^2$ and from the 100 mV layer of the $Z$ map. The top panel has eight sections, each a map of the local FT at a Bragg pixel. The columns are as labeled, $\Re[\tilde{g}(Q_x)](x,y)$, $\Re[\tilde{g}(Q_y)](x,y)$, $\Im[\tilde{g}(Q_x)](x,y)$, and $\Im[\tilde{g}(Q_y)](x,y)$. The bottom panel is comprised of maps of the local nematic order parameters computed from $Z$. The top row of each panel is calculated from the $+45$ map, and the bottom row of each panel is calculated from the $-45$ map.
Figure 3.8: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between +45 map and -45 map, computed from the $Z(x, y, V)$ maps.
Figure 3.9: Maps of the local FT of $R(V)$ at the Bragg pixels and local nematic order parameters calculated from $R(V)$. Each section is $14 \times 14 \text{nm}^2$ and from the $100 \text{mV}$ layer of the $R$ map. The top panel has eight sections, each a map of the local FT at a Bragg pixel. The columns are as labeled, $\Re[\tilde{R}(\vec{Q}_x)](x,y)$, $\Re[\tilde{R}(\vec{Q}_y)](x,y)$, $\Im[\tilde{R}(\vec{Q}_x)](x,y)$, and $\Im[\tilde{R}(\vec{Q}_y)](x,y)$. The bottom panel is comprised of maps of the local nematic order parameters computed from $R$. The top row of each panel is calculated from the $+45$ map, and the bottom row of each panel is calculated from the $-45$ map.
Figure 3.10: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between +45 map and -45 map, computed from the $R(x, y, V)$ maps.
Imaginary, and very low, even negative, for the Amplitude. Based on the apparent susceptibility of the $^3O_n$ to measurement effects, we cannot recommend its use for analysis.

It’s curious that the strength of the nematic order parameter is relatively weaker in the $R$ maps than the $Z$ maps. One of the benefits of the $R$ maps is that they enhance small signals that are integrated all through the energy range, and the nematic order parameter is the same polarity for all energies.

### 3.4 Check of Robustness to Normalization

#### 3.4.1 Case Study Datasets

The complicated dependence of the Fourier properties on energy evident in Figure 3.6 necessitates a more careful look at how these order parameters are energy-dependent and normalization-dependent.

In this section we will use the dataset introduced in Section 2.3 and more thoroughly described in Appendix A.1. It consists of three interleaved spectral surveys, where each of the three spectra were taken in sequence at the same location before moving onto the next point on the grid, in the process described in Section 1.3.4. The three data sets are: a $g(x, y, V)$ map taken with $V_s = -100mV$ (which we will refer to as $g_1$), a $g(x, y, V)$ map taken with $V_s = +100mV$ (which we will refer to as $g_2$), and an $I(z)$ map taken with $V_s = -100mV$. All three were taken with $I_s = 100pA$. The map is nominally $9 \times 9 \text{nm}^2$ and $128 \times 128 \text{pixels}^2$, with 5pixels/atom resolution.

We can compute the nematic order parameters from these maps in a variety of
different normalization schemes and establish to what extent the order parameter that we observe depends on the setup condition and the choice of normalization.

Figure 3.11, in the same format as Figure 3.6, shows the full field of view average (although keep in mind that these maps, at $9 \times 9 \text{nm}^2$, do not have a field of view much larger than the length scale of the local nematic calculation, which is a Gaussian of half-width $L = 5\text{atoms} = 1.91 \text{nm}$) of the weight at the Bragg pixels and the nematic order parameters for the two $dI/dV$ maps. The correlations between the two, shown in the panels below, show that there are serious setpoint effects that skew the computation of the Bragg pixels and the nematic order. The weight at the Bragg pixels, and the nematic order parameters computed from them, have much larger amplitude, in general, on whichever side of the Fermi level they don’t share with $V_s$.

Figures 3.12, 3.13, and 3.14 all show, in the same arrangement, the full field of view average of the weight at the Bragg pixels and the nematic order parameters, as computed from different normalizations. Figure 3.12 shows the result from applying the $Z-$ normalization, which is division of all layers of $dI/dV$ by the lowest energy layer of $dI/dV$, in this case $-100 \text{mV}$. Figure 3.13 shows the result from applying the $Z+$ normalization, which is division of all layers of $dI/dV$ by the highest energy layer of $dI/dV$, in this case $+100 \text{mV}$. Figure 3.14 shows the result from applying the $Z$ ratio map normalization, which is the ratio of $+V$ layers of the $dI/dV$ to the corresponding $-V$ layer. The main conclusion from this zoo of plots is that the local lattice-periodic Fourier properties are highly normalization dependent. The motivation behind applying the $Z-$ and $Z+$ normalizations is that, since division by any energy layer cancels the $\exp(-2\kappa z_\delta)$ prefactor, then a division by an energy layer
Figure 3.11: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between the first $dI/dV$ map taken with $V_s = -100 \, mV$ (referred to in the graph titles as “diag1”), and the second $dI/dV$ map, taken with $V_s = +100 \, mV$ (referred to in the graph titles as “diag2”). Every parameter of the two $dI/dV$ maps is identical except for $V_s$. 
Figure 3.12: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between the $Z-$ map computed from the first $dI/dV$ map, taken with $V_s = -100\, mV$ (referred to in the graph titles as “diag1”), and the $Z-$ map computed from the second $dI/dV$ map, taken with $V_s = +100\, mV$ (referred to in the graph titles as “diag2”). The $Z-$ map is a normalization scheme whereby each energy layer is divided by the lowest energy layer, in this case the $V = -100\, mV$ layer.
Figure 3.13: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between the $Z^+$ map computed from the first $dI/dV$ map, taken with $V_s = -100 \text{ mV}$ (referred to in the graph titles as “diag1”), and the $Z^+$ map computed from the second $dI/dV$ map, taken with $V_s = +100 \text{ mV}$ (referred to in the graph titles as “diag2”). The $Z^+$ map is a normalization scheme whereby each energy layer is divided by the highest energy layer, in this case the $V = +100 \text{ mV}$ layer.
Figure 3.14: Full field averages of the FT at the Bragg pixels and the nematic order parameters, and correlations between the $Z$ ratio map computed from the first $dI/dV$ map, taken with $V_s = -100 \, mV$ (referred to in the graph titles as “diag1”), and the $Z$ ratio map, computed from the second $dI/dV$ map, taken with $V_s = +100 \, mV$ (referred to in the graph titles as “diag2”).
where nothing interesting is happening will cancel the pre-factor without introducing new artifacts. As we can see, there is clearly lattice-periodic electronic structure at all the energy ranges we measure, since each new normalization introduces new artifacts. The fact that each normalization results in properties that appear identical between the two maps taken with different $V_s$ means that this is a real, physical property that is being measured, and it may be possible to extract with a proper normalization. As of now, however, we are unable to cleanly expose the true energy dependence of this order.

### 3.5 Conclusions

In this chapter I have examined how lattice-periodic electronic structure is dependent on measurement conditions and normalization. I have shown in that in addition to the Real nematic order parameter defined by Lawler [28], which quantifies the degree of $C_4 \rightarrow C_2$ symmetry breaking in electronic structure which is in phase with the Cu lattice, there is an arguably equally valid Imaginary nematic order parameter which quantifies $C_4 \rightarrow C_2$ symmetry-breaking in electronic structure which is inversion-symmetry breaking.

Neither the Real nor Imaginary nematic order parameters is sensitive to scan angle, but the same cannot be said for the Amplitude nematic order parameter, which quantifies $C_4 \rightarrow C_2$ symmetry-breaking irrespective of phase with respect to the lattice. We have found that the Amplitude nematic order parameter may be more susceptible to measurement effects and is not a robust order parameter.

All of the lattice-periodic Fourier properties examined in this chapter, whether
Figure 3.15: Figure 3e from Lawler et al. [28]. \( Z(\vec{r}, e = 1) \) image of highly underdoped Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\) with the location and orientation of each Cu and surrounding O overlaid. \( e = 1 \) refers to rescaling by the local pseudogap energy.

the weight at the Bragg pixels themselves or the nematic order parameters, which are comprised of various combinations of Bragg pixels, are highly sensitive to the chosen normalization. The true energy range of this order remains unclear.

It remains in my mind an open question how fundamental these defined nematic order parameters may be. Each of the four Bragg pixels has significant weight and structure, which varies, it seems without pattern, as a function of energy. The strength at the Bragg pixels is not higher than many neighboring random pixels in the Fourier Transform.

Figure 3.15 reproduces Figure 3e from Lawler et al., which is a plot of \( Z(\vec{r}, e = 1) \) showing periodic electronic structure and an overlaid schematic lattice. It is inter-
esting that the clear and present modulation is not actually charge order which is commensurate with the lattice, but rather the $\vec{q}_4$ modulation. The nematic order, calculated from structure which is lattice-periodic, is not visible in this figure. Over a window of finite size, as all of the windows involved in the computation of these local Fourier-space properties must be, an incommensurate and disordered strong modulation at $\vec{q}_4$ will lead to non-zero nematic order, as they are defined in this chapter. We cannot rule out the possibility, and indeed find it likely, that the electronic nematic order parameter as defined by Lawler is not a fundamental order parameter, but rather an artifact of the strong $\vec{q}_4$ modulation.
Appendix A

Experimental and Practical Details of Maps Analyzed

This appendix is a compilation of relevant experimental parameters for the maps analyzed in this dissertation and some miscellaneous other useful details. Some maps are related and are grouped together and some are presented independently.

A.1 Triple Maps

Three different interleaved triple maps were extensively compared. The term “triple map” is used to refer to a collection of three maps, two $dI/dV$ maps and an $I(z)$ map, taken on the same grid and such that at each point at the grid, a spectrum from each map is taken in sequence. In contrast to maps taken on the same grid but where a full map is completed before the next is begun, these interleaved datasets are more similar since each spectrum at a given location is really at the same location
Figure A.1: Schematic showing the relationship between the three triple maps. The red circles represent the atomic lattice. All are the same size, $9 \times 9 \text{ nm}^2$ and $128 \times 128 \text{ pixels}^2$. Control and along were taken centered at the same location, with a 135° rotation between the two. Diag was taken at the same angle as control, at a nearby location. The boxes represent the scanframe. The arrows labeled with ‘$Q_x$’ and ‘$Q_y$’ represent the chosen $Q_x$ and $Q_y$ that define the lattice used for drift-correction. The lower left corner of each scanframe is labeled with a cross. The scans are taken from the bottom left, with $x$ the fast scan direction and $y$ the slow scan direction. Note that for along, $Q_x$ aligns with $x$, whereas for control and diag, there is $45°$ between $Q_x$ and $x$. Our apologies for this confusing nomenclature, which at this point is too deeply entrenched to improve.
Table A.1: Triple Map Parameters and Properties

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<th>Material</th>
<th>Control</th>
<th>Diag</th>
<th>Along</th>
</tr>
</thead>
<tbody>
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<td>$T_c$</td>
<td>Bi$_{2-y}$Pb$_y$Sr$<em>2$CuO$</em>{6+\delta}$</td>
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<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>Pixels</td>
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<td></td>
</tr>
<tr>
<td>Pixels / atom</td>
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<td></td>
<td></td>
</tr>
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<td>0</td>
</tr>
<tr>
<td>$I_s$ ($pA$)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Bias range ($mV$)</td>
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<td></td>
</tr>
<tr>
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<td>$-100$</td>
<td>$-100$</td>
</tr>
<tr>
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<td>$+100$</td>
<td>$+100$</td>
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</tr>
<tr>
<td>$V_{AC}$ ($Hz$)</td>
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<td></td>
</tr>
<tr>
<td>$dI/dV$, numpoints</td>
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<td></td>
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</tr>
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<td>4</td>
<td></td>
<td></td>
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<tr>
<td>$dI/dV$, integration ($ms$)</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.36$\pm$0.07</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>128</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I(z)$, sweep direction</td>
<td>towards surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I(z)$, integration ($ms$)</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ($K$)</td>
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<td>4.75</td>
<td>5.2</td>
</tr>
<tr>
<td>Magnetic field ($T$)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>crop</td>
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<td></td>
</tr>
<tr>
<td>$Q_x$</td>
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<td>(20, 20)</td>
<td>(29, 0)</td>
</tr>
<tr>
<td>$Q_y$</td>
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<td>($-20$, 20)</td>
<td>(0, 29)</td>
</tr>
<tr>
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<td>0.004260</td>
<td>0.002770</td>
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<tr>
<td>$\Re[\tilde{\varepsilon}_{topo}(Q_y)]$</td>
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<td>0.002379</td>
<td>0.005581</td>
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<td>0.000117</td>
<td>0.000280</td>
</tr>
<tr>
<td>$\Im[\tilde{\varepsilon}_{topo}(Q_y)]$</td>
<td>0.000724</td>
<td>-0.000166</td>
<td>0.000471</td>
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</tbody>
</table>
Appendix A: Experimental and Practical Details of Maps Analyzed

Figure A.2: Simultaneously acquired topographs for $dI/dV_1$ in each triple map and its auto-correlation. a) Topograph for control and b) its auto-correlation. c) Topograph for diag and d) its auto-correlation. e) Topograph for along and f) its auto-correlation. All are $9 \times 9 \, nm^2$ and $128 \times 128 \, pixels^2$ and have been drift-corrected. Before finding drift fields, topographs were background subtracted with row polynomial of order 2 (control and diag) and with plane polynomial of order 6 (along).
to a high degree of precision, and since the spectra for each map are separated by only $\sim 2 s$, the environment is more similar. All three triple maps had the same size, number of pixels, and $dI/dV$ spectra parameters. The parameters that were changed between the three triple maps were the applied sample bias during $dI/dV$ maps, the angle with respect to the lattice, and the location. See Table A.1 for details. The map referred to as “control” has exactly the same parameters for the two $dI/dV$ maps, with $V_s = -100 \, mV$ for both. It was taken with the scan direction diagonal to the lattice. The map referred to as “diag” has the same parameters as control except that it is at a different (nearby) location and while the first $dI/dV$ map has the same setup condition, the second $dI/dV$ map has $V_s = +100 \, mV$. The map referred to as “along” has the same parameters as control except that it is rotated $\pi/4$ so that the scan direction is along the direction of the lattice and like the “diag” set, it has a first $dI/dV$ map at $V_s = -100 \, mV$ and second $dI/dV$ map at $V_s = +100 \, mV$. It was taken centered in the same area of the sample as the control map. All three maps have a simultaneously acquired $I(z)$ map as well, allowing us to compare work function maps with precisely registered $dI/dV$ maps.

A few quirks and caveats are worth noting. The tip for all three maps was directional. See Figure A.2 for simultaneously acquired topographs and auto-correlations of those topographs. The first of the simultaneously acquired topographs is shown for each triplemap. The strength of the FFT at each Bragg pixel ($\Re[\tilde{z}_{\text{topo}}(\vec{Q}_x)]$ for the real part at $Q_x$, etc.) is tabulated in Table A.1. A strong directionality makes it difficult to come to robust conclusions about shifts in the average unit cell.

All of the analysis carried out on the triple maps presented in this dissertation
was done with no crop (normally a few pixels are cropped off of the left and bottom edges to remove piezo-drift-related areas that cannot be drift-corrected properly). In retrospect, in light of the drift shown in Figure B.28c and d, it probably would have been a better idea to use a small crop.

The diag and control topographs were best background subtracted using a row polynomial of order 2. It was minimally invasive but made for a satisfactorily flat topograph. Note that the along topographs must be plane subtracted (I used plane polynomial of order 6) because the scan direction is along the lattice so a row subtraction will erase a Bragg pixel. Unfortunately, even such a high order polynomial is unable to fit the temperature-instability related horizontal streak feature that can be seen in Figure A.2e. I attempted to remove bad pixels from the topographs before making drift fields but found that the maps were so stable that no bad pixels were identified to be removed.

The three triple maps do have the advantage that they were taken with an extremely stable tip. Very few of the spectra are unstable (∼10 per map) and the tip is consistent between the three maps.

A.2 Dual Maps

Following the triple maps, two larger dual maps (two interleaved maps, one $dI/dV$ map and one $I(z)$ map) were taken, both with $V_s = -100 \, mV$. These maps have twice the linear size, which makes it easier to compute local quantities with reasonable averaging window without running into edge effects. Unfortunately the tip was far less stable, and there are significant (1-3% of the total, depending on the metric)
Figure A.3: Schematic showing the relationship between the two dual maps. The red circles represent the atomic lattice. Both are the same size, 18 × 18 nm² and 256 × 256 pixels². The boxes represent the scanframe. The arrows labeled with ‘$Q_x$’ and ‘$Q_y$’ represent the chosen $Q_x$ and $Q_y$ that define the lattice used for drift-correction. The lower left corner of each scanframe is labeled with a cross. The scans are taken from the bottom left, with $x$ the fast scan direction and $y$ the slow scan direction. Note that there is 45° between $Q_x$ and $x$. 
### Table A.2: Dual Map Parameters

<table>
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<tr>
<th>Material</th>
<th>Bi$_{2-y}$Pb$_y$Sr$<em>2$CuO$</em>{6+\delta}$</th>
<th>+45</th>
<th>-45</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>16K, overdoped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Size (nm)</td>
<td>18 × 18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pixels</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pixels / atom</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>angle w.r.t. BiO$_2$ lattice</td>
<td>$\pi/4$</td>
<td>$-\pi/4$</td>
<td></td>
</tr>
<tr>
<td>$I_s$ (pA)</td>
<td>125</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Bias range (mV)</td>
<td>±100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_s$ of $dI/dV$ (mV)</td>
<td>−100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_{AC}$ (mV, 0 − p)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$V_{AC}$ (Hz)</td>
<td>1115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dI/dV$, numpoints</td>
<td>51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dI/dV$, integration (ms)</td>
<td>28</td>
<td>32</td>
<td></td>
</tr>
<tr>
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<td>0.36 ± 0.07</td>
<td>0.27 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>$I(z)$, number of points</td>
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<td>64</td>
<td></td>
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</tr>
<tr>
<td>$I(z)$, integration (ms)</td>
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<td>135dual</td>
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</tr>
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<td>crop ([left,right,bottom,top])</td>
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<tr>
<td>Pixels after crop</td>
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<td>230</td>
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<tr>
<td>$Q_x$</td>
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<td>(36, 36)</td>
<td></td>
</tr>
<tr>
<td>$Q_y$</td>
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<td>(−36, 36)</td>
<td></td>
</tr>
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</tr>
<tr>
<td>Filename root</td>
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<td>135m</td>
<td></td>
</tr>
<tr>
<td>crop ([left,right,bottom,top])</td>
<td>[20,235,40,255]</td>
<td></td>
<td></td>
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<tr>
<td>$Q_x$</td>
<td>(33, 33)</td>
<td>(33, 33)</td>
<td></td>
</tr>
<tr>
<td>$Q_y$</td>
<td>(−33, 33)</td>
<td>(−33, 33)</td>
<td></td>
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<td>$\Re[\hat{z}_{\text{topo}}(Q_x)]$</td>
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<tr>
<td>$\Im[\hat{z}_{\text{topo}}(Q_y)]$</td>
<td>0.000057</td>
<td>0.000069</td>
<td></td>
</tr>
</tbody>
</table>
number of bad pixels. The tip was also still quite directional (see topographic images and auto-correlations in Figure A.4). Before finding the drift fields, I removed bad pixels (using the Remove Outliers method with standard deviation 4) and removed by hand two small unstable streaks of less than a row in duration by replacing those pixels with the average of rows above and below. Both topographs can be background subtracted well with a row polynomial of order 2.

I removed bad pixels in a variety of different ways for these maps, and I never found it to make very much of a difference how bad pixels were removed, but it is certainly important to do something. The usual bad pixel removal procedure compares a pixel to its neighbors, but if there are many bad pixels, and especially if they are arranged in stripes along the lattice (as these are) then this works less well. It is possible to run it with a very low bar (standard deviation of 2) or to run it multiple times in a row with a higher bar (standard deviation of 4 or 5). I also experimented with a different kind of bad pixel identifier. The bad pixels in these maps have, in general, much higher RMS noise. So if you step through each point in a spectrum and add up the absolute value of all changes between adjacent points, then you produce a number which is a measure of the average “spikiness” of a spectrum. Do this for every spectrum in the map, and you produce a map of integrated step change throughout each spectrum. You can then apply a cutoff to this map and identify bad pixels, and they can be replaced by an average of all nearest neighbors that are not also bad. This was an arduous process that did not produce significantly different results from applying the standard bad pixel finder a few times in a row.

There is an unfortunate mismatch of nomenclature for one of these maps. In the
Figure A.4: Simultaneously acquired topographs for the $dI/dV$ map in each dual map and its auto-correlation. a) Topograph for +45 and b) its auto-correlation. c) Topograph for -45 and d) its auto-correlation. All are $16.2 \times 16.2 \text{nm}^2$ and $230 \times 230 \text{pixels}^2$ and have been drift-corrected. Before finding drift fields, topographs were background subtracted with row polynomial of order 2 and bad pixels were removed with the remove outliers method with standard deviation 4. The images shown in this figure are from the 45dual / 135dual drift-correction, listed first in Table A.2.
Nanonis software, angles are defined such that positive angles correspond to clockwise rotations. The map which I have identified as “+45” was taken at a scan angle of 61.5°. The map which I have identified as “-45” was taken at a scan angle of -28.5°. When the features in the topograph are compared, it appears that the “-45” map has been rotated 90° clockwise from the +45 map. Because of a convoluted chain of thought which I will not attempt to reproduce here, I have named all files “45” and “135,” since I started my naming scheme after looking at the topographs, but I have made all presentations and communications (including this dissertation) about “+45” and “-45,” to agree with the angles in the headers. Please keep in mind that “-45” and “135” are one and the same map. I apologize for any confusion this may cause.

These maps were drift-corrected two entirely separate times. The first time I found the optimal crop and $\vec{Q}$ for each dataset independently. The datasets were drift-corrected, interesting things (such as maps of local nematic order, as discussed in Chapter 3) computed from them, and then those objects rotated and compared. Files computed from that drift correction are saved with root filenames of “45dual” and “135dual.” The second time, I rotated the 135 map to match the orientation of the 45 map, then drift corrected them both onto exactly the same atomic lattice, with the same $\vec{Q}$ and a crop and shift combination that aligns then onto the same atomically registered locations. This required a more aggressive crop, since the drift-distorted strips on the left and bottom had to be cropped off of the corresponding area of both maps. Outputs from this drift correction can be compared directly. Files computed from this drift correction are saved with root filenames “45m” and “135m.”
A.3 Filenames Cross-referenced to Data Used for Figures

In this section I cross-reference the short, descriptive, monikers that I have used (which except for the unfortunate case of one of the dualmaps as I have described above is an identical or closely-related name for communications, filenames, our Bragg peak database, etc.) with the original, lengthier, date-based filename, and list which maps are shown in each figure (or plots derived from the maps) in this dissertation. The first column in Table A.3 is the name which I have used to refer to datasets in communications. The second column is the filenames which I have used, and which have been carried throughout each file that is generated from the original dataset. The dates in the third column are the date of the lab notebook entry, for Hoffman lab maps. In the case of maps started in the early morning hours, the lab notebook date and the filename date do not correspond, since filename dates roll over at midnight.
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<th>communications</th>
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<th>Original Filename</th>
<th>Date</th>
<th>Figures</th>
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<td>control1</td>
<td>dualsetupDOS1_2011_05_03_BSCCO_001.3ds</td>
<td>5/3/2011</td>
<td>1.6b, A.2ab, B.24</td>
</tr>
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<td>control2</td>
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<td>5/3/2011</td>
<td>B.24</td>
</tr>
<tr>
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<td>controlZ</td>
<td>Zspectro_map2011_05_03_BSCCO_001.3ds</td>
<td>5/3/2011</td>
<td>1.6a, B.24</td>
</tr>
<tr>
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<td>5/5/2011</td>
<td>2.3abc, 2.4abc, 2.5, 2.6, 2.8, 2.9, 2.10, 3.11, 3.12, 3.13, 3.14, A.2cd, B.7, B.8, B.15, B.16, B.25, B.27a, B.28a-d, B.31</td>
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<td>diag2</td>
<td>dualsetupDOS2_2011_05_06_C11B_003.3ds</td>
<td>5/5/2011</td>
<td>2.3def, 2.4def, 2.5, 2.6, 2.8, 2.9, 2.10, 3.11, 3.12, 3.13, 3.14, B.25, B.27b, B.28ab, B.31</td>
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<tr>
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<td>diagZ</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>dualsetupDOS2_2011_05_04_BSCCO_001.3ds</td>
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<td>B.26</td>
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<td>5/4/2011</td>
<td>B.26</td>
</tr>
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</tr>
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<td>6/2/2011</td>
<td>3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 3.10, A.4c, B.9, B.11, B.12, B.13</td>
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</table>
Appendix B

Systematics of Spectroscopic Maps and Drift Correction Algorithm

B.1 Motivation and Contents

This appendix details work done to optimize the parameters used in the drift-correction algorithm introduced in Chapter 3. Specifically, I discuss here the choice of the length scale over which to find the local drift, the question of the best kind of background subtraction and bad pixel removal to be done to a topograph to prepare it before finding drift fields, and the choice of the $\vec{Q}$ to drift correct the raw data onto. At the end is a list of prescriptions and recommendations for future drift-correction.

All drift fields considered in this dissertation were computed by finding the drift fields to the best-fit $\vec{Q}$ and then rescaling those drift fields onto drift fields for orthonormal $\vec{Q}$. I did not compare whether it would be best to instead find drift fields for orthonormal $\vec{Q}$ directly. That issue remains to be investigated.
In characterizing the dependence of the drift field algorithm on various parameters, there are several different things that it may be useful to compare. The first is the drift fields themselves. The second is the effectiveness of the drift fields, measured in the degree to which the Bragg peaks have collapsed onto a single pixel (usually defined by the strength of the Bragg pixel as compared to its nearest neighbors). The third is the amount by which any computed quantity, such as the amplitude of the FT at the Bragg pixels or average unit cells, depend on the parameters used to drift correct the data.

The analysis presented throughout this appendix was done on a variety of different datasets, seemingly at random. In practice, when a question of best practice arose I tended to evaluate the map that was already open, and the dual maps and triple maps (particularly diag) were most often used. In all cases, I checked at least one dataset very carefully (to the point of making a table of comparisons and plotting the dependence of interesting things as a function of the input variable in question) and spot-checked a few more in a quicker manner to make sure that the trend was consistent across datasets. I have not included a description of those quick checks in this appendix.

I also consider a few interesting characteristics of spectroscopic mapping, such as upper limits on systematic drift throughout a spectroscopic measurements and tunneling asymmetry mapping, that are made possible or more rigorous with the drift-correction algorithm.
B.2 How to Evaluate Drift Fields

In this section I will discuss important characteristics to consider when comparing drift fields. Figure B.3 shows several different drift fields computed from the same topograph and can be referred to as an example.

In order to compute a drift field we start with a raw topograph, either a standalone topographic image or a topograph taken simultaneously to a spectroscopic map of some kind. The topographs will have a random overall plane tilt that depends on the sample glue and overall macroscopic alignment of sample to STM head, and will be centered about some z value which may be large. The first thing to do is to remove the overall background slope and offset. The optimal way to do that is discussed later. Second, the topograph may have some distortion at the bottom or left edge which is too extreme to drift correct and must be cropped off. Simultaneous topographs will almost certainly need a crop, due to the scantube not being fully relaxed at the start of a map or being stressed by traveling the return line too quickly. Bad pixels may need to be removed. After those steps, the topograph can be used to find drift fields.

Recall that the drift fields are found by convolving the raw topographic data with a perfect lattice over some length scale larger than the lattice periodicity, computing the phase between the raw lattice and the perfect lattice, and then turning that phase into two image objects. The drift fields $u_x(r)$ and $u_y(r)$ are the amount (measured in pixels) that the data needs to be shifted in $x$ and $y$, respectively, to fall on a perfect lattice.

The mean of a drift field is actually not meaningful; it is just a measure of how much to shift the entire map in order to place the center of a Bi atom at the (0,0).
Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

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pixel. It is a random number that depends only on where the corner of the map grid is placed and the size of the crop. What may be interesting is the variation in the mean between drift fields made from the same topograph prepared in different ways or related topographs. That variation in the averages can give a sense of the precision of the drift field shifts.

The overall texture of a drift field may be interesting (indeed, it is of primary interest in the following section). It can be seen by eye in side-by-side drift fields and is quantified in the statistics column. The standard deviation, listed at SDev in the statistics column, is the positive square root of the variance, or the second central moment about the mean. The mean absolute deviation, listed as MDev, is the mean of the absolute values of all deviations from the mean of the map. The skewness is the third central moment about the mean and a measure of the lopsidedness of the distribution. The kurtosis is the fourth central moment about the mean and a measure of the weight in the tails of the distribution. If a drift field is mostly “flat” to the eye with little variation, that means that the overall shift of the map to place the corner atom is larger than the variable drift that occurred over the course of the map. This is not necessarily meaningful – appearances of “flatness” should always be compared to the overall mean, the pixels/atom of the map, and the standard deviation.

If the drift field has more variation or sharp features at the bottom or at the left, then it is likely that there is some piezo-relaxation area that was not cropped off and that area must be treated with some suspicion for certain kinds of analysis.

In many sections I subtract drift fields that were made from the same topograph
Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

prepared different ways, or related topographs. An example can be seen in Figure B.24. The important thing to consider in those subtracted drift fields is to look at both features and averages. First, how does the magnitude of the average of the difference compare to the averages of the original drift fields? It will always be much smaller, but in some cases it is arguably no different from 0 and in some cases there is a significant, possibly systematic difference. In these difference fields, the overall appearance of “flatness” is actually meaningful. If a difference field is flat, that means there was a systematic shift to the lattice between the two maps, or that a some variable in preparing the topograph created a spurious shift. If the difference field appears to have random features that are unrelated to features in either of the original drift fields, and the magnitude is quite small, then it is likely that these are just random variations and there is no systematic difference between the drift fields. These difference fields give an estimate of the precision of the drift-correction algorithm.

B.3 Make Average Unit Cell Algorithm

One of the outputs most commonly used to determine the impact of input parameters was an average unit cell produced by the Make Average Unit Cell (MAUC) algorithm. The MAUC algorithm is described in detail in Zeljkovic et al. SOM [63]. Starting with a drift-corrected topograph (shown in Figure B.1a), we create an average single-Bi unit cell with more pixels per atom than our raw data (typically 15 × 15 pixels per unit cell). For each pixel in the actual topograph, the location can be calculated with picometer precision in relation to the nearest Bi atom. The data
from that pixel can be placed in the appropriate bin in the average unit cell. This process builds up a histogram of weight at each sub-unit-cell-resolved position in the average unit cell, ultimately showing a high resolution map of an average Bi atom (Figure B.1c). An analogous process can also be used to create an average supercell of any size. The creation of an average supercell allows intra-unit-cell spatial resolution, at the expense of inter-unit-cell variation. This method allows us to detect variations in atomic position as small as a few thousandths of a unit cell. We fit a peak to each of the four “atoms” in order to calculate their exact positions.

An orthorhombic distortion from the tetragonal unit cell was reported in Zeljkovic et al. [63]: the Bi lattice of the surface layer is actually made up of two Bi sublattices, interleaved, and there is a shift of one Bi sublattice of $\sim 1.5\%$ along the $a$ axis of the orthorhombic crystal, displayed schematically in Figure B.2. This shift is resolvable by STM for the first time with the MAUC algorithm. The shift, $d$, is $\sim 1.5\%$ of $a \sim 0.015 \times \sqrt{2} \times 0.383 \text{ nm} \sim 9 \text{ pm}$. In many later figures, I plot the composite atom locations and also the relative shift between the two Bi sublattices. There are a few factors that need to be taken into account for comparison. I plot the shift as a fraction of the tetragonal unit cell, not the orthorhombic, so it will be $\sqrt{2}$ bigger in that basis. I plot the shift between the two Bi sublattices, not between a Bi sublattice and the undistorted Cu lattice, so it will appear twice as large. I plot the shifts along $Q_x$ and $Q_y$ separately, which are each $\sqrt{2}$ of the shift along the orthorhombic direction. Combine all of these, and the relatives shifts I plot should be at most $\sim 2 \times 1.5\%$ of a tetragonal unit cell. In all of the 2X2 average unit cells that you see later in this appendix, the four composite atoms should be very close to their assigned centers.
Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

Figure B.1: A schematic of a drift-corrected topographic image is shown in a) with Bi atoms represented as blue circles. The data is acquired in a pixel grid outlined in black; the center of each pixel is marked with a red dot. The resolution of this image is only slightly better than the Nyquist frequency for resolving atoms. A schematic of the average unit cell is shown in b). We calculate the exact distance of every pixel in a) to the nearest Bi atom (4 example distances are shown in green in (a)), then place it in the average unit cell in b), thus creating a weighted histogram at each sub-unit-cell pixel. The $1 \times 1$ average unit cell is chosen to have a much better spatial resolution than our raw data (typically $15 \times 15$ pixels per unit cell). An example of the final average unit cell obtained from a real topographic image is shown in c).
Figure B.2: A schematic of the orthorhombic shift as observed by scattering and now [63] by STM. The tetragonal unit cell is defined by $Q_x$ and $Q_y$ and the orthorhombic unit cell by $a$ and $b$. The shift, $d$, is, as observed by STM, at most $\sim 1.5\%$ of $a \sim 0.015 \times \sqrt{2} \times 0.383 \text{nm} \sim 9 \text{pm}$. 
and not vary with respect to each other more than $\sim 3\%$. In some of the sections that follow, I will consider the effect of various drift-correction parameters on the average unit cell created by MAUC. If the atoms in a topograph are not centered, or if their positions or shifts with respect to each other are found to depend substantially on an drift-correction input parameter, then we have identified drift-correction parameters that need to be very carefully selected.

The MAUC algorithm can produce an average cell in two different ways. One is a the real-space technique described above, where each pixel is placed in the appropriate bin in the average unit cell, and the other is a Fourier-space technique, where the values at the Bragg pixels $Q_x$ and $Q_y$ (if a 2X2 supercell, along with the values at the orthorhombic pixels $Q_a = (Q_x + Q_y)/2$ and $Q_b = (Q_x - Q_y)/2$) are used to create an average unit cell. I have never found the two techniques to give differences in location of more than $\sim 3\%$ unless the datasets are extremely pathological or have very low signal-to-noise.

### B.4 Choice of Length Scale

One of the first decisions to be made in applying the drift correction algorithm is the length scale, $L_1$, over which to calculate the local drift. If $L_1$ is chosen to be too short, then the drift field algorithm will not have enough Fourier-space resolution and get confused by local variations in the density of states and find spurious drift. If $L_1$ is chosen to be too long, than real drift of the kind we are trying to correct for will be averaged out and fail to be picked up by the algorithm. The analysis in this section was performed on the $+45$ dualmap, which is $18 \times 18$ nm\(^2\) and $256 \times 256$ pixels\(^2\),
Figure B.3: (next page) Dependence of drift fields as a function of the length scale $L_1$ over which the convolution is taken. The first column has the $L_1$ in atoms, where $L_1$ is the half-width of the gaussian window with which the drift field is computed. The second and fourth columns are drift field images, where $u_x(r)$ and $u_y(r)$ are the numbers of pixels to shift the data to align it onto the perfect lattice in $x$ and in $y$, respectively. The $L_1$ drift field picked a different atom as the atom to place at the $(0,0)$ pixel, thus giving it an overall mean one lattice spacing away from the other maps. The key thing to note in the statistics columns are the dependence of the means on $L_1$, which aside from $L_1 = 1$ atom are fairly consistent, and the standard deviations, which decrease steadily as $L_1$ increases. As expected, the drift fields get smoother as a larger area is averaged over to find the local drift field. Drift fields computed for the $+45$ dualmap, which is $16.2 \times 16.2 \, nm^2$ and $230 \times 230 \, pixels^2$. 
## Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

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<tr>
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<th>( u_x ) Statistics</th>
<th>( u_y ) Drift Field</th>
<th>( u_y ) Statistics</th>
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Figure B.4: Dependence of the localization of the Bragg peak on $L_1$. The graphs show linecuts through the Fourier Transform of the drift-corrected topography. As $L_1$ gets larger, the height of the Bragg peak decreases, reflecting how the drift-correction algorithm is doing a less good job of aligning the data with a perfect lattice. a) A linecut through $Q_x$ along the $(0,0)$ to $(1,0)\frac{2\pi}{a_0}$ line in $\Re(\tilde{z})$. b) A linecut through $Q_y$ along the $(0,0)$ to $(0,1)\frac{2\pi}{a_0}$ line in $\Re(\tilde{z})$. c) A linecut through $Q_x$ along the $(0,0)$ to $(1,0)\frac{2\pi}{a_0}$ line in $\Im(\tilde{z})$. d) A linecut through $Q_y$ along the $(0,0)$ to $(0,1)\frac{2\pi}{a_0}$ line in $\Im(\tilde{z})$. Drift fields computed for the +45 dualmap, which is $16.2 \times 16.2 \ nm^2$ and $230 \times 230$ pixels$^2$. 
Figure B.5: Dependence of the localization of the Bragg peak on \( L_1 \). This figure contains the same information as the preceded figure, but presented differently. The graphs show the *relative* strength of the Bragg pixel. The height of the Bragg pixel divided by the average of the absolute values of its nearest neighbors is plotted as a function of \( L_1 \), measured in atoms. a) Relative amplitudes of the Bragg pixels in \( \Re[\tilde{z_{topo}}] \). b) Relative amplitudes of Bragg pixels in \( \Im[\tilde{z_{topo}}] \). Drift fields computed for the +45 dualmap, which is \( 16.2 \times 16.2 \text{ nm}^2 \) and \( 230 \times 230 \text{ pixels}^2 \).
and the 70824A05 map, which is $72 \times 72 \, \text{nm}^2$ and $512 \times 512 \, \text{pixels}^2$. Two other maps (Hudson 0306Q008 and Hoffman 2008_05_21_A001) were analyzed in a similar fashion and exhibit the same dependence on $L_1$.

As can be seen in Figure B.3, for $L_1 = 1$ atoms, the drift field has a pebbly texture and varies quite a lot at the $nm$ length scale, or at much smaller length scales then we would expect temperature or piezo drift to take place. This is spurious drift caused by excessively short $L_1$. The drift fields get smoother by eye and the standard deviation of each map drops steadily as $L_1$ increases.

It is unclear what the actual length scale of drift is, but it is clear from Figure B.4 and Figure B.5 that the relative localization of the Bragg peak onto a single pixel decreases as $L_1$ increases. We want to be sure to re-align the data as well as possible onto a perfect lattice, but do not want to move things around excessively due to spurious drifts, so a moderate value of $L_1$ seems appropriate.

Drift fields were also computed as a function of $L_1$ for a 400 pixel crop of the 70824A05 map, nominally $72 \times 72 \, \text{nm}^2$ and $512 \times 512 \, \text{pixels}^2$. They are similar in appearance to the drift fields shown in Figure B.3 and are not reproduced here. The location of the center each composite atom in a 2X2 average unit cell was found. In Figure B.6 the locations are plotted as a function of $L_1$. While there are four composite atoms in a 2X2 average unit cell, this particular average unit cell was created using Fourier techniques, and the shift was computed using a combination of $Q_x$, $Q_y$, $Q_a$, and $Q_b$, so there are only two distinct atom locations (of the two distinct Bi sublattices). In Figure B.6a, we see that the locations of the centers of the composite atoms are relatively stable for smaller $L_1$ and then move diagonally...
Figure B.6: a) The locations of the two distinct atoms in the 2X2 average unit cell of 70824A05, plotted for $L_1 = 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 13, 17$ atoms. b) The shift between the two atoms, a measure of the orthorhombic distortion in the lattice, as a function of $L_1$. The shift is the distance between the two distinct atoms along $Q_x$ and $Q_y$, respectively. Note that here the shift is along the atomic lattice, so we mean along the direction of $Q_x$ and $Q_y$, not along the scan direction $x$ and $y$. 
across the average unit cell as $L_1$ increases. The drift correction algorithm clearly
does a worse and worse job of placing the atoms accurately at their assigned atom
locations at $L_1$ gets very large. The relative shift between the two atoms, however,
is relatively insensitive to the choice of $L_1$, especially for smaller $L_1$.

We have several competing effects in our choice of $L_1$. We do not want to move
atoms excessively in response to pick-up from longer-length scale electronic structure
(on order $\xi$ lengthscales, or $>3\,\text{nm}$) in the topograph. We also do not want to make
$L_1$ too long because this inhibits our ability correct for real drift. $L_1 = 5\text{atoms}$ was
chosen as a good compromise between competing issues.

### B.5 Choice of Background Subtraction and Bad Pixel Removal

This section deals with the preparation that should be done to a topograph in
order to prepare it to find drift fields, namely background subtraction and bad pixel
removal. I primarily consider the effect on the atoms in the average unit cell made
from a topograph and on the drift fields that are produced, and then conclude with
some remarks are how the information in the drift-corrected topograph is affected by
these choices.

Background subtraction can be done in several different ways. All methods are
based upon fitting either the entire map, or single rows or columns at a time, to a
polynomial, and then subtracting or dividing by that polynomial. The main decisions
to be made are whether to do a plane subtraction or row subtraction and the order
of the polynomial (column subtractions are almost never useful because noise is not
coupled into maps column-wise, and in general we use subtractions instead of divisions
because subtraction is more fundamental than the division – the subtraction is the
difference in z height of the tip, whereas divisions are not well-defined). Higher order
polynomials remove more of the background distortion but are also more invasive.

Some maps can be subtracted quite well with a plane polynomial of fairly high
order (like 5 or 6). Plane subtraction removes only a few pixels at the center of
the FT, where the change is unlikely to affect any future analysis we might want
to do. Sometimes a plane subtraction does not do a good job at the very bottom
few percent of the image where there is more scantube relaxation artifact. Some
maps have temperature change events, for example if the level of liquid Helium in the
dewar belly drops below a certain level and then the temperature control feedback
loop responds over the course of an hour. It is likely that this is the reason for the
horizontal feature that can be seen in the topograph of B.9. A row subtraction does an
excellent job of removing temperature variation background ripples, but has the effect
as well of removing a stripe through the vertical center of the FT of a topograph.
This is not a problem if your goal is to find some drift fields and then analyze a
spectroscopic map, but it is very important to remember that you have erased some
data (including potentially the orthorhombic distortion peak, if the map was taken
at 45° to the lattice, if your goal is to analyze the topograph itself. Background
subtraction with a row polynomial will erase a Bragg pixel if the map was taken
aligned with the lattice, and then the drift correction algorithm will not work.
B.5.1 Effect of Background Subtraction on Average Unit Cell

This section concerns the effect of background subtraction on the average unit cell that is produced by the MAUC algorithm and the shifts of the four composite atoms in the 2X2 supercell as a function of background subtraction method. The simultaneous topograph from the diag $dI/dV_1$ map was background subtracted using plane and row polynomial fits of order 2 and 6, drift fields were found and applied, and then 2X2 average unit cells were computed from the drift-corrected topographs.

Figure B.7 shows the drift-corrected topographs in the middle column. In the top row, the topograph that was produced by a plane polynomial subtraction of order 2 shows a sharper horizontal darker streak on the bottom, likely due to incomplete removal of early-map piezo-relaxation, and a smooth overall warp to the map. For this particular map, the plane polynomial subtraction of order 6 produces a very similar effect to a row polynomial subtraction of order 2. This is not true in general. It is interesting to note that the row polynomial subtraction of order 6 appears to have actually removed some of the $\xi$-length scale electronic structure from the topograph. The depressed areas appear to be less dark than in the other topographs.

The 2X2 average unit cells look fairly similar by eye. There is some streaky noise which becomes less pronounced as more aggressive background subtractions are performed. We get our first hint here that the long length-scale order is implicated in the pixelated look of the average unit cell. This will be discussed more fully in later sections.

The fitted locations of the centers of the four composite atoms in the 2X2 average
Figure B.7: Topograph and 2X2 average unit cell of the diag dI/dV₁ simultaneous topograph, which is $9 \times 9 \text{nm}^2$ and $128 \times 128\text{pixels}^2$. The details about the background subtraction performed on the topograph before drift fields were found and applied are listed in the first column. All topographs were drift-corrected onto $Q_x = (19, 19)$. 
Figure B.8: Locations of the four composite atoms in the 2X2 average unit cell, for the four different topograph background subtraction methods shown in Figure B.7. Shifts of the four atoms in the a) $Q_x$ direction and b) $Q_y$ direction are plotted. If the drift-correction worked perfectly, the four atoms would be centered around 0, and an orthorhombic distortion would cause two atoms to appear shifted at most $\sim 3\%$ from the other two.
unit cell can be seen in Figure B.8. There is some variation with background subtraction, but aside from the plane polynomial of order 2, which pretty clearly seems insufficient, they are tightly clustered, within 0.5% of a unit cell of each other.

The key thing to note from this section is that the topographs themselves and their average unit cells are affected by choice of background-subtraction method. We will see in the next section that the choice of background subtraction has a negligible effect on the drift fields themselves. If your goal is to simply make some drift fields and study the spectroscopic map, then background subtraction can be done a little more cavalierly. However, if the goal is the learn anything about the topograph, then you can see from Figure B.7 that the best-suited background subtraction method should be very carefully selected, based on the size of the image, orientation to the lattice, noise, features due to temperature instabilities, etc.

B.5.2 Combination of Background Subtraction and Bad Pixel Removal

The analysis carried out in this subsection was done on the -45 dualmap, on both the simultaneous topograph of the $dI/dV$ map and the simultaneous topograph of the $I(z)$ map. The -45 dual map is fairly noisy and had a less stable tip than would be ideal, as can be seen in A.4c.

Bad pixel removal can be done in a few different ways. Sometimes there are isolated bad pixels caused by momentary tip instabilities. The best way to remove them is to use the Image Process > Remove Bad Pixels > Remove Outliers > N=x standard deviations. x is largely at your discretion. I never formed a strong opinion
Figure B.9: Topographs and drift field statistics for the $-45 \, dI/dV$ map simultaneous topograph. The details about the topograph preparation are in the first column.
### Figure B.10: Topographs and drift field statistics for the -45 $I(z)$ map simultaneous topograph.

The details about the topograph preparation are in the first column.

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<tr>
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<th>Topograph</th>
<th>$u_x$ Statistics</th>
<th>$u_y$ Statistics</th>
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<td>Mean: $-0.9413635$ SDDev: $0.61551885$ Variance: $0.37786546$ Kurtosis: $-0.072680216$ Median: $-0.08945664$</td>
<td>Mean: $2.0928385$ SDDev: $0.47840411$ Variance: $0.22887432$ Kurtosis: $-0.64230311$ MDDev: $0.83195815$ Median: $2.1500896$</td>
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Figure B.11: Drift fields computed for the -45 \(dI/dV\) simultaneous topograph, with row subtraction polynomial order 2 and bad pixel removal. These are the same drift fields whose statistics are given in the last row of Figure B.9. The drift fields are presented as representative images. All of the computed drift fields look the same by eye. The statistics are for this particular set of drift fields, and provide context for evaluating the statistics of the differences of the drift fields.

A long such streak can be seen in the second topograph from the top in B.9 (they are easier to see with row subtraction than plane subtraction) and several shorter ones are also visible throughout the map. Those sometimes need to be identified and removed by hand, by writing a little custom piece of code that sets that unstable section equal to the average of the rows above and below it.

In this subsection section I go through a few different combinations of background subtraction and bad pixel removal. I consider both subtraction of a plane polynomial of order 6 and subtraction of a row polynomial of order 2. I consider both no bad pixel removal at all and removal of outliers with \(N=2\) standard deviations plus the removal of the single large streak. I apply the combinations of these to both the \(dI/dV\) simultaneous topograph and the \(I(z)\) simultaneous topograph.

The key things to notice in Figures B.9 and B.10 are the visible differences between topographs and the variation in averages between drift fields. The standard
Figure B.12: (next page) Drift field difference images, produced by subtracting drift fields computed from topographs shown in Figures B.9 and B.10. In the first column, the descriptor(s) in bold are the things that are different between the topograph used to make the subtracted drift fields, and the descriptor(s) in italics are the things that are the same about the topographs used to make the subtracted drift fields.
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- $\Delta d/dV - l[z]$
  - both plane polynomial 2
  - both no bad pixel removal

- $\Delta d/dV - l[\lambda]$
  - both row polynomial 2
  - both no bad pixel removal

- $\Delta d/dV - l[z]$
  - both plane polynomial 6
  - both bad pixel removal state = 2

- $\Delta d/dV - l[\lambda]$
  - both row polynomial 2
  - both bad pixel removal state = 2

- $\Delta d/dV$
  - both
  - plane polynomial 6
  - row polynomial 2
  - both no bad pixel removal
Figure B.13: (next page) Drift field difference images, produced by subtracting drift fields computed from topographs shown in Figures B.9 and B.10. In the first column, the descriptor(s) in bold are the things that are different between the topograph used to make the subtracted drift fields, and the descriptor(s) in italics are the things that are the same about the topographs used to make the subtracted drift fields.
### Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

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<th>Image</th>
<th>Statistics</th>
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Skewness: 1.15939157  
Kurtosis: 0.021542124  
Median: 0.00003254711 |

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| Both plane polynomial 6-row polynomial 2 | ![Image](image2.png) | Mean: 0.00062395162  
Variance: 8.685772e-006  
Skewness: 1.7468521  
Kurtosis: 0.018808136  
Median: 0.00093080781 |

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| Both plane polynomial 6-row polynomial 2 | ![Image](image3.png) | Mean: 0.0006448495  
Variance: 8.667709e-006  
Skewness: 2.37836258  
Kurtosis: 0.018015093  
Median: 0.0002341487 |

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| Both plane polynomial 6-row polynomial 2 | ![Image](image4.png) | Mean: 0.00062395162  
Variance: 8.685772e-006  
Skewness: 1.7468521  
Kurtosis: 0.018808136  
Median: 0.00093080781 |

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| Both plane polynomial 6-row polynomial 2 | ![Image](image5.png) | Mean: 0.0006448495  
Variance: 8.667709e-006  
Skewness: 2.37836258  
Kurtosis: 0.018015093  
Median: 0.0002341487 |

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<th>Statistics</th>
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| Both plane polynomial 6-row polynomial 2 | ![Image](image6.png) | Mean: 0.00062395162  
Variance: 8.685772e-006  
Skewness: 1.7468521  
Kurtosis: 0.018808136  
Median: 0.00093080781 |

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<th>Image</th>
<th>Statistics</th>
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</table>
| Both plane polynomial 6-row polynomial 2 | ![Image](image7.png) | Mean: 0.0006448495  
Variance: 8.667709e-006  
Skewness: 2.37836258  
Kurtosis: 0.018015093  
Median: 0.0002341487 |
deviations are pretty consistent between all computed drift fields. Comparisons of the averages shows that there is more difference between topographs with different bad pixel removal than between topographs with different background subtractions.

In Figure B.11 I show computed drift fields for one of the prepared topographs, for context. The drift fields do not look different by eye so it is not useful to show all of them.

The useful findings of this section are in Figures B.12 and B.13. The key take-home message is that the drift fields are remarkably insensitive to topograph preparation, and the maximum average difference between computed drift fields from the same topograph prepared in different ways is only about 1.5% of a pixel. For a 5pixel/atom map, this is only 0.003 of the inter-atomic spacing, or 0.00078 nm. However, a single bad pixel can locally affect the drift field. There are sharp features in the difference fields with different bad pixel removal effects. The local effect of bad pixels is $4 - 5\%$ of a pixel (in these maps, for these particular bad pixels).

Conclusions for the three points of comparison:

- There is a difference between the topograph of the $dI/dV$ map and the $I(z)$ map that may be systematic. Since the topographs were taken with the same setup conditions, they should be identical. It is possible that if $(x,y)$ is not fully stabilized before spectroscopic measurements begin, there will be some systematic drift in the fast scan direction between the first and second of the interleaved datasets. These difference drift fields show that if there is such a systematic drift, it is in this particular map $0.032 \pm 0.014$ of a pixel, and is not consistent throughout the map (as can be seen by how the difference fields do
not look “flat”.) This effect will be considered more fully in Section B.9.

- Drift fields computed from topographs that have been background subtracted in different ways are essentially identical – the difference drift fields are not meaningfully different from 0. This is not surprising because the drift field finding procedure is essentially a Fourier-space technique, and any background tilt will only be present in the center few pixels.

- Drift fields computed from topographs that have had different bad pixel removal preparations are very close to identical, and not different enough to get worried about the “right” way to remove bad pixels. It is a good idea to remove bad pixels, since a bad pixel may be able to locally screw up a drift field.

In summary, it is entirely unimportant what kind of background subtraction you do to the topograph (if you are going to use the computed drift fields to drift correct and then analyze a spectroscopic map), it is a good idea to remove bad pixels, and if there is systematic drift between subsequent topos in an interleaved set, it is in this map roughly $0.032 \pm 0.014$ of a pixel.

### B.6 Choice of $\vec{Q}$

One of the key choices that needs to be made while drift-correcting maps is the set of $\vec{Q}$ onto which to align the lattice. A typical FT of a topograph taken simultaneously to a spectroscopic map is shown in Figure B.14. The Bragg peaks start out non-isotropic blobs which may or may not be centered on orthonormal vectors. The example in Figure B.14 has Bragg peaks centered at $(38.13, 36.40)$ and
Figure B.14: Fourier Transform of a topograph taken simultaneous to a spectroscopic map. The map is $18 \times 18 \text{ nm}^2$ and $256 \times 256 \text{ pixels}^2$, which gives roughly 5 pixels/atom resolution. The insets show the Bragg peaks, which a 2d gaussian peak find gives as centered at $(38.13, 36.40)$ and $(-37.24, 35.66)$. The erased stripe down the center vertical is the result of row-subtraction background removal. Fourier Transform image is Amplitude, no window.

It is not obvious which set of orthonormal $\vec{Q}$ between $Q_x = (35, 35)$ and $Q_x = (38, 38)$ is the right choice. This section details some analysis that was done to see what kinds of things depended on the choice of $\vec{Q}$. Only orthonormal $\vec{Q}$ were considered.

It is difficult to evaluate the best choice of $\vec{Q}$ in a spectroscopic map, since it is unclear what is the proper metric. The question of $\vec{Q}$ choice was evaluated in two somewhat indirect ways. First, I considered how the choice of $\vec{Q}$ location affected the location of the atoms in an average unit cell of a topograph made by the MAUC
algorithm. Second, I made simulated data and evaluated how the choice of $\vec{Q}$ to

drift-correct it onto affected the location of atoms in the average unit cell.

B.6.1 How $\vec{Q}$ Choice Affects Atom Locations in a Drift Corrected Topograph

First we will consider the effect of $\vec{Q}$-choice variation on the 2X2 average unit
cell. The diag dataset, with size $9 \times 9 \text{nm}^2$ and $128 \times 128\text{pixels}^2$ and original $\vec{Q}$ of

$Q_x = (19, 20)$ and $Q_y = (-18, 21)$, was analyzed for orthonormal $\vec{Q}$ choices ranging

from $Q_x = (17, 17)$ to $Q_x = (21, 21)$. Drift fields were found for the best-fit Bragg

vectors and rescaled onto the set of orthonormal $\vec{Q}$. The drift-corrected topographs

and the 2X2 average unit cell can be seen in Figure B.15. The topographs do not

vary very much visually; they are presented mainly so the flat drift-correction artifact

stripe at the edges can give a sense of scale of lattice stretching or smushing. The

computed average unit cells show that it is not only the background subtraction which

plays a key role in the pixelated appearance of the average unit cell, but rather the

combination of the size of the lattice and the background subtraction. It is natural to

speculate that the stripes and checkerboard-type noise are manifestations of beating

between the longer-wavelength structure in the topograph and the atomic lattice.

The plot of the locations of the centers of the four composite atoms as a function

of $\vec{Q}$ can be seen Figure B.16. A striking dependence of location on $\vec{Q}$ can be seen.

Interestingly, the four composite atoms travel through the average unit cell on a
diagonal path as a function of $\vec{Q}$ magnitude. The shift of fitted atom centers from the

nominal center locations is smallest for $Q_x = (19, 19)$ and $Q_x = (20, 20)$, which are
Figure B.15: Topograph and 2X2 average unit cell of the diag $dI/dV_1$ simultaneous topograph, which is $9 \times 9 \text{nm}^2$ and $128 \times 128\text{pixels}^2$. The $\vec{Q}$ which the topograph was drift-corrected onto are listed in the first column. All topographs were background subtracted with plane polynomial of order 2 before drift-correcting.
Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

Figure B.16: Locations of the four composite atoms in the 2X2 average unit cell, for the five different sets of $\vec{Q}$ shown in Figure B.15. Shifts of the four atoms in the a) $Q_x$ direction and b) $Q_y$ direction are plotted. c) The relative shifts, defined as the distance between the composite atoms in each Bi sublattice in the $Q_x$ and $Q_y$ directions. This is a measure of the orthorhombic shift. If the drift-correction worked perfectly, the four atoms would be centered around 0, and an orthorhombic distortion would cause two atoms to appear shifted at most $\sim 3\%$ from the other two.
the $\vec{Q}$ that are closest to the original non-orthonormal best-fit $\vec{Q}$. It is clearly very important to drift-correct onto the $\vec{Q}$ that most closely fit the locations of the Bragg peaks in the raw data.

Another interesting observation is that the orthorhombic shift, a measure of which is plotted in Figure B.16c, shows a $\vec{Q}$ dependence for $\vec{Q}$ smaller than the optimal size (which corresponds to a stretched lattice) but not for $\vec{Q}$ which are larger than the optimal size (which corresponds to a smushed lattice). It is not surprising that it is not a great idea to try to pretend you have better spatial resolution than you do by stretching your lattice. Given a choice between two orthonormal $\vec{Q}$ which are equally close to the best-fit $\vec{Q}$, it is better to drift-correct onto the slightly larger set.

B.6.2 How $\vec{Q}$ Choice Interacts with Background Subtraction to Affect Atom Locations in a Drift-Corrected Topograph

Expanding this discussion to include the interaction of these effects, now we will consider a combination of both $\vec{Q}$ variation and background subtraction variation, in the $+45$ map, which with the standard crop is $16.2 \times 16.2 \text{ nm}^2$ and $230 \times 230 \text{ pixels}^2$ and has un-corrected Bragg vectors centered at $Q_x = (34, 33)$ and $Q_y = (-34, 32)$. The drift-corrected simultaneous topograph of the $dI/dV$ map is shown in Figures B.17 and B.18. In Figure B.17 is a set of topographs with background subtraction of plane polynomial of order 2, close to the least aggressive possible background subtraction, and $Q_x = (31, 31), (33, 33)$, and $(35, 35)$. Figure B.18 shows the same set but with background subtraction of row polynomial of order 6, the most aggressive possible
background subtraction.

The plane polynomial of order 2 background subtraction is clearly insufficient to remove the very-long-length scale piezo-drift or temperature-drift which has caused some strong horizontal features. The row polynomial of order 6 background completely removes all of that artifact. Unlike what we saw in Figure B.7, the $\xi$-length-scale variations in electronic structure are not significantly affected by this aggressive row subtraction, probably because the larger spatial extent of this map as compared to the diag map makes it impossible for a $6^{th}$ order polynomial to fit an entire row.

Most strikingly, the 2X2 average unit cell shows the strongest striping for the case of $Q_x = (33, 33)$, which we might have guessed to be the best-choice $\bar{Q}$ from comparison to the original $\bar{Q}$ in the raw data. However, the combination of this particular size, longer-length-scale structure, and magnitude of $\bar{Q}$ has produced a strong interaction. It is mitigated but not eliminated by a more aggressive background subtraction. This shows how important it is to compute the average unit cell of the topograph after drift-correcting to check and see if any unfortunate beating is occurring which could be eliminated by a different choice of crop or $\bar{Q}$.

The plot of the locations of the centers of the four composite atoms as a function of $\bar{Q}$ can be seen Figure B.19. The largest outliers from the crowd are those from average unit cells computed from topographs that were drift-corrected onto the $Q_x = (31, 31)$ lattices, confirming again that it is a better idea to err on the side of larger $\bar{Q}$ than smaller. Even though the appearance of the average unit cell computed from topographs drift-corrected onto $Q_x = (33, 33)$ shows a strong diagonal striped noise feature, the fits to the locations of the centers of the composite atoms seem
Figure B.17: Topograph and 2X2 average unit cell of the +45 dI/dV simultaneous topograph, which is 16.2 × 16.2 nm² and 230 × 230 pixels². All were background subtracted by a plane polynomial of order 2. $\vec{Q}$ which the topograph was drift-corrected onto are listed in the first column. Bad pixels were removed from all topographs with standard deviation=2 before drift-correcting.
Figure B.18: Topograph and 2X2 average unit cell of the +45 $dI/dV$ simultaneous topograph, which is $16.2 \times 16.2 \text{nm}^2$ and $230 \times 230 \text{pixels}^2$. All were background subtracted by a row polynomial of order 6. $\vec{Q}$ which the topograph was drift-corrected onto are listed in the first column. Bad pixels were removed from all topographs with standard deviation=2 before drift-correcting.

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<td><img src="image5" alt="drift-corrected topo" /></td>
<td><img src="image6" alt="2X2 average unit cell" /></td>
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Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

Figure B.19: Locations of the four composite atoms in the 2X2 average unit cell, for the six different combinations of background subtraction and $\vec{Q}$ shown in Figure B.17 and B.18. Shifts of the four atoms in the a) $Q_x$ direction and b) $Q_y$ direction are plotted. c) The relative shifts, defined as the distance between the composite atoms in each Bi sublattice in the $Q_x$ and $Q_y$ directions. This is a measure of the orthorhombic shift. If the drift-correction worked perfectly, the four atoms would be centered around 0, and an orthorhombic distortion would cause two atoms to appear shifted at most $\sim 3\%$ from the other two.
to be unaffected. The measure of orthorhombic distortion plotted in Figure B.19 shows a strong $\vec{Q}$ dependence for the less aggressive background subtraction and a much smaller $\vec{Q}$ dependence for the very aggressive background subtraction. If the features of the topograph are the area of study, then it seems like a more aggressive background subtraction, coupled with a good choice of $\vec{Q}$, is necessary. Care should be taken that the background subtraction is not so aggressive that it removes features in the topograph, however.

**B.6.3 Choice of $\vec{Q}$ in Simulated Data**

In order to more fully understand the effect of the choice of $\vec{Q}$ on the average unit cells, simulated topographs were produced, drift-corrected, and then made into average unit cells. I chose to make data with $128 \times 128$ pixels$^2$ and 5 pixels/atom, in order to compare to the diag datasets, which had been most heavily studied.

The topographs are shown in the central column of Figure B.20. They are not particularly interesting except for the drift-correction artifact stripe along the edges, which gives a sense of scale to the degree to which the lattice was stretched or smushed. The 2X2 average unit cells appear identical, which means that variation of $\vec{Q}$ alone cannot explain the stripes or other features in the average unit cell.

The location of the centers of the four composite atoms in the 2X2 average unit cells shows exactly the same strong dependence on $\vec{Q}$ seen in Figure B.16, confirming that it is the question of lattice stretch or compression which is responsible for this movement. The measure of orthorhombic shift plotted in Figure B.21c also shows identical behavior, with a strong $\vec{Q}$ for $\vec{Q}$ smaller than optimal and stability for larger
Figure B.20: Simulated topograph and 2X2 average unit cell, $9 \times 9 \text{nm}^2$ and $128 \times 128 \text{pixels}^2$. The simulated topographs contain only a perfectly sinusoidal atomic lattice, with no structure are any other wavelengths. $\vec{Q}$ which the topograph was drift-corrected onto are listed in the first column.
Figure B.21: Locations of the four composite atoms in the 2X2 average unit cell, for the five different \( \vec{Q} \) shown in Figure B.20. Shifts of the four atoms in the a) \( Q_x \) direction and b) \( Q_y \) direction are plotted. c) The relative shifts, defined as the distance between the composite atoms in each Bi sublattice in the \( Q_x \) and \( Q_y \) directions. This is a measure of the orthorhombic shift. If the drift-correction worked perfectly, the four atoms would all be exactly at 0 with no orthorhombic distortion, since the simulated lattice was a perfect tetragonal lattice.
Because of the extreme simplicity of this simulated data, the similarity Figure B.16 and Figure B.21 is an excellent confirmation that we understand the effect of varying $\vec{Q}$.

### B.7 Effect of Order at Non-Bragg Wavelengths on Average Unit Cell of Simulated Maps

This section is a minor tangent into the analysis of slightly more realistic simulated images. I used a simple model of a $dI/dV$ in which I took an atomic lattice, added warps of various kinds, and then found drift-fields from the perfect lattice and applied them to the more complicated object. Like the simple simulations in the previous section, the data was $128 \times 128 \text{pixels}^2$ and $5 \text{pixels/atom}$.

The drift-corrected maps can be seen in the center column of Figure B.22. The atomic lattice is on the same scale as the lattices shown in the Figure B.20, but warps are so strong that it is not visible.

The warp fields were simply added to the atomic lattice. They are as follows:

1. **warp1**: a very long wavelength slow row-wise sinusoidal variation, like temperature drift or long time-scale piezo-creep, and a strong checkerboard order at $\sim 1/4\vec{Q}$

2. **warp2**: a very long wavelength slow row-wise sinusoidal variation, like temperature drift or long time-scale piezo-creep, and a strong checkerboard order at $\sim 3/4\vec{Q}$ (note that the apparent atomic lattice in the second row of Figure B.22 is actually a strong $3/4\vec{Q}$ structure)
Figure B.22: Simulated “dI/dV” layer and 2X2 average unit cell, 9 × 9 nm² and 128 × 128 pixels². The simulated maps contain a perfectly sinusoidal atomic lattice and a variety of structure at other wavelengths. See the text for details about the warp maps. $\vec{Q}$ which the topograph was drift-corrected onto are listed in the first column.
Figure B.23: Locations of the four composite atoms in the 2X2 average unit cell, for the five different simulated maps shown in Figure B.22. Shifts of the four atoms in the a) \( Q_x \) direction and b) \( Q_y \) direction are plotted. c) The relative shifts, defined as the distance between the composite atoms in each Bi sublattice in the \( Q_x \) and \( Q_y \) directions. This is a measure of the orthorhombic shift. If the drift-correction worked perfectly, the four atoms would all be exactly at 0 with no orthorhombic distortion, since the simulated lattice was a perfect tetragonal lattice.
3. warp3: several very long wavelength slow row-wise sinusoidal variations, like
temperature drift or long time-scale piezo-creep, of various periodicities, and a
strong checkerboard order at $\sim 3/4\vec{Q}$ of two similar periodicities, and a strong
checkerboard order at $\sim 1/4\vec{Q}$ of two similar periodicities

In addition to these warps, the maps were intentionally drift-corrected onto non-
ideal $\vec{Q}$. The first three had an original atomic lattice of $Q_x = (19, 19)$ and were
drift-corrected onto $Q_x = (18, 18)$. The fourth and fifth had, in addition to warp3, a
significantly distorted initial lattice. Initially, $Q_x = (17, 16)$ and $Q_y = (-20, 20)$ for
the fourth and $Q_x = (20, 20)$ and $Q_y = (-17, 17)$ for the fifth. Note that the lattice
vectors are not orthogonal and not of equal magnitude. These maps were then drift-
corrected onto orthonormal $\vec{Q}$ with $Q_x = (18, 18)$. These lattices are distorted worse
than any raw data that has been analyzed in this dissertation, but not by a ridiculous
amount. For comparison, the Bragg vectors of the raw diag $dI/dV_1$ simultaneous
topograph are centered at $Q_x = (19, 20)$ and $Q_y = (-18, 21)$.

Unsurprisingly, the 2X2 average unit cell of these maps are really ugly. The
different stripe and pixelation patterns of the average unit cell show that it is indeed
the longer-wavelength structure in the topograph which is beating with the atomic
lattice and creating periodic noise. The locations of the centers of the four composite
atoms in the 2X2 average unit cell are plotted in Figure B.23. The longer-wavelength
structure alone does have the effect of shifting the centers of the composite atoms
away from the nominal center, especially in the $Q_x$ direction, but the (spurious)
orthorhombic distortion remains quite small ($< 0.2\%$ of a unit cell). The maps which
have a distorted initial lattice and strong warp are significantly more problematic,
and show spurious shifts of up to 12% of a unit cell and orthorhombic shifts of up to 1% of a unit cell. It is unclear why the fourth map is so much more strongly pathological than the fifth, since they had similar degrees of distortion and identical warps.

B.8 Summary of Prescriptions

This section contains an ordered list describing my current method for drift-correcting datasets, based on all of the analysis of systematic effects that has been described in this appendix. Some of the steps that follow are physically meaningful, some particular to our code, and some are just advice to make your life easier. Below is a set of instructions sufficient to drift-correct a straight-forward dataset. If the dataset has particularly bad temperature instability resulting in a lot of row-wise streakiness, or if there is a tip change, or if there is a particularly high percentage of bad pixels, then more care and creativity will be required, and many decisions will have to be made on a case-by-case basis.

• If possible, start by taking a dataset that is easier to drift-correct. When relaxing the scantube over the map area, keep adjusting the scan size, the scan angle, and if necessary the $x$ and $y$ piezo calibration and be patient until the following things are true:

  – the Bragg pixels fall on orthonormal pixels – at 90° and equal magnitude
  – if 2201, that the scan angle is 45° to the lattice and the orthorhombic distortion wavevector is on the horizontal where it will not be erased by
row subtraction

– if 2212, that the scan angle is a few degrees off of 45° to the lattice so that
the orthorhombic distortion vector won’t get erased by row subtraction.

– the temperature is stable to $\leq 2 \, mK$

– the scantube is relaxed

• open the simultaneous topograph and rename it something sensible and descriptive and save it (this step is important because Util_BraggPeakDatabase uses the filename string to look for a match, so if the windowtitle matches the entry but the filename does not, then it will not be found).

• Background subtract the topograph using poly back row 2.

• Remove bad pixels, standard deviation 5.

• FFT the topograph, no window, amplitude, and to find the centers of the $Q_x$ and $Q_y$ Bragg pixels, do Analysis > 2d peak fit > fit simple gaussian. Force isotropic and redo fit. Note the peak center locations.

• Make a new entry in Util_BraggPeakDatabase, using some part of your descriptive filename as the identifier and the Bragg peak locations that you just found.

• Promote to layerobj.

• Find drift fields, using length scale of 5 atoms and flip before unwrapping. Do not force orthogonal or force even. Start with no crop.
• It is very likely that your drift fields will not unwrap properly at the bottom. Add a square crop to the find drift field algorithm gui (select the crop Before option). Slowly increase the size of the crop (you probably just want to crop only from bottom and left, since that is where the most drift occurs) until you get drift fields that unwrap properly.

• Now go back to your topograph, crop it by that same amount, re-find the Bragg pixels, and adjust the entry in Util_BraggPeakDatabase to reflect the new size and the new Bragg vectors. This is optional but I found that it led to far less confusion about $Q_x$ and $Q_y$ in the long run.

• Find drift fields.

• Save the topograph with “drift field source” appended to the end of the filename so that you know where your drift fields came from.

• If the Bragg vectors that you found via the 2d peak find were not orthonormal, then rescale your drift fields to orthonormal Bragg vectors. Choose Bragg vectors that are as close as possible to the Bragg vectors in the raw data, but with a strong preference to make them slightly larger rather than slightly smaller. This has the effect of compressing the atomic lattice slightly and is much better than stretching it.

• Save the drift fields.

• Drift correct the topograph and save it.
• Check the drift correction by looking at the Bragg pixels in the FFT of the topograph. The amplitude at the real $Q_x$ and $Q_y$ should be much larger (at least an order of magnitude) than neighboring pixels and the strength at the imaginary $Q_x$ and $Q_y$ should be much less than the real $Q_x$ and $Q_y$.

• Turn to your $dI/dV$ map. Rename it the same sensible and descriptive thing you named your topograph.

• Crop the $dI/dV$ map to the same size as the topograph.

• Remove bad pixels (standard deviation 4).

• Apply drift fields.

• Remove bad pixels (standard deviation 4).

• Save the drift-corrected $dI/dV$.

If the goal is to drift correct several different datasets onto the same lattice in order to compare changes as a function of temperature or magnetic field, then I would advise that you go quickly through the drift-field finding procedure, but not drift-correct each spectroscopic map, and find the smallest crop that will work for the entire set of maps. It may be necessary to shift the maps with respect to each other. The easiest way to do this is to drift correct the topographs and then put the images in a powerpoint file, one topograph per slide, and carefully size them the same and put them in the same location. Flipping rapidly through the slideshow helps you to see whether or not a shift is needed. If so, use the 2011 Analysis $>$ cross-correlate procedure and find the amounts that need to be added to the drift fields.
If the goal is to get a drift-corrected map of $\phi$ or $\kappa$, then in my opinion it makes the most sense to find $\phi$ or $\kappa$ from the $I(z)$ map, and then drift correct that 2d image. Since each $I(z)$ spectrum might have some variation or random noise that is pixel-by-pixel dependent, it makes the most sense to find the $\phi$ or $\kappa$ from each spectrum and then to drift correct something that is physically meaningful. The same argument applies if you are going to divide something by $I_s$ in order to remove some of the setpoint effect. The noise in $I_s$ is measurement-specific and pixel-specific, so it makes more sense to do the division and then the drift-correction.

B.9 Upper Limit of Systematic Drift

Here I return to the question of systematic drift throughout a multiple-map that was broached in Section B.5. We can use the simultaneous maps to calculate the upper limit on systematic drift that may occur throughout the course of a spectral measurement and to evaluate the amount of error introduced by long length-scale (length scales of order $\xi = 2.2 \text{ nm}$) variations in a topograph used to find drift fields. The analysis in the following section was carried out on all three triple maps.

This analysis provides a way to quantify what we mean when we say that the interleaved maps of a triple map were taken at the “same” location. Figures B.24 through B.26 are tables that show the drift fields that were found for the three simultaneous topographs of each triple map and differences between them.

The first interesting observation that can be made by comparing the simultaneous topographs from the same triplemap is the degree to which the drift-correction algorithm is affected by longer-length scale differences in topographs. It is really key
Figure B.24: Drift fields computed for the three simultaneous topos of the control triplemap. Background subtracted using row polynomial order 2. Bad pixel removal was attempted, but the map was so stable that no bad pixels were identified.
Figure B.25: Drift fields computed for the three simultaneous topos of the diag triplemap. Background subtracted using row polynomial order 2. Bad pixel removal was attempted, but the map was so stable that no bad pixels were identified.
Figure B.26: Drift fields computed for the three simultaneous topos of the along triplemap. Background subtracted using plane polynomial order 6. Bad pixel removal was attempted, but the map was so stable that no bad pixels were identified.
to note the scalebars of all the images in this discussion. Figure B.27 shows the three simultaneous topographs of the diag triple map. The first $dI/dV$ map (referred to hereafter as 1) and the $I(z)$ map (referred to as Z) were taken with a bias setup condition of $-100 \text{ mV}$ and are essentially identical. The second $dI/dV$ map (referred to as 2) was taken with a bias setup condition of $+100 \text{ mV}$ and shows clear differences in $\xi$-length scales from the other two topos. Recall that the topograph contains the integral of the local DOS from the Fermi level to the bias setup condition (refer to Equation 1.9). Because the lattice of each of these topographs is identical, the drift correction algorithm should be able to place them perfectly on top of each other.

Figure B.28a and b show the difference between 1 and 2, both before and after drift-correction. The clearly visible lattice in Figure B.28b suggest that either the drift-correction algorithm gets distracted by long length scale differences between 1 and 2 and shifts them differently depending on local background or aligns the atomic lattices perfectly but because theyre sitting on different backgrounds they do not subtract cleanly. The drift-correction does not seem to have changed a and b much with respect to each other, which may mean that differences are due to legitimate differences in the map, not to mis-registry, or that mis-registry is not fixed by the drift-correction algorithm.

The interesting thing is to see how the 1-2 comparisons (a and b) look in contrast to the 1-Z comparisons (c and d). The 1-Z subtraction clearly shows a little bit of lattice mis-registry which was visibly reduced but not eliminated by the drift-correction algorithm, and its also clear how much worse it is on the left edge, both before and after drift-correction. In fact, the drift correction seems to have spread the
Appendix B: Systematics of Spectroscopic Maps and Drift Correction Algorithm

Figure B.27: The three simultaneous topographs for the three spectroscopic maps in the diag dataset. a) from $dI/dV_1$ map and c) from the $I(z)$ show topographs taken with $-100\, mV$ bias setup condition, and b) from $dI/dV_2$ shows a topograph taken with $+100\, mV$ bias setup condition. All three had a current setpoint of 100 $pA$.

Another interesting observation is that the difference between drift fields computed from topographs of subsequent maps may show a systematic transient shift in $x$. In the dual map analyzed in Section B.5, we saw that there was an apparent systematic shift along $x$ between subsequent maps of $0.032 \pm 0.014$ pixels. In the triple map drift fields we see a hint of the same phenomenon, although we see a smaller magnitude and the means are not clearly larger than standard deviations. For lattice-shift analysis it is best to compare the first and last simultaneous topographs because they were all taken with the same bias voltage of $-100\, mV$ and should be identical. The difference along $x$ is $0.016 \pm 0.019$ pixels for control, $0.015 \pm 0.010$ pixels for diag, and $0.026 \pm 0.009$ pixels for along. These differences are consistent with the
Figure B.28: The difference between subsequent simultaneous topographs of the diag dataset. Topograph from $dI/dV_1$ (bias=$-100 \text{ mV}$) - topograph from $dI/dV_2$ (bias=$+100 \text{ mV}$) a) before and b) after drift correction. Topograph from $dI/dV_1$ (bias=$-100 \text{ mV}$) - topograph from $I(z)$ (bias=$-100 \text{ mV}$) c) before and d) after drift correction.
hypotheses of systematic transient drift in $x$, but are smaller and less convincingly
outside of the standard deviation than in the case of the dualmap. Differences in
$u_y$ drift fields are an order of magnitude smaller, not consistent between the three
triple maps, and likely random uncertainty because the means are smaller than the
standard deviations. If we compare the three control (the map where all three si-
multaneous topographs were taken at the same bias voltage) drift fields, then it is
possible to see a hint of the time dependence of the shift. The difference between
the first and second map, $\sim 1$ s apart in time, is an average of 0.015 pixels, and the
average between the second and third, another $\sim 1$ s later, is an order of magnitude
smaller, with an average of 0.0015 pixels. The triple maps had less settling time than
the dual maps (see Section C.4 for a full discussion) so it is not clear why, if there
was a systematic shift along the fast scan direction, it should be larger in the dual
maps than in the triple maps.

The comparison between identical topographs taken $\sim 2$ s apart show that there
is probably a systematic shift between subsequent maps in a triplemap, but its really
tiny. The drift-correction does do a decent job of aligning the 1 and Z maps to
each other. It remains an open question how well the drift correction algorithm
does at aligning lattices that are in topographs with different setup conditions, or
temperatures, or magnetic fields.

B.10 Setup Condition Effects

This section concerns observations of tunneling asymmetry that are not really
anything to do with drift correction, but are made possible by drift correction. In
this section I will use energy and voltage interchangeably, since they differ by only a factor of $e$.

Recall the expression for $dI/dV$ spectra (Equation 1.13) that we arrived at after the discussion in Section 1.3.3:

$$\frac{dI(x, y, z_\delta, V)}{dV} \propto \frac{eI_s}{\int_{-eV}^{0} DOS(x, y, E)dE} DOS(x, y, E)$$  \hspace{1cm} (B.1)

In arriving at this equation we assumed several things, among them that the DOS of the tip is an energy-independent constant, that the tunneling matrix element $|M|$ is an energy-independent constant, and that $z_\delta$ is held constant throughout the course of the measurement. If all of those assumptions are true, then the prefactor to the DOS,

$$\frac{eI_s}{\int_{-eV}^{0} DOS(x, y, E)dE}$$  \hspace{1cm} (B.2)

is truly just a constant, and spectra taken at the same location with different setup conditions will differ by only a multiplicative factor which is constant in energy. The triple maps provide an opportunity to test these assumptions. In these maps we have two drift-corrected and therefore perfectly aligned maps, taken with either identical or two different bias setup conditions. Let us define the ratio, $R$, of two $dI/dV$ spectra as

$$R(x, y, z_\delta, V_{s1}, V_{s2}, V) = \frac{dI(x, y, z_\delta, V_{s1}, V)}{dV} / \frac{dI(x, y, z_\delta, V_{s2}, V)}{dV}$$  \hspace{1cm} (B.3)

Because the $DOS(x, y, E)$ in both expressions for $dI/dV$ is the true, physical DOS of the sample at that point, that piece drops out, as does, if the pre-factor is
Figure B.29: A typical ratio, $R(V)$, at a single pixel from the diag map. This particular $R(V)$ is of a $-100 \text{ mV}$ bias setup map over a $+100 \text{ mV}$ bias setup map. The standard deviation of this $R(V)$ is 0.058.

We test the assumption of prefactor energy-independence by looking at $R(V)$ for each location. A typical ratio is shown in Figure B.29. This is not the most stringent test of energy-independence because these spectra are taken as part of a full spectral survey, and due to timing constraints have less averaging and less integration time than would be ideal. The standard deviation of the noise on the $R(V)$ shown in Figure B.29 is 0.058, and the average of the $128 \times 128$ standard deviations of all the $R(V)$ in the whole diag map is 0.061. A more careful check of energy-independence would require taking a few point spectra at the same location with much higher
Figure B.30: Setup condition effects. The distributions of $\langle R \rangle_V$ over a full map for the three different triple maps. a) The ratio for the control map; first map was taken with $V_s = -100\,meV$ and second map was taken with $V_s = -100\,meV$. Mean is 1.016 and standard deviation is 0.137. This gives a measure of the uncertainty in $z_\delta$ due to imperfect control over $I_{set}$, since ratio should be exactly 1 for all spectra. b) The ratio for the diag map; first map was taken with $V_s = -100\,meV$ and second map was taken with $V_s = +100\,meV$. Mean is 0.959 and standard deviation is 0.163. c) The ratio for the along map; first map was taken with $V_s = -100\,meV$ and second map was taken with $V_s = +100\,meV$. Mean is 0.887 and standard deviation is 0.131.

signal-to-noise and several different bias setup conditions. But because we have full maps we can compare, we can see if there are spatial patterns in $\mathcal{R}(V)$.

We start by looking at the ratio of the two $dI/dV$ maps in the control dataset. Since these two maps were taken with identical setup and timing parameters, we expect the spectra to be exactly identical. We do, as expected, find that these $\mathcal{R}(V)$ have no energy-dependence, so we average over all $V$ to reduce noise. We find that the distribution of energy-averaged ratios, $\langle R \rangle_V$, between same-location point spectra is peaked at 1.01 and has a standard deviation of 0.137, which gives us a way to quantify the imperfection in our tunneling current feedback loop and the error in $z_\delta$. The full histogram of ratios is seen in Figure B.30a.
Now we turn to the maps where were taken with different bias setup conditions. Like the control maps, we find no discernible energy-dependence in $R(V)$ (although keep in mind that the RMS noise of $R(V)$ is relatively high), which confirms the assumptions that went into the derivation of Equation 1.13. If we compute $\langle R \rangle_V$ and compare maps which were taken at the same locations with different bias setup conditions, we see that the distributions are not peaked at 1.0. The distribution for the diag maps, shown in Figure B.30b, has an average of 0.959 and standard deviation of 0.163. The distribution for the along maps, shown in Figure B.30c, has an average of 0.887 and standard deviation of 0.131. These distributions are a measure of the tunneling asymmetry – the ratio of the ease of extracting electrons to the ease of injecting electrons.

One of the most interesting aspects of this exercise is the map of $\langle R(x, y, V_{s1}, V_{s2}) \rangle_V$. An example is shown in Figure B.31a. This figure compiles several different ways to visualize the spatial variation of the tunneling asymmetry. In Figure B.31a, we show

$$\langle R(x, y, -100 \text{ mV}, +100 \text{ mV}) \rangle_V = \frac{\int_{0}^{e(+100 \text{ mV})} DOS(x, y, E)dE}{\int_{e(-100 \text{ mV})}^{0} DOS(x, y, E)dE}$$

(B.5)

Note that both maps were taken with a tunneling current setpoint of 100 pA. In Figure B.31c we show the $0 \text{ mV} = E_F$ layer of the $dI/dV$ map taken bias setup condition of $-100 \text{ mV}$, or

$$\frac{e(-100 \text{ mV})}{\int_{e(-100 \text{ mV})}^{0} DOS(x, y, E)dE} DOS(x, y, 0)$$

(B.6)

In Figure B.31d we show the $0 \text{ mV} = E_F$ layer of the $dI/dV$ map taken bias setup condition of $+100 \text{ mV}$, or
Figure B.31: (next page) Different ways to visualize the spatial variation of the tunneling asymmetry. All images are from the diag triple map. a) Energy-wise averaged ratio of the two $dI/dV$ maps, $\langle R(x, y, -100 \text{ meV}, +100 \text{ meV}) \rangle_V$. b) The ratio of the two simultaneous topographies taken with different bias setup conditions, $z_{+100\text{ mV}}/z_{-100\text{ mV}}$. c) The 0 $\text{meV}$ layer of the $-100 \text{ mV}$ bias map. d) The 0 $\text{meV}$ layer of the $+100 \text{ mV}$ bias map. e) The simultaneous topography of the $-100 \text{ mV}$ bias map. f) The simultaneous topography of the $+100 \text{ mV}$ bias map. A colorbar is not included for b) because it is produced by dividing two objects whose offset from zero is unknown, so the actual numbers are not physically meaningful.
\[
\frac{e^{(+100 \text{ mV})}}{\int_0^{e^{(+100 \text{ mV})}} DOS(x, y, E) \, dE} DOS(x, y, 0)
\] (B.7)

Figure B.31a is the (noise-reduced by energy-averaging) ratio of Figure B.31c over Figure B.31d. In Figure B.31e we show the simultaneous topography of the \(dI/dV\) map taken with bias setup condition of \(-100 \text{ mV}\), or

\[
z_{\text{topo}}(x, y, -100 \text{ mV}) = -\frac{1}{2\kappa(x, y)} \ln \left[ \frac{100 \text{ pA}}{\int_{e^{(-100 \text{ mV})}}^0 DOS(x, y, E) \, dE} \right]
\] (B.8)

In Figure B.31f we show the simultaneous topography of the \(dI/dV\) map taken with bias setup condition of \(+100 \text{ mV}\), or

\[
z_{\text{topo}}(x, y, +100 \text{ mV}) = -\frac{1}{2\kappa(x, y)} \ln \left[ \frac{100 \text{ pA}}{\int_{e^{(+100 \text{ mV})}}^0 DOS(x, y, E) \, dE} \right]
\] (B.9)

In Figure B.31b, we show the ratio of the two topographies, or

\[
\ln \left[ \frac{100 \text{ pA}}{\int_{e^{(-100 \text{ mV})}}^0 DOS(x, y, E) \, dE} \right] \div \ln \left[ \frac{100 \text{ pA}}{\int_{e^{(+100 \text{ mV})}}^0 DOS(x, y, E) \, dE} \right]
\] (B.10)

It is striking how while (a) is equal to the ratio of the integrated DOS, as derived from the tunneling Equation 1.8, and (b) is the ratio of the natural log of the tunneling current, arrived at from ratios of entirely different experimentally acquired signals, maps of the two quantities look remarkably similar.

In summary, we find that as we expect, to the limits of our signal-to-noise, the ratio of \(dI/dV_1\) to \(dI/dV_2\) is a constant, independent of energy. We show the spatial variation of the ratio, a map of the tunneling asymmetry.
Appendix C

Timing Parameters of Spectroscopic Measurements

This appendix contains a detailed description of the procedure and adjustable timing parameters for taking point spectra and spectroscopic maps, using the Nanonis controller with software version 2678. It was written in collaboration with Michael Yee and with assistance from George Lengel.

C.1 Point $I(V)$ and $dI/dV$ Spectrum

Using the lock-in technique, $I(V)$ and $dI/dV$ spectra are recorded simultaneously into different software channels with the same timing parameters. For each spectrum, the number of points of the spectrum, `numpoints`, and the bias voltage range, from $V_{start}$ to $V_{end}$, is chosen. The bias voltage range is almost always chosen to be symmetric about the Fermi energy with an odd number of points so as to
capture the Fermi energy as well. The bias voltage $V$ is stepped through the array $V_i = V_{\text{start}} + (V_{\text{end}} - V_{\text{start}}) \times i / \text{numpoints}$, pausing at each $V_i$ to integrate over $10 - 30$ lock-in cycles. We use a lock-in modulation frequency of $1115 \text{ Hz}$. The bias modulation amplitude, $V_{\text{AC}}$, varies with the energy resolution of interest, and closely tracks the spacing between adjacent $V_i$. We typically use $0.5 - 3.0 \text{ mV}0 - \text{peak}$.

In Figure C.1 is a schematic description of how the bias voltage is ramped in time throughout a spectrum and the order of different steps. The routine is described in the list below, and typical values for timing parameters are given in Table C.1

1. Begin with the lock-in amplifier turned on, modulating $V$ with $V_{\text{AC}}$ and demod-
Appendix C: Timing Parameters of Spectroscopic Measurements

ulating $I(V)$, and recording both $I(V)$ and $dI/dV$ in separate channels.

2. Hold the tip in feedback, defined by $I_s$ and $V_s$, at a set $(x, y)$ location. Average $z$ for $z$ averaging time and call that value $z_0$.

3. Set $z = z_0$ and disengage feedback (Z-controller hold mode). Record this value $z_0$ as the height at which the spectrum is taken.

4. Ramp $V$ from $V_s$ to $V_{start}$, the first point of the spectrum, with the ramp speed set by maximum slew rate. Frequently, but not always, $V_s = V_{start}$.

5. Wait at $V_{start}$ for initial settling time.

6. For each point in the spectrum, $i$,

   (a) Ramp the bias voltage to $V_i$, with the ramp speed set by maximum slew rate. (Note that for first point only, this step is skipped because already $V = V_{start}$.)

   (b) Wait settling time.

   (c) Integrate the $I(V)$ and $dI/dV$ channels for integration time and record these values.

7. Ramp $V$ from $V_{end}$ to $V_s$, with the ramp speed set by maximum slew rate.

8. Wait for end settling time with the feedback off.

9. Re-engage the feedback and stabilize at the same $(x, y)$ location for $z$ control time. This $z$ is labeled as $z^*$. 
Appendix C: Timing Parameters of Spectroscopic Measurements

Table C.1: Typical Timing Parameters of $I(V)$ and $dI/dV$ Measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>initializing – z averaging time ($ms$)</td>
<td>50</td>
</tr>
<tr>
<td>initializing – initial settling time ($ms$)</td>
<td>10</td>
</tr>
<tr>
<td>sweep – settling time ($ms$)</td>
<td>2</td>
</tr>
<tr>
<td>sweep – integration time ($ms$)</td>
<td>10-35</td>
</tr>
<tr>
<td>sweep – maximum slew rate ($V/s$)</td>
<td>Inf</td>
</tr>
<tr>
<td>end – settling time ($ms$)</td>
<td>10</td>
</tr>
<tr>
<td>end – z control time ($ms$)</td>
<td>10</td>
</tr>
<tr>
<td>bias modulation frequency ($Hz$)</td>
<td>1115</td>
</tr>
</tbody>
</table>

The maximum slew rate controls the speed at which the bias is ramped. We typically leave it set to Inf, which means that it slews as quickly as the hardware is able to. The DACs are 200 kHz so their update rate is $5 \mu s$, but they can update by any arbitrary voltage, not just one least significant bit. Regardless of the update rate, the bias passes through a 2 kHz low pass filter so the actual bias slew rate is not faster then that.

The total time for a single point spectrum is given by $z$ averaging time + initial settling time + (numpoints)($settling \text{ } time + integration \text{ } time$) + end settling time + $z$ control time + slew rate($V_s \rightarrow V_{start} + V_{start} \rightarrow V_{end} + V_{end} \rightarrow V_s$). In practice the slew rate is not deterministic or well-defined, so there will be some small uncertainty to the total amount of time that a spectrum will take.

### C.2 Point $I(z)$ Spectrum

An $I(z)$ point spectrum is taken with exactly the same sequence of events, but with the key difference that $z$ is ramped rather than $V$ and only $I$ is recorded. Typical timing parameters for an $I(z)$ spectrum are given in Table C.2. Far less integration
Table C.2: Typical Timing Parameters of $I(z)$ Measurements

<table>
<thead>
<tr>
<th>Timing Parameter</th>
<th>Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initializing – $z$ averaging time</td>
<td>50</td>
</tr>
<tr>
<td>initializing – initial settling time</td>
<td>10</td>
</tr>
<tr>
<td>sweep – settling time</td>
<td>2.5</td>
</tr>
<tr>
<td>sweep – integration time</td>
<td>3</td>
</tr>
<tr>
<td>end – settling time</td>
<td>5</td>
</tr>
<tr>
<td>end – $z$ control time</td>
<td>200</td>
</tr>
</tbody>
</table>

time at each point is required, since the signal of interest is $I$ rather than $dI/dV$, but far longer end settling time is required. The scantube is ramped through a range of $z$ during the spectrum and needs sufficient time to relax back into $z_0$.

### C.3 Grid Spectroscopy, Single Map

A grid of points can be defined and at each point a single spectrum ($dI/dV$, $I(z)$, or any arbitrary type, using Nanonis Generic Sweep) taken, building up a three-dimensional dataset. The timing parameters for each individual point spectrum are identical to the list enumerated in Section C.1. Note that the height $z_0(x, y)$ at which the spectrum is taken is recorded as a single pixel in the simultaneous topograph (in the parameters section of the .3ds) that accompanies each spectral map. If ‘record scan channels’ is selected, then the $z$ during the $z$ control time, $z^*$, can also be recorded as a post-spectrum simultaneous topograph.

The timing sequence for grid spectroscopy is as follows:

1. The tip is moved to the lower left corner of the defined grid.

2. For each point in a row,
(a) Wait for a pre-measure delay time (currently set to 10 ms). This is a Nanonis built-in parameter that is controlled in the Experiments on a Grid tab.

(b) A point spectrum is taken using the sequence of events described in the enumerated list in Section C.1.

(c) The tip is moved one step to the right at scan speed on the defined grid of \((x,y)\) locations (this direction is defined as the fast scan direction, sometimes referred to as \(x\)).

3. At the end of the row, the tip is moved back to the left-most \((x,y)\) point on the next row up at scan speed (this is defined as the slow scan direction, sometimes referred to as \(y\)).

This process is performed by a module written by Nanonis. Adjustable parameters are the grid size, location, angle, number of points, scan speed, pre-measure delay, and all of the setup condition, timing, and lock-in amplifier parameters discussed in Section C.1.

## C.4 Grid Spectroscopy, Multi Maps

Using the Nanonis Programming Interface, a module which takes multiple interleaved spectral surveys was written by Michael Yee in May of 2011. Many of the maps discussed in this dissertation take advantage of this capability. In a multi map, in contrast to the procedure described above, at each point on the defined grid, \(n\) spectra of any kind are taken. Prior to each spectrum, feedback is re-engaged. The
tunneling setup condition that is enforced prior to each spectrum at a given pixel need not be the same.

The grid is defined the same way as it is for a single map: the start point is the lower left corner and the grid is completed row-wise. At each point in the defined grid, the timing sequence for a multi map is described in the list below. The subscript \( j \) is used to refer to the index of the spectrum with \( j = 1 \) to \( n \). The subscript \( j = 0 \) is used to refer to the setup conditions while traveling between grid points.

1. Move the tip in feedback, defined by \( I_{s,0} \) and \( V_{s,0} \), to a grid point at a set \((x,y)\) location.

2. Repeat the following \( n \) times, where \( n \) is the number of interleaved maps.

   (a) Execute **Set Feedback Condition VI**:

      i. Average \( z \) in feedback, defined by \( I_{s,j-1} \) and \( V_{s,j-1} \), for a user-settable time *switch off delay time* (5 ms).

      ii. Disengage \( z \)-controller feedback.

      iii. The Nanonis computer queries Nanonis RC4 controller whether feedback has been disengaged, repeating every 5 ms until the RC4 returns off. This process happens as fast as possible but does lead to an unavoidably non-deterministic settling time at each point.

      iv. Change bias and current setpoints to \( I_{s,j} \) and \( V_{s,j} \).

      v. Wait with feedback disengaged for *settling time before feedback* (2 ms).

      vi. Re-engage \( z \)-controller feedback, with feedback defined by \( I_{s,j} \) and \( V_{s,j} \).

      vii. Wait in feedback for *settling time after feedback* (50 ms).
Appendix C: Timing Parameters of Spectroscopic Measurements

(b) Execute a spectrum as described in Section C.1.

3. If $I_{s,n}$ and $V_{s,n}$ are not equal to $I_{s,0}$ and $V_{s,0}$ then switch to traveling setup condition using **Set Feedback Condition**.

While in theory $n$ can be any arbitrary number, all multi maps collected to date have had $n = 2$ or 3, with one or two $dI/dV$ spectra and one $I(z)$ spectrum, taken in that order. For all multi maps discussed in this dissertation, the setup condition used for the $I(z)$ spectrum is the same as $I_{s,0}$ and $V_{s,0}$ so Step 3 is unnecessary. Later maps have used a traveling setup condition with much larger tunneling junction resistance ($10 \, G\Omega$) than the setup condition used for the spectra ($\leq 1 \, G\Omega$).

Initial multi maps were taken while the module was still in a state of development and consequently there is some variation in timing parameters. All multi maps except for the first, the control map, were taken using the procedure and timing parameters enumerated above.

As initially written, and used to take the control map on May 3\textsuperscript{rd}, the multi map module did not switch off z-controller feedback while changing bias and current setpoint. Instabilities in the feedback were observed during the subsequent multi map attempt on May 5\textsuperscript{th}, and the module was modified to switch off the z-controller during setpoint changes and add settling times. The process for the control map used similar timing sequences to those described above except that **Set Feedback Condition** was significantly more basic. Its functionality for the control map is listed below.

1. Average $z$ in feedback for *switch off delay time* (5ms).

2. Change the bias and current setpoints to the desired spectroscopy setpoints.
$V = V_{s,j}$ and $I = I_{s,j}$.

### C.5 Types of Data in a 3ds File

Four classes of data are saved to Nanonis .3ds files: Headers, Parameters, Spectroscopy Channels and Scan Channels.

The Header of a 3ds file contains values that are constant throughout the full spectral survey, such as software version, date and time, spectrum timing parameters, grid size and location, numbers of pixels, setup condition, lock-in parameters, etc. In addition, users may write a subVI which saves other information, such as temperature or magnetic field, to the header. Unlike other classes of data, they are saved as a list at the beginning of the file rather than as a grid. The information that goes into the header is selected from menus in a variety of different windows, such as the Scan Control window, the spectroscopy window, and the lock-in window.

Spectroscopy Channels can be thought of as the real 3d data. Each $(x, y)$ position will have a curve of data (e.g. $I(V)$, $I(z)$, $dI/dV$, etc.). The Spectroscopy Channels that are saved are selected from the menu within the Bias spectroscopy module or Z spectroscopy module. For Bias spectroscopy curves, we normally save “Current (A)” and “LIY (A).” “LIY (A)” is the channel which contains the demodulated Current, or the $dI/dV$ information. For Z spectroscopy curves we typically save “Current (A)” only.

Parameters differ from Spectroscopy Channels in that at each $(x, y)$ position a single value is recorded (e.g. $z$, integration time, etc) instead of a full curve. The most interesting parameter is $z$, which when plotted on the grid, $z(x, y)$, is the simultaneous
topography of the grid spectroscopy measurement. Parameters are automatically saved when Nanonis writes a .3ds file and cannot be selected by the user.

On the other hand, unlike Parameters, Scan Channels allow the user to select additional data (still one value per \((x,y)\) position) that is not automatically saved within the parameters. STM1 does not presently have a need for Scan Channel data. To enable the recording of Scan Channels, in the Scan tab of the ‘Scan Control’ module, select the channels of interest under the ‘Data Acquisition’ tab, then in the ‘Grid’ tab enable the ‘Save scan channels’ checkbox.
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