ORDERING AND SUPERCONDUCTIVITY: 
SCANNING TUNNELING SPECTROSCOPY OF 
UNCONVENTIONAL SUPERCONDUCTORS

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Abstract

In this thesis I present scanning tunneling microscopy (STM) studies that probe the interplay between ordering phenomena and superconductivity in two classes of materials: heavy fermions (CeCoIn$_5$ and URu$_2$Si$_2$) and cuprates (Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212)). In CeCoIn$_5$, these measurements detect the emergence of heavy quasiparticles with lowering of temperature, as well as their composite nature. Interference of these quasiparticles allow their energy-momentum structure to be resolved as a function of temperature. Analysis of the tunneling spectra reveal signatures of energy-temperature scaling associated with a quantum critical point. In URu$_2$Si$_2$, spatially resolved spectroscopy is used to examine the electronic states that emerge from the uranium $f$-states. As the temperature is lowered, the spectrum develops into a Fano resonance which characterizes the onset of heavy-fermion coherence below $\approx 120$ K. At $T = 17.5$ K, URu$_2$Si$_2$ is known to undergo a second-order phase transition into a phase with a hidden order parameter. Tunneling spectroscopy identifies a bias-asymmetric energy gap with a mean-field temperature dependence that develops in the hidden order state. In Bi-2212, combined STM and resonant elastic x-ray scattering (REXS) measurements are used to establish the formation of charge ordering. Depending on the hole concentration, the ordering in Bi-2212 occurs with the same period as those found in Y-based or La-based cuprates. This charge ordering also displays the analogous competition with superconductivity found in the other compounds. Together these results indicate the universality of charge organization competing with superconductivity across different families of cuprates. Finally, investigations of the influence of anisotropic tip structures on STM conductance maps establish, with a model calculation, the presence of a tunneling interference effect within an STM junction that induces an artificial nematic signal. This effect is experimentally confirmed on different correlated electron systems, including Bi-2212, and is shown to be a sensitive probe of changes in the band structure of the sample.
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\textsuperscript{1}Occasionally the seed was planted by considering alternative life paths. Such was the case when observing the “knitting man” or the “man in the tiger costume”. 

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Chapter 1

Introduction

The discovery of superconductivity by Heike Kamerlingh Onnes in 1911 has now already surpassed 100 years. Still, it took almost half a century before the development of a microscopic theory which not only correctly described the already known phenomena but whose predictions could be verified. This microscopic description takes the name BCS theory after Bardeen, Cooper and Schriefer [1] who received the Nobel prize in 1972 for their work. Indeed, superconductivity in conventional metals is well understood in terms of the ideas provided by BCS.

In 1979, superconductivity was discovered in the compound CeCu$_2$Si$_2$ [2] below 0.5 K. It was soon followed by the discovery of superconductivity in other materials which contained actinide or rare-earth elements [3]. For reason discussed below, these materials are known as heavy-fermions (see section 1.1) and they are characterized by the presence of magnetic 4$f$ and 5$f$ ions. In conventional superconductors, which are accurately described by BCS theory, magnetic impurities are detrimental to superconductivity. Therefore, at first glance, the presence of magnetic ions should have made heavy-fermion superconductivity impossible. But by 1987, an observation that had been on the minds of some researchers is that heavy-fermion superconductivity occurs in compounds that are very close to becoming antiferromagnetic [4].

Around that time efforts in understanding heavy-fermion superconductivity were shifted to a new puzzle when, in 1986, Bednorz and Müller [5] discovered supercon-
ductivity in layered copper oxides. Superconductivity in these materials is obtained by doping charge carriers into a transition-metal oxide which is antiferromagnetic in nature. Again, based on the understanding provided by BCS theory, it was quite surprising to find out that very poor conductors of electricity (ceramics) allowed a dramatic enhancement of the transition temperature ($T_c$). Indeed the highest transition temperatures up to 1986 were around 25 K, but by 1993 $T_c$ in the cuprates had reached 135 K at ambient pressure. Needless to say, this increase in $T_c$ above liquid nitrogen temperatures has sparked technological dreams associated with the possibility of a room-temperature superconductor.

More broadly, we can classify heavy fermions and cuprates as unconventional superconductors: materials that display the macroscopic properties of superconductivity such as zero electrical resistance and the expulsion of magnetic fields, but whose mechanism is not explained by the usual BCS formalism. As already suggested above, one of the many aspects that have puzzled scientists over the decades is that superconductivity in these materials develops in proximity to ground states which are related to magnetism. These nearby ground states are usually characterized by some kind of ordering phenomena ranging from antiferromagnetism to more exotic types such as unidirectional periodic patterns of spins and charge, known as stripes. At a basic level, it is important to know the relevance of these orders to superconductivity. Therefore, key to understanding the superconducting phenomenon in these materials is the correct identification of coexisting orders, their microscopic nature, and whether they are in competition with superconductivity. Following this logic, it is crucial to determine what ordering phenomena are unique to specific materials and which are universal to unconventional superconductors.

My doctoral thesis work is based on the investigation of electronic ordering phenomena in unconventional superconductors using spectroscopic imaging with the scanning tunneling microscope (SI-STM). In the hope of separating material-specific effects from phenomena common to different materials, my work has been focused on two different classes of unconventional superconductors: heavy-fermion systems
(URu$_2$Si$_2$, and the 115 family of Ce-based materials, e.g. CeCoIn$_5$) and the high-temperature superconducting cuprates, primarily Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212).

In the remainder of this chapter I will provide a brief overview of the physics specific to heavy fermions and cuprates. This is not aimed to be a comprehensive introduction but rather a focused discussion to, not only prepare the reader for the material described in subsequent chapters, but also to point out the similarities between the two classes of materials. I will conclude the chapter with a summary of the results presented in this thesis. Additionally, in chapter 2 I will make a brief description of the STM technique, and explain the types of measurements that were performed to obtain the data which served as the source for the discussion in chapters 3 through 6.

1.1 Heavy-fermion Materials

One of the most important goals of modern condensed matter physics is to understand the role of the coupling between magnetic and electronic degrees of freedom in correlated electron systems, and more specifically in unconventional superconductors. Examples of materials in which such a coupling is thought to be a key ingredient to their novel states include high-temperature cuprate superconductors in which hole doping of the magnetic Mott insulator state leads to superconductivity. Heavy-fermion materials, whose name was coined to describe electronic excitations corresponding to an effective electronic mass ($m^*$) as high as 1000 times the mass of the bare electron ($m_e$), offer an alternative route to understand the importance of magnetic order to unconventional superconductors. At low temperatures, heavy-fermions display a wide range of quantum phases such as superconductivity and antiferromagnetism, as well as the formation, at higher temperatures, of a magnetic state known as the Kondo lattice from which these phases emerge. Heavy-fermion materials contain rare-earth or actinide ions, forming a lattice of magnetic moments due to the localization of $f$-electron spins. Therefore the relevant physical behavior results
from the presence of these magnetic ions immersed in the Fermi sea of conduction electrons. The mechanism by which the coupling between the spin degrees of freedom of the localized $f$-electrons and the conduction electrons takes place is analogous to the Kondo effect [6].

Experimentally, the Kondo effect is observed on dilute alloys of magnetic ions. At high temperatures the ions behave as free paramagnetic moments exhibiting Curie-Weiss behavior. But at low temperatures the conduction electrons interact with the magnetic impurity, effectively screening the local magnetic moment (see Fig. 1.1(a)).\(^1\) This transition happens continuously and the characteristic temperature scale is known as the Kondo temperature. This screening manifests itself in dramatic ways. The most well known is the logarithmic increase of the resistivity at low temperatures. This happens due to the strong enhancement of the electron scattering cross-section. Kondo [6] found a new term on the expansion of the resistivity proportional to $J \ln(T)$, where $J$ is the exchange between the local magnetic moment and the conduction electrons. This is a surprising result since this effect in the resistivity occurs even in the very dilute limit where the impurity density can be of the order of one part per million.

Heavy-fermions display an analog of the dilute limit Kondo effect, but in the very dense limit instead. In a simplified scenario one could perceive the Kondo lattice as a matrix of magnetic impurities each susceptible to their own Kondo effect (see Fig. 1.1(b)). Now we are in position to understand where the name of these materials comes from, for the Kondo lattice effect can be thought of as the process by which these otherwise localized $f$-electron spins become mobile and form electronic excitations carrying an effective mass orders of magnitude larger than in normal metals, such as copper. In the single Kondo problem, the presence of the magnetic impurity creates discrete energy levels which lead to a resonance in the density of states of

\(^1\)The widely disseminated cartoon picture of a Kondo cloud, depicted as free conduction electrons in a blob around a spin (see Fig. 1.1(a)) is dangerously inaccurate. In fact, the correlation length of this interaction can be on the order of hundreds of lattice constants.
Figure 1.1: Schematics of the Kondo effect (a) and Kondo lattice (b). (c) Heavy fermion band structure, characterized by the hybridization between the conduction band (green) and renormalized heavy band (red).

the conduction electrons. But in the Kondo lattice we expect to have one resonance created in each lattice site. Bloch’s theorem guarantees that the scattering between these resonances results in the formation of a highly renormalized band of width $T_K \sim D e^{-\frac{1}{2\pi\rho J}}$, where $D$ is the unrenormalized band width, $J$ represents the strength of the Kondo coupling, and $\rho$ is the conduction electron density of states at the Fermi energy. In terms of the band-structure, one expects the formation of a heavy band near the Fermi energy due to coherent scattering of this matrix of resonances. This heavy band can, in principle, hybridize (mix) with the pre-existing light band (the one responsible for the conduction prior to the formation of the Kondo lattice) and consequently form a hybridized band structure (see Fig. 1.1(c)). Despite its acceptance, direct spectroscopic measurements of the formation of this hybridized band structure with lowering of temperature had not been achieved. In chapter 3 I will describe STM experiments that directly visualize this process of heavy-fermion Kondo lattice formation.

However, the Kondo lattice is not the only stable ground state accessible to heavy-fermion systems. The interaction that develops between the conduction electrons and the localized moments can lead to different ground states. In the dense limit this interaction can lead to a Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect antifer-
Temperature exchange between the local moments. At low temperatures the RKKY interaction gives rise to an ordered antiferromagnetic state, characterized by an energy scale (or Néel temperature) $T_N \sim J^2 \rho$.

The presence of two energy scales in the problem naturally leads to a competition between ground states. For small $J \rho$, $T_N \gg T_K$ and the system evolves into an antiferromagnet at low temperatures. For large $J \rho$ the inequality is reversed and the system achieves a heavy Fermi liquid ground state. The resulting phase diagram proposed by Doniach [7] is shown in Fig. 1.2, where a zero-temperature second-order phase transition occurs at a critical value $J \rho_c$, therefore characterizing a quantum critical point (QCP).

In heavy fermions, a QCP can be achieved by a non-thermal control parameter, such as chemical doping, magnetic field, or pressure. At finite temperatures above the QCP (see Fig. 1.3) the system is in a state of fluctuations between the competing ground states. Remarkably, it is in this quantum critical region that the
emergence of superconductivity is observed in heavy-fermion materials [3], suggesting that antiferromagnetic quantum criticality can provide a mechanism for superconductivity in these materials. This puts heavy-fermion systems in direct analogy to high-temperature superconductors, where spin fluctuations have played a central role in trying to understand the pairing mechanism.

1.2 Copper-based High-temperature Superconductors

High-temperature superconductors, are more than simply high-temperature analogues of conventional BCS superconductors. The parent compounds of the cuprates are layered metal oxides, where superconductivity occurs by doping of the CuO$_2$ planes, as depicted in the phase diagram for hole-doped cuprates (see Fig. 1.4). On
one extreme, the undoped cuprates are Mott insulators, where electrons subject to a local strong Coulomb repulsion have a tendency to localize and adopt an antiferromagnetic spin configuration. Notice that the physical origin of antiferromagnetism in the cuprates is different than in heavy fermions where the moments are formed due to the localized $f$-orbitals. Nevertheless, in both materials the antiferromagnetic ground state can be destabilized toward a superconducting one by a tuning parameter (chemical doping in Fig. 1.4). In the cuprates as doping is increased, $T_c$ first increases and then decreases, forming a dome of superconductivity. On the underdoped regime (low doping part of the dome), superconductivity emerges from an exotic “normal” state characterized by the mysterious pseudogap phenomenon [12]. This *pseudo* gap in the excitation spectrum encompasses a large portion of the phase diagram, and onsets at relatively high temperatures (see Fig. 1.4).

Though an appropriate theory that explains this phenomenon is still lacking, experiments have shown that the pseudogap fosters a variety of phenomena such as stripe order, charge density wave, superconducting fluctuations and antiferromagnetic
fluctuations [10,11,13–16]. Taken at face value these experiments would suggest that a complete theory of high-$T_c$ superconductivity must incorporate all these ingredients. However, these experimental evidences come from a variety of different materials and techniques. This disparity is not the result of poor decision making by researchers, but is rather due to the fact that specific experimental techniques couple more favorably to specific materials. For example, whereas quantum oscillation experiments require a high carrier-mobility and have so far only been detected in Y-based cuprates, surface sensitive techniques such as STM and angle-resolved photoemission spectroscopy (ARPES) require a non-polar cleaving plane, making Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ the sample of choice for those measurements. Therefore, one of the current challenges in the field of high-temperature superconductivity is to find experimental connections between different materials or different techniques.

Nevertheless, some aspects of cuprate phenomenology are agreed upon. Firstly, the phase diagram for the hole-doped cuprates discussed above seems to be universal to all classes of cuprates. Second, from a band structure perspective, there is a consensus on the basic topology of the Fermi surface. Since the charge carriers are confined to the CuO$_2$ planes, the Fermi surface of the cuprates can be represented by
Figure 1.6: Schematic layout of the Fermi surface in Bi-2212 UD75 sample, consistent with ARPES measurements [18]. The green and white segments represent the Fermi arc as determined by ARPES below and above $T_c$, respectively [19].

a two-dimensional slice of reciprocal space. ARPES experiments on Bi-based cuprates confirm the basic high-temperature topology displayed in Fig. 1.5 [17]. From this high-temperature Fermi surface the pseudogap and the superconducting gap emerge. In underdoped cuprates, the pseudogap appears in the anti-nodal region, leaving behind a Fermi surface above $T_c$ characterized by finite arcs (see white region in Fig. 1.6). It is on top of these arcs that superconductivity appears below $T_c$ in the form of a d-wave gap which is anisotropic in momentum space, starting from zero at the nodes, increasing as we move away from the nodes, and deviating from its characteristic functional form as it reaches the anti-nodal pseudogap region. Defining the finite arc-length where this deviation happens, we obtain the green region in Fig. 1.6.

Regardless of details, this basic Fermi surface phenomenology provides a way to connect ordering phenomena to either superconductivity or to the pseudogap. Periodic ordering in real space can be characterized in momentum space by a wavevector $\vec{Q}$. In terms of the quantum states $\vec{k}$ of the system on the Fermi surface, the ordering is expected to mix $\vec{k}_1$ and $\vec{k}_2$ states that are separated by $\vec{k}_2 - \vec{k}_1 = \vec{Q}$. Therefore, by identifying the regions on the Fermi surface that are connected by $\vec{Q}$, it is possi-
ble to establish the relationship of this order to either the pseudogap (if it connects anti-nodal regions) or to superconductivity (if it connects regions on the Fermi-arc).

1.3 Summary of Results

Below I give a summary of the results presented in this thesis. Chapters 3, 4 and 6, in slightly modified form, have been published in peer reviewed journals: references [20], [21], and [22] respectively. These works have also been presented publicly at scholarly conferences and meetings. A list of these presentations can be seen in appendix E.

Chapter 3 describes SI-STM measurements on the prototypical heavy-fermion CeCoIn$_5$ that provide us with a way to visualize how these low-energy quasiparticles develop their heavy mass by resolving their energy-momentum structure as a function of temperature and chemical composition. This allowed for a detailed analysis of the lifetime of the emergent heavy excitations showing that the high temperature state from which superconductivity emerges at $T_c = 2.3\text{K}$ is indeed characterized by quantum fluctuations [20]. As it will be presented in chapter 4, the situation is drastically different in URu$_2$Si$_2$ ($T_c = 1.5\text{K}$). Our high-temperature spectroscopic measurements confirm that whereas URu$_2$Si$_2$, much like CeCoIn$_5$, is a Kondo lattice, their corresponding precursor states (from which superconductivity emerges at low temperatures) are peculiarly different. While in CeCoIn$_5$ superconductivity emerges from a state of quantum fluctuations between antiferromagnetic and heavy Fermi liquid ground states, URu$_2$Si$_2$ undergoes a phase transition into a hidden order state ($T_c < T_{HO} = 17.5\text{K}$). Our results further showed that this transition is characterized by the appearance of an energy gap with mean-field temperature dependence below $T_{HO}$ [21]. Though the first step of characterizing the precursor states has been achieved, the link between fluctuations and hidden order is still missing, in part because the order parameter for the hidden order state has yet to be identified. How-
ever, the connection between these different precursor states and superconductivity at sub-Kelvin temperatures remains an ongoing effort in the field.²

The situation is even more complicated for the cuprates where there has been an escalating amount of evidence for ordering phenomena coming from different probes and materials, and which are apparently dissimilar amongst themselves. Bulk measurements coming from thermoelectric transport [24], Hall resistance [25], and quantum oscillations [26] on YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) point to Fermi surface reconstruction and electronic ordering. Additionally, scattering experiments have detected stripe order in La-based compounds [13], and charge density wave order (CDW) in YBCO [15, 16] (neutron scattering and x-ray scattering, respectively). Simultaneous to those discoveries there has been an increasing amount of evidence for a propensity toward charge ordering in the pseudogap phase coming from surface sensitive techniques such as ARPES [27] and STM [28], though these were obtained in yet another family of cuprate materials, the Bi-based compounds. Hence the link between these different findings remains a matter of debate.

If the propensity for CDW formation or other unconventional instabilities such as stripe formation or electronic nematic ordering is a universal property of high-temperature superconductors, then the connection between different materials and experimental techniques needs to be settled. Only once the universality of a particular order is determined can we further investigate its relation to superconductivity. Recently we performed a comprehensive doping- and temperature-dependent study that revealed a correlation between the onset of the pseudogap phase and incipient order in Bi-2212 [29]. Regarding the energy dependence of this ordering, precise modeling of its energy-momentum structure showed how to disentangle it from local scattering effects, and confirmed its incipient nature near optimally doped samples [30, 31]. However, at that point we were only able to indirectly detect the presence of charge ordering from the STM data. In the last two years the primary focus of my research

²Recently we have performed STM experiments at mili-Kelvin temperatures and high magnetic fields, that probe the superconducting order parameter in CeCoIn$_5$ [23]. Those results will not be presented in this thesis.
has been to correctly characterize the charge ordering detected by STM. Chapter 5 describes our most recent efforts to directly visualize the charge ordering in Bi-2212. Higher spatial resolution measurements more precisely identify the period of these modulations and over what energy range they occur in underdoped samples. These new measurements suggest a connection of the charge ordering observed in STM with the stripe ordering in La-based cuprates, and the recent experiments in YBCO. Additionally, we have performed resonant elastic x-ray measurements (REXS)\(^3\) that allow us to show for the first time that the charge modulations detected on the surface of Bi-2212 are also present in the bulk. Altogether the studies presented in chapter 5 establish that a charge ordering in competition with superconductivity is a universal property of cuprate high-temperature superconductors.

In parallel to so many experimental results, several theoretical ideas have also been proposed to inhabit the underdoped region of the cuprate phase diagram. One proposal that has recently gained vast interest in the field of high-temperature superconductivity describes a ground state where the ordinary four-fold electronic symmetry of the system (imposed by the crystal structure) is broken in favor of a two-fold symmetric state. This state of broken symmetries is usually referred to as an electronic nematic\(^4\) state when it is not accompanied by translational symmetry breaking [32]. Recently, an STM study reported the presence of an electronic nematic state in the pseudogap of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\). The interpretation of the STM data in [33] provided a specific approach to detect nematic order in other materials with the STM. Following their results we performed similar measurements on the three materials which are the focus of this thesis CeCoIn\(_5\), URu\(_2\)Si\(_2\), Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\), where the first served as a control experiment since no claims of nematic order had ever been associated to it. Unfortunately, our measurements find similar “nematic” signals in all samples, and show that the signatures of rotational symmetry breaking in the STM previously as-

\(^3\)In collaboration with the group of Prof. Bernhard Keimer at the Max Planck Institute for Solid State Research in Germany, and with the group of Prof. Andrea Damascelli at the University of British Columbia

\(^4\)Borrowing the name from liquid crystal theory.
associated to nematic order are the result of a tip-induced quantum interference effect. As explained in chapter 6 the presence of this effect is associated with an anisotropic tip probe, rather than nematic states in the material. Nevertheless, this effect displays an energy dependence associated with the underlying quantum states of the material [22]. Hopefully, this newly discovered quantum interference effect within an STM tunneling junction will provide a novel way to probe the band structure of solids.
Chapter 2

Brief Introduction to STM

The scanning tunneling microscope was invented by Binnig and Rohrer in 1982 [34], and for their invention they were awarded the Nobel prize in 1986. As the name suggests, the basic principle behind this technique is the phenomenon of quantum tunneling through vacuum. STM has become one of the most prominent techniques in the study of correlated electron systems, in particular due its success in the study of the high-temperature superconductors [35]. Not only it is a real-space probe, capable of sub-lattice resolution or single atom spectroscopy [36], recently it has also been pioneered as an indirect probe of momentum space (Fourier-transform space) [37].

In its most basic conceptualization the STM consists of a sharp metallic tip, ideally consisting of a single atom at its end, brought to close proximity (within a fraction of a nanometer) of a sample. The wavefunction of the electrons on the sample overlaps with the wavefunction of the electrons on the tip, therefore allowing the possibility for electrons to tunnel between the sample and the tip. Upon the application of a bias voltage to the sample, a tunneling current is established and measured. As a function of tip-sample separation the tunneling current is expected to decay exponentially in the length scale of a few Angströms. A current amplifier is used to convert the tunneling current to a voltage. This converted voltage is used through a feedback circuit which adjusts the tip position in the z-direction in order to maintain a constant current condition. In other words, this negative feedback circuit maintains a constant
tunneling current (predetermined by the user) by adjusting the distance between the
tip and the surface. The tip can then be moved in the $x$- and $y$-directions to scan the
desired area. During the scan, the height of the piezoelectric tube is recorded and
a two-dimensional topography of the surface is produced. This mode of operation is
schematically depicted in Fig. 2.1, and examples of such topographic measurements
are shown in Fig. 2.2

Though the topographic mode of measurement has been shown to provide struc-
tural information about the surface of the sample, as we will see below, the tunneling
current also contains information about the electronic density of states of the material.
Therefore the STM provides the unique ability to measure the local density of states
with sub-atomic resolution, and to correlate these measurements with simultaneously
acquired structural information.

2.1 Basic Theory of the STM Measurement

We can make the tunneling process more precise. By considering the tunneling
between two locations (A and B) separated by an insulating barrier, and taking into
Figure 2.2: (a) STM topographic image (540 × 400 Å²) of Bi₂Sr₂CaCu₂O₈₊δ acquired at −300 mV bias and 200 pA current, and showing a square lattice along the diagonal, together with a unidirectional structural distortion along the orthorhombic b-axis. (b) STM topographic image (33 × 33 Å²) of U-lattice of URu₂Si₂ acquired at +200 mV bias and 60 pA current. (c) STM topographic image (1000 × 1000 Å²) of the Ru-exposed surface of URu₂Si₂ acquired at +100 mV bias and 200 pA current. Inset shows a blow-up of the region in the black square.
account the transition rate from A to B and the reverse process, an expression for the tunneling current at non-zero temperature can be obtained [38,39]:

\[
I = \frac{2\pi e}{\hbar} \int_{-\infty}^{+\infty} \left[ f(E_F - eV + \epsilon) - f(E_t + eV) \right] \rho_A(E_F - eV + \epsilon) \rho_B(E_F + \epsilon) |M|^2 d\epsilon. \tag{2.1.1}
\]

Here \(V\) is a bias energy applied between A and B, \(M\) is the tunneling matrix element between A and B, and \(\rho_A/B\) represents the density of states. The Fermi-Dirac function is \(f(E) = \left(1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]\right)^{-1}\). For \(k_B T\) less than the energy resolution \((E - E_F)\), the Fermi-Dirac distribution can be approximated by a step function. Then the tunneling current is

\[
I = \frac{2\pi e}{\hbar} \int_{0}^{eV} \rho_A(E_F - eV + \epsilon) \rho_B(E_F + \epsilon) |M|^2 d\epsilon. \tag{2.1.2}
\]

Here, note that \(M\) contains information about the interference between the sample and tip (A and B) wave functions. For now, it suffices to use the approximation in which the tip is metallic (\(\rho\) is expected to be constant near \(E_F\)) and isotropic. Following these approximations Tersoff and Hamman [39] were able to show that

\[
\frac{dI}{dV} \propto \rho_A(E_F - eV). \tag{2.1.3}
\]

Consequently, we conclude that \(dI/dV\) is proportional to local density of states of the sample. This is the single most important result to be learned from this section and it is the basis for most of the measurements displayed in later chapter.

As an example, it is instructive to consider tunneling into a conventional BCS superconductor. At high temperatures these materials behave as normal metals. Below \(T_c\) phonons mediate an attractive interaction between electrons of opposite momenta and spins, causing electrons to pair into bosons. This process is called Copper pairing and its result in the electronic excitation spectrum is to remove states below a certain energy from the Fermi energy. This absence of electronic states is represented by a gap in the density of states near the Fermi energy and is beautifully
Figure 2.3: Differential conductance $G (dI/dV)$ as a function of the voltage $V$ between the tip and the sample showing a gap in the density of states of superconducting Al. Red line represents a fit to BCS gap function. Courtesy of Brian Zhou.

captured by tunneling measurements (see Fig. 2.3 for an example of a superconducting gap measured on elemental Al).

Despite its wide use for the interpretation of STM measurements, Eq. 2.1.3 (local proportionality of $dI/dV$ to $\rho$) required several approximations. Specifically, the assumption of an isotropic tip can have dire consequences to the interpretation of STM data in the context of rotational symmetry breaking. In chapter 6 I will present experimental results, together with model calculations, which will show how a realistic (anisotropic) tip can cause an apparent rotational symmetry breaking in STM data. Nevertheless, for the purpose of interpreting most STM results, Eq. 2.1.3 is an appropriate start.

2.2 Spectroscopic Imaging with the STM

Another kind of measurement that can be performed with the STM is spectroscopic imaging. As I will argue below, this measurement can obtain indirect information about the momentum states probed by the STM tip on the surface of the
material. This allows the STM experiments to be compared with angle resolved photoemission spectroscopy (ARPES) and quantum oscillation experiments, the usual techniques used to probe the band structure and Fermi surface of materials, respectively. It also works as a complementary technique, since the STM can measure with high energy-resolution (limited only by the temperature), whereas the best ARPES resolution is restricted to $\approx 3\text{ meV}$ and only energies below $E_F$. Furthermore measurements of quantum oscillations are only sensitive to the Fermi surface and are performed in the presence of magnetic fields, therefore making the connection to zero-field measurements non-trivial.

Mechanically the measurements occur as follows. Sequentially the tip moves to points on a pre-selected grid, where at each position the feedback loop is opened, the tip-sample bias swept and the $dI/dV$ is recorded as a function of voltage. The resulting data is a three-dimensional set $(x, y, \text{and energy } E)$ of the local density of states (LDOS). Modulations of the LDOS can have different physical origins, from long-range spatial structures associated with periodic modulations of the charge, to short-range interference patterns originating from quasiparticles scattering near point defects. Not only this kind of measurement is very challenging from an acquisition point of view, but it is also very difficult to interpret. Figure 2.4 shows an example of the simultaneously acquired conductance map and topography which display very different spatial structures.

Much of this thesis is dedicated to the correct identification of the physical origin of LDOS modulations in STM measurements. At this stage, it is instructive to consider a common interpretation of SI-STM data, the so-called quasiparticle interference effect (QPI). In a completely homogenous system one would expect no spatial variations of the LDOS, or at most that it modulates following the underlying crystalline structure as a result of the discrete translational symmetry of the system. However, the introduction of a few local impurities (allowing the local breaking of symmetry) can result in short-range wave-like patterns. Treating the presence of the
Figure 2.4: Comparison of the $dI/dV$ map ($-70$ mV) and topography simultaneously acquired on the surface of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$. The spatial modulations in the $dI/dV$ map originate from the location of the Hg dopants as determined from the topography.
impurities as a small local perturbation\(^1\), the eigenstates of the unperturbed system remain good quantum states. Of course, in a periodic potential, Bloch’s theorem guarantees that the eigenfunctions can be written as the product of a plane wave \( e^{i\vec{k} \cdot \vec{r}} \) and function \( u_{\vec{k}}(\vec{r}) \) which has the same periodicity as the potential (in our case the lattice). For simplicity, let us consider just two degenerate eigenfunctions \( \psi_1 = e^{i\vec{k}_1 \cdot \vec{r}} \) and \( \psi_2 = e^{i\vec{k}_2 \cdot \vec{r}} \), with distinct wavevectors in reciprocal space, \( \vec{k}_1 \) and \( \vec{k}_2 \) respectively. Here, without loss of generality, I have assumed a common \( u_{\vec{k}}(\vec{r}) \) for both and I have therefore dropped it. The presence of the impurity potential allows an interaction between these two otherwise orthogonal eigenstates, resulting in a mixed state of the form

\[
\psi_1 + \psi_2 = e^{i\vec{k}_1 \cdot \vec{r}} + e^{i\vec{k}_2 \cdot \vec{r}}. \tag{2.2.1}
\]

Then, taking the square modulus of this wave function, we obtain the local density of states around the impurity:

\[
\rho \propto |e^{i\vec{k}_1 \cdot \vec{r}} + e^{i\vec{k}_2 \cdot \vec{r}}|^2 = 2 + \cos(\vec{q} \cdot \vec{r}), \tag{2.2.2}
\]

where \( \vec{q} = \vec{k}_2 - \vec{k}_1 \) represents the momentum transfer. Therefore modulations with periodicity \( 2\pi/|\vec{q}| \) are expected to emerge around impurity defects. An example of this kind of modulation can be seen in Fig. 2.4 for the case of CeCo(\( \text{In}_{0.9985}\text{Hg}_{0.0015} \))\(_5\), where it is clear that the LDOS modulations originate from impurity-induced scattering. Of course the mixing of the eigenstates, or the transition probabilities for the \( \vec{k}_2 \rightarrow \vec{k}_1 \) processes, depend on details of the full microscopic Hamiltonian. Nevertheless, it is expected that the LDOS modulations originating from the QPI effect yield information about the \( \vec{k} \) states of the sample. In a Fermi liquid, with well defined quasiparticles, the \( \vec{k} \) states at a particular energy are determined by the band structure. Therefore, a hallmark of the QPI effect is an energy dependence of the \( \vec{q} \) modulations as a function of \( V \).

\(^1\)Notice this is a very special approximation, where the impurity potential is infinitely localized and infinitely weak. Nevertheless it will suffice for the discussion presented here.
Figure 2.5: Comparison of the $dI/dV$ map (+15 mV) and topography simultaneously acquired on the surface of underdoped Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ ($T_c = 35$ K).

Since ARPES measures the DOS as a function of $\vec{k}$ and $E$, it is expected that the $\vec{q}$ measured by STM connects points of high DOS along the contours of constant energy in $\vec{k}$-space. Not surprisingly, autoconvolution of ARPES data is often used in comparison or support of SI-STM data [40–42]. Additionally, if the observed $\vec{q}$ can be associated with particular bands (with the aid of ARPES or local-density approximation (LDA) calculations), one can use the energy dispersion of the $\vec{q}$’s to calculate the band curvature and therefore its mass. Such results can, of course, be compared to quantum oscillation measurements which can measure $m^*$ very accurately.

Finally, impurity-induced QPI is not the only origin of LDOS modulations in the STM data. Figure 2.5 shows simultaneously acquired topography and conductance map on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. Here the LDOS modulations look more long range than the ones observed in CeCoIn$_5$ (see Fig. 2.4). This is an example of a charge ordering phenomenon, not impurity-induced QPI. However, in a very inhomogeneous and doped system, QPI ripples such as the ones seen in Fig. 2.4 might overlap, and therefore make it hard to distinguish between QPI effects from charge ordering. One way to
distinguish these two phenomena is to look at their energy dependence. Whereas QPI is expected to follow the band structure and therefore be energy-dependent, charge ordering should have a fixed periodicity as a function of energy. In chapter 5 I present STM experiments that help us disentangle these two phenomena. The presence of charge ordering in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ is confirmed by resonant elastic x-ray scattering (REXS), which is an experiment sensitive to charge organization phenomena.
Chapter 3

CeCoIn$_5$

In solids containing elements with $f$-orbitals, the interaction between $f$-electron spins and those of itinerant electrons leads to the development of low-energy fermionic excitations with a heavy effective mass. These excitations are fundamental to the appearance of unconventional superconductivity and non-Fermi liquid behavior observed in actinide- and lanthanide-based compounds. In this chapter I present results where spectroscopic mapping with the scanning tunneling microscope is used to detect the emergence of heavy excitations with lowering of temperature in a prototypical family of Ce-based heavy fermion compounds. We demonstrate the sensitivity of the tunneling process to the composite nature of these heavy quasiparticles, which arises from quantum entanglement of itinerant conduction and $f$-electrons. Scattering-induced interference of the composite quasiparticles is used to resolve their energy-momentum structure and to extract their mass enhancement, which develops with decreasing temperature. Remarkably, the lifetime of the emergent heavy quasiparticles reveals signatures of enhanced scattering and their spectral lineshape shows evidence of energy-temperature scaling. These findings demonstrate that proximity to a quantum critical point results in critical damping of the emergent heavy excitation of our Kondo lattice system. This chapter is based on a paper I coauthored which appeared in Nature in 2012 [20].
A local magnetic moment occurs when a strongly interacting quantum state, such as an atomic $d$- or $f$-orbital, cannot be doubly occupied due to strong on-site Coulomb repulsion [43]. In the presence of a dilute concentration of such magnetic moments in a metal, spin-flip scattering of conduction electrons from these local moments results in their collective magnetic screening below a characteristic temperature called the Kondo temperature $T_K$ (Fig. 3.1(a), also see section 1.1). In materials where local moments are arranged in a dense periodic array, the so-called Kondo lattice, the deconfinement of localized orbitals through their hybridization with the conduction electrons results in composite low-energy excitations with a heavy effective mass (Fig. 3.1(b)). Tuning the hybridization between $f$-orbitals and itinerant electrons can destabilize the heavy Fermi liquid state towards an antiferromagnetically ordered ground state [44–49]. In proximity to such a quantum phase transition, between itinerancy and localization of $f$-electrons, many heavy fermion systems exhibit unconventional superconductivity at low temperatures (Fig. 3.1(c)) [3].

Thermodynamic and transport studies have long provided evidence for heavy quasiparticles, their unconventional superconductivity and non-Fermi liquid behavior in a variety of material systems [3,50–54]. However, the emergence of a coherent band of heavy quasiparticles near the Fermi energy in a Kondo lattice system was still not well understood [54–57]. Part of the challenge had been the inability of spectroscopic measurements to probe the development of heavy quasiparticles with lowering of temperature and to characterize their properties with high-energy resolution. Such precise measurements of heavy fermion formation are not only required for understanding the nature of these electronic excitations close to quantum phase transitions [58] but are also critical to identifying the source of unconventional superconductivity near such transitions.

Recent advances in the application of STM to heavy fermions have provided a new approach to examining the correlated electrons in these systems with high energy and spatial resolutions. STM and point-contact experiments on heavy fermion compounds have shown evidence for hybridization of the conduction electrons with the $f$-orbitals
Figure 3.1: Schematic representations of a single-impurity Kondo effect (a) and a Kondo lattice (b) illustrating the screening (hybridization) of the local moments (red arrows) by the itinerant conduction electrons (green arrows). (c) Schematic phase diagram of heavy-fermion systems where the electronic ground state can be tuned from antiferromagnetism (AFM) with localized f-moments to a heavy Fermi liquid (HFL) with itinerant f-electrons. At low temperatures, superconductivity (SC) sets in near the quantum critical point (QCP) from a non-Fermi liquid (NFL). (d) Bare electronic bands (dashed lines) and hybridized heavy fermion bands (HF) (solid lines) displaying a direct (2ν) and an indirect (∆h) hybridization gaps. (e) Tunneling spectra computed from the hybridized band structure in (d) for a tunneling ratio tf/tc = −0.025 showing sensitivity to the direct hybridization gap (2ν). (f) Similar spectra computed with tf/tc = −0.37 showing sensitivity to the indirect gap (∆h). See section 3.1.1 for details of the model. Reproduced from [20].
and have been used to probe the so-called *hidden order* phase transition involving heavy $f$-electrons in URu$_2$Si$_2$ [21, 59–61]. As it will be explained in chapter 4, the sudden onset of the hidden order phase appears to give rise to strong modification of the band structure in URu$_2$Si$_2$ as detected by STM measurements [21, 60]. However, these changes are correlated with the phase transition into the hidden order at 17.5 K rather than the generic physics of heavy Fermi liquids that should appear at higher temperatures and evolve smoothly with lowering of temperature. Therefore, the results presented in the current chapter represent the first direct experimental observation of the gradual formation of heavy quasiparticles with temperature and evidence of their composite nature, which is ubiquitous to all heavy fermions. Additionally, these results offer a novel way to examine their properties in proximity to quantum critical points (QCPs), which had remained out of the reach of STM and other spectroscopic measurements.

### 3.1 Tunneling into a Kondo Lattice

The emergence of composite heavy fermions in a Kondo lattice can be considered as a result of the hybridization of two electronic bands: one dispersing band due to conduction electrons and one weakly dispersing (nearly flat) band originating from localized $f$-electrons (dashed lines in Fig. 3.1(d)). This hybridization generates low-energy quasiparticles that are a mixture of conduction- and $f$-electrons with a modified band structure characterized by the so-called direct ($2\nu$) and indirect ($\Delta h$) hybridization gaps, as shown in Fig. 3.1(d) [57, 62]. Various theoretical approaches, including several numerical studies, remarkably reproduce the generic composite band structure in Fig. 3.1(d) [63–67].

Recent theoretical modeling has also shown that tunneling spectroscopy can be a powerful probe of this composite nature of heavy fermions [68–71]. Depending on the relative tunneling amplitudes to the light conduction ($t_c$) or to the heavy $f$-like ($t_f$) components of the composite quasiparticles, and due to their interference, tunneling
spectroscopy can be sensitive to different features of the hybridized band structure. Figures 3.1(d-f) show examples of model calculations illustrating the sensitivity to predominantly tunneling to the light (Fig. 3.1(e)) or heavy (Fig. 3.1(f)) electronic states. For the reader who may be interested in the details of the model calculations section 3.1.1 provides a review of the phenomenological Green’s function method used to simulate the tunneling into a composite quasiparticle. Though recommended the next section can be skipped without loss of continuity.

3.1.1 Modeling the Tunneling Density of States

To understand the experimentally observed spectroscopic lineshapes (section 3.3) and the quasiparticle interference (QPI) patterns (section 3.4) and show that they are consistent with the emergence of heavy fermions, we model the \( dI/dV \) following a recent theoretical description of a coherent Kondo lattice state \([70]\) described below. Though the model describes the formation of heavy fermions using the Kondo-Heisenberg Hamiltonian within the framework of a large-N approach, it shares the basic phenomenology of heavy fermion hybridization in Fig. 3.1. The significance of the model comes from the introduction of two different tunneling amplitudes \( t_f \) and \( t_c \) to the two different electronic states (heavy \( f \)-band and light conduction band). The ratio between these tunneling paths and their interference determines the experimental lineshapes of the spectra.

The starting point is a light hole-like conduction \( (c) \) band \( E_{k}^c = 2t[\cos(k_x) + \cos(k_y)] - \mu \) and a heavy \( (f) \) band \( E_{k}^f = -2\chi_0[\cos(k_x) + \cos(k_y)] - 4\chi_1\cos(k_x)\cos(k_y) + \epsilon_f^0 \) near the Fermi energy, where \( t \) (not to be confused with \( t_f \) or \( t_c \)) and \( \mu \) represent the nearest neighbor hopping of the conduction electrons and the chemical potential, respectively, and \( \chi_0, \chi_1, \) and \( \epsilon_f^0 \) represent the nearest and next-nearest site spin correlations, and the position of the heavy band with respect to the Fermi energy,
respectively. The differential conductance \( \frac{dI}{dV} \) is given by

\[
\frac{dI}{dV}(\vec{k}, \omega) = -\frac{2e}{\hbar} T \sum_{i,j=1}^{2} \left[ \hat{t} \hat{G}(\vec{k}, \omega) \hat{t} \right]_{ij}.
\]

(3.1.1)

In Eq. 3.1.1 the ratio of tunneling to the \( c \)- and \( f \)-bands is controlled by the matrix

\[
\hat{t} = \begin{pmatrix}
t_c & 0 \\
0 & t_f \\
\end{pmatrix}.
\]

(3.1.2)

Here, we consider a metallic tip and take its density of states \( T \) to be unit. The composite Green’s function is written as

\[
\hat{G} = \begin{pmatrix}
G_{cc} & G_{cf} \\
G_{fc} & G_{ff} \\
\end{pmatrix},
\]

(3.1.3)

In Eq. 3.1.3 each component already describes the hybridization between \( c \)- and \( f \)-electron bands:

\[
G_{ff}(\vec{k}, \omega) = \left[ (G_{ff}^0(\vec{k}, \omega))^{-1} - \nu^2 G_{cc}^0(\vec{k}, \omega) \right]^{-1},
\]

(3.1.4)

\[
G_{cc}(\vec{k}, \omega) = \left[ (G_{cc}^0(\vec{k}, \omega))^{-1} - \nu^2 G_{ff}^0(\vec{k}, \omega) \right]^{-1},
\]

(3.1.5)

\[
G_{cf}(\vec{k}, \omega) = G_{cc}^0(\vec{k}, \omega) \nu G_{ff}(\vec{k}, \omega).
\]

(3.1.6)

where \( \nu \) is the hybridization energy scale. The bare Green’s functions are given in their usual form by

\[
G_{cc}^0(\vec{k}, \omega) = (\omega - E_{\vec{k}}^c + i\gamma_c)^{-1},
\]

(3.1.7)

\[
G_{ff}^0(\vec{k}, \omega) = (\omega - E_{\vec{k}}^f + i\gamma_f)^{-1},
\]

(3.1.8)

and the lifetimes of the \( c \) and \( f \)-electron states are \( \gamma_c^{-1} \) and \( \gamma_f^{-1} \) respectively. The upshot is the typical hybridization picture where the poles of the above (hybridized)
Green's function yield two heavy fermion bands $E_{\vec{k}}^{\pm}$:

$$E_{\vec{k}}^{\pm} = \frac{E_{\vec{k}}^c + E_{\vec{k}}^f}{2} \pm \sqrt{\left(\frac{E_{\vec{k}}^c - E_{\vec{k}}^f}{2}\right)^2 + \nu^2},$$  \hspace{1cm} (3.1.9)$$

where as before $\nu$ represents the hybridization amplitude between the $c$ (light) and $f$ (heavy) bands.

Figure 3.2 shows a plot of the bare heavy and light electronic bands (dotted lines) and the hybridized heavy fermion bands (solid lines) and Fig. 3.3 displays the computed differential conductance using the same band structure of Fig. 3.2 for several selected values of $t_f/t_c$. For small $t_f/t_c$, the predominant tunneling channel is into the light conduction band and the differential conductance exhibits a gap. For larger $t_f/t_c$, tunneling becomes more sensitive to the $f$-orbitals and the differential conductance exhibits two sharp peaks reflecting the electronic density of states of the split heavy fermion bands and the opening of the small indirect hybridization gap $\Delta_h$. 

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Figure 3.3: A $dI/dV$ computed using the same band structure parameters as in Fig. 3.2 for selected values of $t_f/t_c$. The inverse quasiparticle lifetimes used are $\gamma_c = 0.03t$ and $\gamma_f = 0.03t$. 
To speculate the quasiparticle interference data, the Fourier transform of the \(dI/dV\) (\(q\)-space) is computed:

\[
S(\vec{q}, \omega) = \frac{dI}{dV}(\vec{q}, \omega) = \frac{2\pi e}{\hbar} T \sum_{i,j=1}^{2} \left[ \hat{t} \hat{N}(\vec{q}, \omega) \right]_{ij} .
\]  

In Eq. 3.1.10 the single impurity scattering between points on the contours of constant energy of the hybridized band structure is present in

\[
\hat{N}(\vec{q}, \omega) = \frac{1}{\pi} \text{Im} \int \frac{d^2 \vec{k}}{(2\pi)^2} \hat{G}(\vec{k}, \omega) \hat{U} \hat{G}(\vec{k} + \vec{q}, \omega) ,
\]

with \(U_c\) and \(U_f\) being the scattering potential in the \(c\)- and \(f\)-electron channels in

\[
\hat{U} = \begin{pmatrix} U_c & 0 \\ 0 & U_f \end{pmatrix} .
\]

Figure 3.4 shows \(S(\vec{q}, \omega)\) computed for a scattering potential of \(U_c = 1\) and \(U_f = 0\) for two values of \(\gamma_f\) showing the momentum-energy signatures of the hybridization.

Overall, the calculation presented above demonstrates how the existence of two tunneling paths and their interference can significantly alter the tunneling spectrum as well as the QPI. In sections 3.3 and 3.4 I will present the experimental realization of the ideas developed above. The tuning of the tunneling ratio \(t_f/t_c\) will come from tunneling on different chemical terminations of CeCoIn\(_5\), providing different sensitivities to tunneling into the \(f\)-component of the composite quasiparticles. First we must explore the different surface terminations made available for STM measurements by the cleaving of CeCoIn\(_5\).

### 3.2 CeMIn\(_5\) as a Model Heavy-Fermion System

To provide a controlled study of the emergence of heavy fermion excitations within a Kondo lattice system that can be tuned close to a QCP, we carried out studies on
Figure 3.4: The QPI band structure $S(q,\omega)$ for $U_c = 1$ and $U_f = 0$ using the same band structure parameters as in Fig. 3.2 for selected values of $\gamma_f$. Reproduced from [20].

The Ce$M$In$_5$ (with $M = \text{Co, Rh}$) material system. These so-called 115 compounds offer the possibility to tune the interaction between the Ce’s $f$-orbitals and the itinerant $spd$ conduction electrons using isovalent substitutions at the transition metal site within the same tetragonal crystal structure. Consequently, the ground state of this system can be tuned (in stoichiometric compounds) between antiferromagnetism, as in CeRhIn$_5$ (Neél temperature, $T_N = 3.5$ K), to superconductivity, as observed in CeCoIn$_5$ (superconducting transition temperature, $T_c = 2.3$ K) and CeIrIn$_5$ ($T_c = 0.4$ K) [3]. Previous studies indicate that CeCoIn$_5$ is very close to a QCP [72–75], while CeRhIn$_5$ can be tuned close to this transition with application of pressure [48, 76]. These experiments confirm that superconductivity in the 115 system emerges at low temperatures close to a QCP from the development of heavy low-energy excitations at high temperature [3, 48, 76]. More specifically, transport studies show a drop in the electrical resistivity in CeCoIn$_5$ around 50 K, which has been interpreted as evidence for the development of a coherent heavy quasiparticle band, followed by a linear resis-
tivity at lower temperature (above $T_c$) \[77\] – a behavior that has been associated with the proximity to the QCP. Quantum oscillations and thermodynamic measurements find a heavy effective mass ($10-50 m_0$, bare electron mass) for CeCoIn$_5$, while in the same temperature range the $f$-electrons in CeRhIn$_5$ are effectively decoupled from the conduction electrons \[78,79\].

Figure 3.5 shows STM images of a single crystal of CeCoIn$_5$ that has been cleaved in situ in our variable temperature ultra-high vacuum STM. In this family of compounds the cleaving process results in exposing multiple surfaces terminated with different chemical compositions. The crystal symmetry necessarily requires multiple surfaces for cleaved samples, as no two equivalent consecutive layers occur within the unit cell. Therefore breaking of any single chemical bond will result in different layer terminations on the two sides of the cleaved sample. Experiments on multiple cleaved samples have revealed three different surfaces, two of which are atomically ordered (termed surfaces A and B in Figs. 3.5(a,b)) with a periodicity of approximately 4.6 Å corresponding to the lattice constant of the bulk crystal structure, while the third surface (termed surface C, Fig. 3.5(b)) is reconstructed. Comparison of the relative heights of the sub-unit cell steps between the different layers (Figs. 3.5(c,d)) to the crystal structure determined from scattering experiments \[80\] suggests that the exposed surfaces A, B, and C correspond to the Ce-In, Co, and In$_2$ layers, respectively. Experiments on CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ and CeRhIn$_5$ reveal similar results, where cleaving exposes the corresponding multiple layers in those compounds (see appendix A.1). Hg defects in CeCoIn$_5$ at this concentration have negligible influence on its thermodynamic and transport properties \[81\] and are introduced for scattering experiments described in section 3.4.
Figure 3.5: (a) Constant current topographic image (+200 mV, 200 pA) showing an atomically ordered surface (termed surface A) with a lattice constant of approximately 4.6 Å. (b) Topographic image (−200 mV, 200 pA) showing two consecutive layers: a distinct atomically ordered surface (termed surface B; lattice constant approximately 4.6 Å) and a reconstructed surface (termed surface C). (c) Constant current topographic image (−150 mV, 365 pA) displaying all three surfaces (the derivative of the topography is shown to enhance contrast). (d) A line cut through the different surfaces (solid line in (c)) showing the relative step heights compared to the bulk crystal structure. Insets in (a) and (b) show blow-ups (45 × 45 Å²) of the three different surfaces. Reproduced from [20].
3.3 Signatures of Hybridization and Composite Excitations

Spectroscopic measurements of CeCoIn$_5$ show the sensitivity of the tunneling process to the composite nature of the hybridized heavy fermion states. As shown in Fig. 3.6(a), tunneling spectra on surface A (identified as the Ce-In layer) of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ and CeCoIn$_5$ (shown in appendix A.2) show that upon cooling the sample dramatic changes develop in the spectra in an asymmetric fashion about the Fermi energy. The redistribution of the spectra observed on this surface is consistent with a tunneling process that is dominated by coupling to the light conduction electrons and displays signatures of the direct hybridization gap (2$\nu$) experienced by this component of the heavy fermion excitations (e.g. see Figs. 3.1(d,e)). In contrast to these observations, similar measurements on the corresponding surface of CeRhIn$_5$ show spectra that are featureless in the same temperature range (Fig. 3.6(a), dashed line) and are consistent with the more localized nature of the Ce $f$-orbitals in CeRhIn$_5$ as compared to CeCoIn$_5$. The hybridization gap structure in CeCoIn$_5$ is also centered above the chemical potential (8 meV, see Fig. 3.6(a)), which makes it difficult for angle-resolved photoemission experiments [82–84], the typical technique to probe electronic band structures in solids, to access.

The composite nature of the heavy fermion excitations manifests itself by displaying different spectroscopic characteristics for tunneling into the different atomic layers. Figure 3.6(b) shows spectra measured on surface B (identified as Co) of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ that looks remarkably different than those measured on surface A (Fig. 3.6(a)). In the same temperature range where spectra on surface A (Fig. 3.6(a)) develop a depletion of spectral weight near the Fermi energy, surface B shows a sharp enhancement of spectral weight within the same energy window (Fig. 3.6(b)). With further lowering of temperature, the enhanced tunneling on surface B evolves into a double-peak structure. As a control experiment, measurements on the corresponding surface in CeRhIn$_5$, once again, display no sharp features in the
Figure 3.6: (a) Averaged tunneling spectra ($-150$ mV, 200 pA) measured on surface A of CeCo(In_{0.9985}Hg_{0.0015})_5 for different temperatures (solid lines) and on the corresponding surface A of CeRhIn$_5$ at 20 K (dashed line). (b) Averaged tunneling spectra ($-150$ mV, 200 pA) measured on surface B of CeCo(In_{0.9985}Hg_{0.0015})_5 for different temperatures (solid lines) and on corresponding surface B of CeRhIn$_5$ at 20 K (dashed line). (c),(d) Tunneling spectra computed for $t_f/t_c = -0.01$ (c) and $t_f/t_c = -0.20$ (d) for selected values of $\gamma_f$. See section 3.1.1 for details of the model. Reproduced from [20].
same temperature and energy windows (Fig. 3.6(b), dashed line). The spectroscopic features of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$’s surface B display the characteristic signatures of dominant tunneling to the $f$-component of the heavy quasiparticles, which reside near the Fermi energy and are expected to display the indirect hybridization gap ($\Delta_h$) (see Fig. 3.1(d,f)).

The model calculation for tunneling to composite heavy excitations in section 3.1.1 can reproduce well our spectroscopic measurements on the two different atomically ordered surfaces of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$. The results of our calculations (Fig. 3.6(c,d)) are sensitive to the ratio of tunneling ($t_f/t_c$) into the heavy $f$-states versus the light conduction band – a behavior that explains the differences between the tunneling processes on the different cleaved surfaces (Fig. 3.6(a,b)). While naïvely one would expect that tunneling to the heavy excitations would be more pronounced on the Ce-In layer, recent first principles calculations show that the amplitude of the hybridization of the $f$-states with the out-of-plane $spd$-electrons can be remarkably larger than with those in-plane [64].

### 3.4 Visualizing quasiparticle mass enhancement

To directly probe the energy-momentum structure of heavy quasiparticles in the 115 material systems, we have carried out spectroscopic mapping with the STM that enables us to visualize scattering and interference of these quasiparticle excitations from impurities or structural defects. Elastic scattering of quasiparticles from these imperfections gives rise to standing waves in the conductance maps at wavelengths corresponding to $2\pi/|\vec{q}|$ where $\vec{q} = \vec{k}_f - \vec{k}_i$ is the momentum transfer between initial ($\vec{k}_i$) and final ($\vec{k}_f$) states at the same energy. We expect that $\vec{q}$ vectors with the strongest intensity connect regions of high density of states on the contours of constant energy and hence provide energy-momentum information of the quasiparticle

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1To generate the spectra in Figs. 3.6(c,d) the band structure of Fig. 3.2 was used for $\gamma_c = 0.03t$ and for different values of $\gamma_f$. 

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excitations. We characterize the scattering $\vec{q}$ vectors using discrete Fourier transforms (DFTs) of STM conductance maps measured at different energies. The presence of Hg substitutions in CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ provides a sufficient number of scattering centers to enhance signal to noise ratio for such quasiparticle interference (QPI) measurements.

Figure 3.7(a) shows examples of energy-resolved STM conductance maps on surface A of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ measured at 20 K displaying signatures of scattering and interference of quasiparticles from defects and step edges. These conductance maps show clear changes of the wavelength of the modulations as a function of energy. Perhaps the most noticeable are the changes around each random defect. Fig. 3.7(b) shows DFTs of such maps that display sharp non-dispersive Bragg peaks (at the corners, $(\pm 2\pi/a, 0)$, $(0, \pm 2\pi/a)$) corresponding to the atomic lattice, as well as other features (concentric square-like shapes) that rapidly disperse with energy, collapse (Fig. 3.7(b); 0 meV), and disappear (Fig. 3.7(b); 9 meV) near the Fermi energy. We have carried out such measurements both at low temperatures (20 K, Fig. 3.7(b)) where the spectrum shows signatures of hybridization between conduction electrons and $f$-orbitals, as well as at high temperatures (70 K, Fig. 3.7(c)) where such features are considerably weakened (e.g. Fig. 3.7(c); 2 meV, 10 meV). As a control experiment, we have also carried out the same measurements on the corresponding surface of CeRhIn$_5$ (Fig. 3.7(d)), for which signatures of heavy electron behavior are absent (e.g. Fig. 3.6(a)) in the same temperature window (20 K). While understanding details of the QPI in Fig. 3.7 requires detailed modeling of the band structure of the 115 compounds, the square-like patterns observed in the data correspond to scattering wavevectors that can be identified from the calculated LDA band structure [85] (see appendix A.3).

We find that analyzing the features of the energy-resolved DFT maps provide direct evidence for mass enhancement of quasiparticles, in unison with related signatures in the tunneling spectra. Figures 3.8(a,b) show line cuts of the DFT maps plotted along two high-symmetry directions as a function of energy for
Figure 3.7: Real space (a) and corresponding DFT (b) of conductance maps ($-200$ mV, 1.6 nA) at selected energies measured on surface A of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ at 20 K. Similar DFTs for CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ at 70 K ($-150$ mV, 1.5 nA) (c) and on the corresponding surface A for CeRhIn$_5$ at 20 K ($-200$ mV, 3.0 nA) (d) at selected energies. The arrow indicates the position of the Bragg peaks at $(2\pi/a, 0)$ and $(0, 2\pi/a)$. All DFTs were four-fold symmetrized (due to the four-fold crystal symmetry) to enhance resolution. The intensity is represented on a linear scale. Reproduced from [20].
CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ at 20 K and in Fig. 3.8(c) we show their corresponding spatially averaged spectrum. The square-like regions of enhanced quasiparticle scattering in Fig. 3.7(b) appear in the line cuts of Figs. 3.8(a,b) as energy-dependent bands of scattering, which become strongly energy dependent near the Fermi energy. Clearly the scattering of the quasiparticle excitations in the energy window near the direct hybridization gap have flatter energy-momentum structure as compared to those at energies away from the gap. This is the direct signature of the quasiparticles acquiring heavy effective mass at low energies near the Fermi energy. Detailed analysis of one of the QPI bands estimates the mass enhancement near the Fermi energy to be about $30m_0$ (Fig. 3.8(a) inset), a value which is close to that seen in quantum oscillation studies of CeCoIn$_5$ [78, 79]. Notice that the experimental results presented here are in qualitative agreement with the calculation for the QPI presented in section 3.1.1.

Contrasting low temperature QPI patterns on CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ to measurements on the same compound at high temperatures (70 K, Figs. 3.8(d,e)), where the hybridization gap is weak (Fig. 3.8(f)), or to measurements on CeRhIn$_5$ (20 K, Fig. 3.8(g,h)), where signatures of a hybridization gap are absent in the tunneling spectra (Fig. 3.8(i)), confirms that the development of this gap results in apparent splitting of the bands which are responsible for both the scattering and the heavy effective mass in the QPI measurements. Furthermore, these measurements show that the underlying band structure responsible for the scattering wavevectors away from the Fermi energy is relatively similar between CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ and CeRhIn$_5$. Only when $f$-electrons of the Kondo lattice begin to strongly hybridize with conduction electrons and modify the band structure within a relatively narrow energy window (30 meV), we see signatures of heavy fermion excitations in QPI measurements, signaling a transition from small to large Fermi surface (see appendix A.3).
Figure 3.8: Energy-momentum structure of the QPI bands extracted from line cuts (solid white lines in Fig.3.7(b)) along the atomic direction \((2\pi/a, 0)\) (a) and along the zone diagonal \((\pi/a, \pi/a)\) (b) in CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ at 20 K. The solid red line represents a fourth-order polynomial fit to the data. Inset in a shows the effective mass \(m^*/m_0\) as a function of momenta obtained from the curvature \((\hbar^2/4d^2E/dq^2)^{-1}\) of the outer band (solid red line in (a)). (c) Average spectrum on surface A of CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ at 20 K reflecting the suppression of scattering in the QPI bands. Similar measurements performed in CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ at 70 K (d), (e), (f) and in CeRhIn$_5$ at 20 K (g), (h), (i). PSD, power spectral density. The intensity is represented on a linear scale. Reproduced from [20].
3.5 Signatures of Quantum Criticality

The ability to tunnel through the \( f \)-component of the heavy quasiparticles on CeCo(In\(_{0.9985}\)Hg\(_{0.0015}\))\(_5\)’s surface B provides an opportunity to probe the lifetime of the heavy quasiparticles as a function of temperature in a system that is close to a QCP. The narrow dispersion of the \( f \)-band results in a direct connection between the experimentally measured width of the peak in the density of states near the Fermi energy (Fig. 3.6(b)) and the lifetime of the heavy quasiparticles. Analysis of this width measured at different temperatures is displayed in Fig. 3.9(a) (see appendix A.4) and shows a strong temperature dependence with a finite intercept (\( \approx 3.5 \text{meV} \)) in the limit of zero temperature. The finite width at zero temperature can be understood as a consequence of a small but finite dispersion of the \( f \)-band as well as a finite probability of tunneling into the \( spd \) electrons (see section 3.1.1). However, the large linear slope (even after thermal deconvolution of the data) in Figure 3.9(a) indicates that the \( f \)-electrons lifetime, as opposed to thermal broadening, is strongly influencing the spectra and its temperature dependence. Consistent with this observation, we also find that to capture the temperature evolution of the spectra in Fig. 3.6b, we have to use rather large values of scattering rate (inverse lifetime) of the \( f \)-component of the heavy quasiparticles \( \gamma_f = \hbar/\tau_f \) in our model calculations (Fig. 3.6(d)).

A linear scattering rate (or inverse lifetime) for the heavy quasiparticles is consistent with the expectation that CeCoIn\(_5\) is close to a QCP, since for systems tuned close to such transitions, temperature is the only relevant energy scale available to determine the quasiparticle lifetime, resulting in \( \hbar/\tau_f \propto k_B T \) [58, 86]. Yet, a more precise signature of a QCP would be the observation of energy-temperature scaling of experimental quantities near such transitions. In fact, recent theoretical work suggests that the instability of the Fermi surface near a QCP should result in scaling properties of the single-particle excitation that can be directly probed in measurements of the tunneling density of states [87]. To test this hypothesis, we examine the lineshape of the tunneling spectra on surface B near the chemical potential at different
Figure 3.9: (a) Full width at half maximum (FWHM) of the heavy quasiparticle peak (red squares) as a function of temperature extracted from a Gaussian fit to the sharp lineshape of the spectra of Fig. 3.6(b) after a smooth background subtraction (see appendix A.5). Blue squares represent the thermally deconvoluted FWHM corresponding to the intrinsic width in the absence of thermal broadening. The error bars represent one standard deviation. (b) Energy-temperature scaling of the different spectra of Fig. 3.6(b), after the removal of a temperature independent background (see appendix A.5), within a narrow energy window near the Fermi energy. Inset shows the ‘goodness of the collapse’ as a function of the critical exponents $\alpha$ and $\beta$. Reproduced from [20].
temperatures and attempt to scale the data (Fig. 3.6(b)) by plotting \((dI/dV)_S(k_B T^\alpha)\) as a function of \(E/(k_B T)^\beta\) where \((dI/dV)_S\) is the background subtracted spectra of Fig. 3.6(b) (see appendix A.5) and \(E\) is the energy of the tunneling quasiparticles. We find that using the exponents \(\alpha = 0.53\) and \(\beta = 1\) results in a collapse of the data at different temperatures on a single curve in the low bias region (Fig. 3.9(b) and see appendix A.5). Although an understanding of the value of the exponent \(\alpha\) is currently lacking, the linear power \(\beta\) confirms our hypothesis of energy-temperature scaling associated with proximity to a QCP. These results indicate that the heavy quasiparticles in CeCoIn\(_5\) are damped because of critical fluctuations rather than the typical scattering that is expected in a Fermi liquid \((T^2\) dependence). Similar energy-temperature scalings, with anomalous exponents \((\alpha)\), have been previously observed in the dynamical spin susceptibility of other heavy fermion systems near QCPs [44,46,88,89]. However, here we show for the first time that the signatures of scaling and critical phenomena appear in the spectroscopic properties of the quasiparticle excitations.

### 3.6 Summary of CeCoIn\(_5\)

The experimental results and the model calculations presented here provide a comprehensive picture of how the heavy fermion excitations in the 115 Ce-based Kondo lattice systems emerge with lowering of temperature or as a result of chemical tuning of the interaction between the Ce \(f\)-electrons and the conduction electrons. The changes in the scattering properties of the quasiparticles directly signal the flattening of their energy-momentum structure and the emergence of heavy quasiparticles near the Fermi energy. Such changes are also consistent with the predicted evolution from small to large Fermi surface as the localized \(f\)-electrons hybridize with the conduction electrons. The sensitivity of the tunneling to the surface termination and the successful modeling of these data provide direct spectroscopic evidence of the composite nature of heavy fermions and offer a unique method to disentangle their components.
Our experiments also demonstrate that the emergent heavy quasiparticles in our system are strongly scattered and show signatures of scaling associated with critical damping of excitations in proximity to a QCP. Like many other heavy fermion systems, thermodynamic and transport studies of the 115 systems have shown evidence of quantum criticality, but never before such signatures have been isolated in an electron spectroscopy measurement as described here. Such spectroscopic signatures are a direct evidence for the breakdown of coherent fermionic excitations approaching a QCP. Future extension of our measurements to lower temperatures can probe the interplay between quantum fluctuations and the appearance of superconductivity, an issue which continues to be one of the most debated in condensed matter physics.\textsuperscript{2}

\textsuperscript{2}We have recently performed such experiments in the superconducting state of CeCoIn\textsubscript{5}. These results are available elsewhere [23].
Chapter 4

URu\textsubscript{2}Si\textsubscript{2}

4.1 Brief Review of the Hidden Order in URu\textsubscript{2}Si\textsubscript{2}

Among the heavy fermion compounds perhaps the most enigmatic is the URu\textsubscript{2}Si\textsubscript{2} system, which undergoes a second-order phase transition with a rather large change in entropy (see Fig. 4.1) [50, 90, 91] at 17.5 K from a paramagnetic phase with Kondo screening to a phase with an unknown order parameter [92]. This material possesses low-energy commensurate and incommensurate spin excitations, which are gapped below the hidden order (HO) transition temperature [93–96]. These features are believed to be signatures of a more complex order parameter, the identification of which has so far not been possible despite numerous investigations [95–101]. Moreover, analogous to other correlated systems, this unusual conducting phase is transformed into an unconventional superconducting state at 1.5 K [50, 91, 102], the understanding of which hinges on formulating the correct model of the HO state.

In this chapter I will describe STM measurements on URu\textsubscript{2}Si\textsubscript{2} single crystals that allow atomic scale examination of this system in the paramagnetic Kondo phase and its phase transition into the HO state. We isolate electronic signatures of the Kondo lattice state and their transformation at the HO transition. Although there have long been reports on modification of the electronic structure of URu\textsubscript{2}Si\textsubscript{2} at the onset of the HO transition, such as those in specific heat [50, 91] as well as opti-
Figure 4.1: Specific heat of URu$_2$Si$_2$ plotted as $C/T$ vs. $T^2$ (above) and vs. $T$ (below) showing the phase transition at 17.5 K. Reproduced from [50].
cal [103,104], point contact [104,105], and angle resolved photoemission spectroscopy measurements [100, 106, 107], our experiments provide an unprecedented determination of these changes with high energy and spatial resolutions. We find a particle-hole asymmetric energy gap that turns on with a mean-field temperature dependence near the bulk HO transition. More importantly, spectroscopic mapping as a function of temperature further reveals that the HO gap is spatially correlated on the atomic scale with the electronic signatures of the Kondo lattice state. This chapter is based on a paper I coauthored which appeared in the Proceedings of the National Academy of Sciences in 2010 [21].

4.2 Chemical Identification of Cleaved Surfaces

As it was the case for CeCoIn$_5$ (see appendix A.1) the crystal structure of URu$_2$Si$_2$ does not show identical consecutive, mirror-like layers along the c-axis, and multiple surfaces are expected to be accessible from the cleaving process. The STM topographies show that cleaved surfaces can be terminated with primarily two types of surfaces, one of which is atomically ordered with a lattice spacing corresponding to either the U or the Si layer (Fig. 4.2A; termed surface A), whereas the other is reconstructed (Fig. 4.2B; termed surface B) (see more information in appendix B). The occurrence of surfaces A and B with roughly equal probabilities (55% and 45%, respectively) implies that these surfaces are the two sides of the same cleave, suggesting that the cleaving process involves breaking of a single type of chemical bond. Moreover, the relative height between surfaces A and B shown in Fig. 4.2C reveals that surface A lies $\approx 1.5\,$Å above and $\approx 3.3\,$Å below surface B. This asymmetry allows us to uniquely identify surfaces A and B as the U and Si layers, respectively (see Fig. 4.2E). Any other possibility (i.e., Fig. 4.2F) will require the breaking of two bonds, the result of which would be the observation of four surfaces with 25% probabilities. Occasionally ($< 5\%$ of the time), small patches of a different surface (termed surface C) have also been observed (Fig. 4.2D). The presence of multiple
surfaces for cleaved URu$_2$Si$_2$ samples indicates that obtaining local surface structure information is critical to identifying which spectroscopic properties are most related to the bulk properties. This requirement puts other surface sensitive spectroscopic techniques, such as angle resolved photoemission or point contact spectroscopy, at a disadvantage.

### 4.3 Signatures of Kondo Lattice Formation

The temperature evolution of the spatially averaged STM spectra on the atomically ordered terraces (U terminated, surface A), shown in Fig. 4.3B, reveals the development of electronic correlations in URu$_2$Si$_2$ below 120 K, which evolve into dramatic spectroscopic signatures of the HO phase as the temperature is reduced (Fig. 4.3 C and D). At high temperatures (above 120 K), the spectrum presents a broad feature that has weak energy dependence, although it shows a slightly asymmetric density of states (DOS) for electron or hole tunneling. As the temperature is lowered, we find that the background is modified with an asymmetric resonance near the Fermi level, which sharpens as the temperature is reduced. On further cooling below the HO transition, we find the opening of a low-energy gap that widens with decreasing temperature and reveals an unusual asymmetry relative to the Fermi energy and an even sharper structure within the gap (Fig. 4.3D). The unusual shape of the low-energy spectral properties and their dramatic evolution with temperature provide important clues to the underlying correlations responsible for the thermodynamic phases of URu$_2$Si$_2$.

Focusing on the spectroscopic features above the HO transition, we note that the asymmetric line shape near the Fermi level developing below 120 K is reminiscent of a Fano spectral line shape [68, 108, 109] measured for single Kondo impurities on the surface of noble metals [110–112]. Recent calculations of the local electronic DOS on URu$_2$Si$_2$ reveal a Kondo resonance with a Fano line shape on the U layer in qualitative agreement with our data [101]. Previous thermodynamic and transport
Figure 4.2: STM topography. (A and B) Constant current topographic image (200 mV, 60 pA, 33 Å) showing an atomically ordered surface (termed surface A) and (100 mV, 200 pA, 90 Å) showing an atomic layer with surface reconstruction (termed surface B), respectively. (C) The relative heights between surfaces A and B. (D) Constant current topographic image (50 mV, 100 pA) over a 185 × 140 Å² area showing a (21) reconstructed surface (surface C) lying ≈ 2.2 Å above surface A. A horizontal line cut through the data in C and D is shown on the bottom panels. (E) Schematic diagram illustrating the different atomic layers of URu₂Si₂. U is identified as the atomically ordered surface (surface A) that lies 1.24 Å above and 3.56 Å below surface B. In this case, obtaining surfaces A and B requires breaking of a single bond only (U-Si; see arrows). (F) Schematic diagram illustrating a different possibility for the cleaved surfaces, which requires the breaking of two bonds (Ru-Si and U-Si; see arrows). This scenario cannot explain why surfaces A and B occur with roughly equal probabilities. The step heights in A and B are obtained (or calculated) from ref. [50]. Reproduced from [21].
Figure 4.3: STM topography and spectroscopy on URu$_2$Si$_2$. (A) Constant current topographic image (200 mV, 60 pA) over a 200-A area showing the atomically ordered surface where the spectroscopic measurements are performed. (B and C) Averaged electronic DOS above (B) and below (C) the HO temperature. The red lines in B and C are the results of least squares fit described in the text and appendix B. Spectra are offset by 0.25 nS for clarity. (D) Averaged electronic DOS at low temperatures showing additional features within the gap. Spectra are offset by 1 nS for clarity. Reproduced from [21].
studies have also identified the temperature range above the HO transition as being dominated by Kondo screening of the $f$-electron moments [50, 91, 102]. The STM spectroscopic line shape expected for tunneling into a Kondo lattice has already been described in section 3.1.1. In the limit of dominant tunneling to the $spd$ component of the hybridized electrons, the spectroscopic lineshape takes a specific form known as the Fano line shape. This lineshape naturally occurs because of the presence of two interfering tunneling paths from the STM tip, one directly into the itinerant electrons, and the other indirectly through the Kondo resonance. The Fano lineshape, which takes the simple form

$$G(V) \propto \frac{((V - E_0)/\Gamma + q)^2}{1 + ((V - E_0)/\Gamma)^2}, \quad (4.3.1)$$

is characterized by the resonance energy $E_0$, its width $\Gamma$, and the ratio of probabilities between the two tunneling paths $q$. In terms of the formalism developed in section 3.1.1, $E_0$ represents the energy of a flat band of $f$-character, $\Gamma$ phenomenologically takes into account the coherence of the heavy states and $q$ relates to the relative tunneling probabilities ($t_f/t_e$). The addition of this line shape to the high temperature background DOS accurately fits the spectroscopic data over a wide range of temperatures (red line in Fig. 4.3B; see also appendix B), and therefore provides a convenient way to extract the temperature dependence of the heavy electron coherence ($\Gamma$). The extracted values of $q = 1.3 \pm 0.3$ and $E_0 = 5 \pm 2$ meV show no significant temperature dependence within the uncertainty of our fits above the HO transition, whereas $\Gamma$ clearly broadens with increasing temperature as shown in Fig. 4.4A. Results for the single channel spin one-half Kondo impurity model in a Fermi liquid regime have been used to describe the temperature dependence of $\Gamma$,

$$\Gamma = 2\sqrt{(\pi k_BT)^2 + 2(k_BT_K)^2}, \quad (4.3.2)$$

and to extract the value of the Kondo temperature, $T_K = 129 \pm 10$ K (Fig. 4.4A).

The success of this model at describing the spectra above the HO transition points to a strong disparity between URu$_2$Si$_2$ and CeCoIn$_5$. While the broadening of the
spectroscopic lineshape in CeCoIn$_5$ is proportional to temperature and indicates proximity to a quantum critical point, the temperature dependence of $\Gamma$ for URu$_2$Si$_2$ follows the Fermi liquid prediction. Since CeCoIn$_5$ has a higher $T_c$ than URu$_2$Si$_2$, our results suggest that quantum fluctuations may be an essential ingredient for superconducting pairing in this compounds.

To obtain information about the influence of the periodic arrangement of Kondo “resonances” in our lattice, we now turn to the spatial dependence of the STM spectra. Obtaining topographies and STM differential conductance maps ($dI/dV$) with sub-Angström resolution, we find that the DOS modulates with the same periodicity as the atomic lattice (Fig. 4.4 C and D). Fitting individual spectra at each location with the Fano line shape, we find that the extracted ratio $q$, which describes the relative strength for tunneling into the Kondo resonance and the spd bands, shows measurable variation on the atomic scale (Fig. 4.4E). Naïvely, we would expect $q$ to be maximal when the tip is over the U atoms. However, the orientation and shape of the atomic orbitals also plays a role in the tunneling into the Kondo resonance [113]. In fact, the spatial dependence of $q$ shows enhanced tunneling into the resonance when the tip is over the locations between the surface U atoms. A schematic of the orientation of the U’s $f$ orbitals at a cleaved surface, shown in Fig. 4.4B, provides a possible way to understand such spatial dependence.

4.4 Mean-Field Signature of Hidden Order Formation

As illustrated by the spectra in Fig. 4.3, the development of the HO has a dramatic influence on the Kondo-Fano resonance and contains key information on the electronic correlations responsible for this transition. In order to isolate the spectroscopic changes at the onset of the HO, we divide the spectra obtained at temperatures below $T_{HO} = 17.5$ K with the spectrum measured at 18 K just above the bulk HO transition, as shown in Fig. 4.5 A and B (see appendix B for details of the analy-
Figure 4.4: Kondo lattice. (A) Temperature dependence of the Kondo resonance width $\Gamma$ extracted from the fits in Fig. 4.3B. The red line represents the temperature dependence for a single Kondo impurity described in the text, which results in a Kondo temperature $T_K = 129 \pm 10$ K. (B) Crystal structure of URu$_2$Si$_2$ indicating the different atomic layers and a schematic of the orbitals that bond the Si atoms to the U atoms. (C) A high-resolution constant current topography of 44 atoms taken at 18 K. (D) Conductance map at 6 mV (Kondo resonance energy) corresponding to the topography in C showing atomic scale modulations. (E) The dimensionless $q(\vec{r})$ map on the same area as in C obtained by fitting the spectra at each location to a Fano line shape. The larger values of $q$ (indicating higher tunneling probability to the $f$-like states) lie in between the atomic sites as depicted by the black square. Reproduced from [21].
sis). The normalized spectra reveal the onset of a low-energy gap centered at an energy below the Fermi level. Whereas the presence of a gap associated with the HO has been indicated by previous thermodynamic [50,91] and spectroscopic measurements [103–105,114], our high-resolution data and their spatial dependence allows identification of several of its fundamental features.

A phenomenological way to characterize the HO gap, $\Delta_{HO}$, is to fit the spectra to a thermally convoluted DOS with a Bardeen-Cooper-Schrieffer (BCS) functional form, from which we can extract the magnitude and temperature dependence of $\Delta_{HO}(T)$.\footnote{We do not mean to associate the hidden order gap to superconductivity. The choice of a BCS functional form to fit the gap is simply a generic choice in the context of mean-field theories of phase transitions.} Following this procedure (Fig. 4.5 A and B), we extract $\Delta_{HO}(T)$, which evolves more rapidly than simple thermal broadening (see appendix B). However, as we approach the transition temperature, $\Delta_{HO}$ becomes comparable to thermal broadening, making the precise determination of the onset temperature difficult. Regardless, we find the temperature dependence of $\Delta_{HO}(T)$ to follow a mean-field behavior with an onset temperature of $T_{HO} \approx 16$ K (Fig. 4.5C). Broken symmetry at the surface is likely to influence the HO state and may account for the slightly reduced observed onset temperature relative to that of bulk measurements. An important aspect of the $\Delta_{HO}$ is the fact that it develops asymmetrically relative to the Fermi energy and it shifts continuously to lower energies upon lowering of the temperature (Fig. 4.3 C and D). We quantify the changes to $\Delta_{HO}$ and its offset by fitting the data to a BCS function form with an offset energy relative to $E_F$ (Fig. 4.3 C and D and Fig. 4.5D; see the caption of Fig. 4.5).

The low temperature extrapolation, $\Delta_{HO}(0) = 4.1 \pm 0.2$ meV, yields the value of $2\Delta_{HO}(0)/k_B T_{HO} = 5.8 \pm 0.3$, which together with the value of the specific heat coefficient $\gamma_c = C/T$ for $T > T_{HO}$ (8) within the BCS formalism results in a specific heat jump at the transition of $\Delta C = 6.0 \pm 1.3$ JK$^{-1}$ mol$^{-1}$, consistent with previous measurements [90,91,95]. The partial gapping of the Fermi surface observed in our spectra also corroborates the recently observed gapping of the incommensurate
Figure 4.5: Temperature dependence of the HO gap. (A and B) The experimental data below $T_{HO}$ divided by the 18 K data. The data are fit to the form $D(V) = (V - V_0 - i\gamma) / \sqrt{(V - V_0 - i\gamma)^2 - \Delta^2}$, which resembles an asymmetric BCS-like DOS with an offset from the Fermi energy $E_F$. $V_0$, $\gamma$, and $\Delta$ are the gap position (offset from the Fermi energy), the inverse quasi-particle lifetime, and the gap magnitude, respectively. A quasi-particle lifetime broadening of $\gamma \approx 1.5$ mV was extracted from the fits. (C) Temperature dependence of the gap extracted from the fits in A (Black Squares) and from a direct fit to the raw data of Fig. 4.3C (Blue Circles). Both results are comparable within the error bars. The transition temperature $T_{HO} = 16.0 \pm 0.4$ K is slightly lower than the bulk transition temperature presumably as a consequence of the measurement being performed on the surface. (D) Temperature dependence of the gap position $V_0$ extracted from the fits. The line is a guide to the eye. Reproduced from [21].
spin excitations by inelastic neutron scattering experiments [95]. Finally, the spectrum develops additional, sharper features within $\Delta_{HO}$ at the lowest temperatures (Fig. 4.5B). Such lower energy features may be related to the gapping of the commensurate spin excitations at the antiferromagnetic wave vector below $T_{HO}$ also seen in inelastic neutron scattering at an energy transfer of about 2 meV [94–96].

4.4.1 Spatial Structure of the Hidden Order Gap

The spatial variation of the STM spectra provides additional information about the nature of redistribution of the electronic states that gives rise to $\Delta_{HO}$. In Fig. 4.6, we show energy-resolved spectroscopic maps measured above and below $T_{HO}$, all of which show modulations on the atomic scale. The measurements above $T_{HO}$ show no changes in their atomic contrast within the energy range where the $\Delta_{HO}$ is developed. In fact, the modulations in these maps (Fig. 4.6 B-E) are because of the surface atomic structure but occur with a contrast that is opposite to that of the STM topographies of the same region (Fig. 4.6A). However, observation of reverse contrast in STM conductance maps is expected as a consequence of the constant current condition. Similar measurements below $T_{HO}$ are also influenced by the constant current condition, as shown in Fig. 4.6 GJ; nonetheless, these maps show clear indication of the suppression of contrast associated with $\Delta_{HO}$ at low energies (within the gap; see Fig. 4.6F) and the consequent enhancement at high energies (just outside the gap).

To isolate the spatial structure associated with $\Delta_{HO}$ and to overcome any artifacts associated with the measurement settings, we divide the local conductance measured below $T_{HO}$ by that above for the same atomic region, as shown in Fig. 4.6 L-O. Such maps for $|V| < \Delta_{HO}$ illustrate that the suppression of the spectral weight principally occurs in between the surface U atoms. These maps are essentially the spatial variation of the conductance ratios, shown in Fig. 4.5A. Therefore, consistent with the BCS-like redistribution of spectral weight, we find that conductance map ratios at energies just above $\Delta_{HO}$ illustrate an enhancement between the surface U atoms. Quantifying these spatial variations further, we also plot the correlation between the
Figure 4.6: Atomic origin of the HO. (A) A constant current topography at $T = 18$ K corresponding to 55 atoms. Spatial conductance maps on the area in A at different bias voltages $V$ obtained at 18 (B-E) and 6.6 K (G-J). The junction is stabilized at 100 mV and 100 pA. All conductance maps are normalized to their mean value to emphasize the atomic contrast. The maps display an atomically periodic modulation. (F) Average $dI/dV$ spectra at 18 and 6.6K. The arrows indicate the energies where the conductance maps are performed. (LO) Division of the $G(r, V, T = 6.6$ K) maps with the $G(r, V, T = 6.6$ K) maps showing a contrast reversal of the conductance when moving from outside the gap (L; $V = 6$ mV) to within the gap (M and N). The loss of the spectral weight in the gap and the transfer to higher energies occurs principally between the surface U atoms as is shown by the white square boxes. (K) Correlation of the conductance maps with the atomic locations above and below the HO temperature showing a dramatic change of correlation (change of contrast) within the gapped region between the surface U atoms. Homogeneous gapping should result in no change of correlation. Reproduced from [21].
conductance map ratios and the atomic locations above and below $T_{HO}$ (Fig. 4.6K) to show that $\Delta_{HO}$ is strongest in between the surface U atoms – i.e., at the same sites where tunneling to the Kondo resonance is enhanced (Fig. 4.4E). Our observation that the modulation in the tunneling amplitude into the Kondo resonance correlates with the spatial structure of the HO gap shows that the two phenomena involve the same electronic states.

4.5 Summary of URu$_2$Si$_2$

Our finding of an asymmetric mean-field-like energy gap would naively suggest the formation of a periodic redistribution of charge and/or spin at the onset of the HO because of Fermi surface nesting. However, consistent with previous scattering experiments [91, 94–96], we find no evidence for any conventional density wave or charge ordering in our experiments. Recently, it has been suggested that the opening of a gap may be a consequence of hexadecapole ordering emerging from the crystal field splitting of U’s 5$f^2$ states [101]. Whereas the experimentally observed gap can be the consequence of the hexadecapole ordering, no signatures of the higher temperature crystal field splitting was observed in our data. Other proposals indicate that the development of the gap is the effect of a hybridization gap [69, 70]. Though a conventional hybridization gap should not manifest itself as a second-order phase transition with a mean-field-like order parameter, an exotic form of hybridization accompanied by orbital ordering can be a possible candidate for the HO phase. Regardless, our spatial mapping, which reveals the enhancement of the Kondo-Fano signature between the surface U atoms and the relatively stronger HO gap at these same locations, provides additional information to identifying the electronic states responsible for these phenomena and therefore the understanding of the nature of the HO phase.
Chapter 5

Charge Ordering in the Cuprates

Understanding the properties of the copper-based high-temperature superconductors has remained one of the most puzzling problems in all of condensed matter physics. In these materials, modification of the chemical composition by hole-doping of the CuO$_2$ plane can lead to the development of superconductivity reaching an optimal value at a value of hole concentration near $x = 0.16$ (hole/Cu) (see Fig. 1.4). Still, it is not clear why superconductivity is weakened as the hole-doping concentration is decreased from its optimal value. One possibility is the presence of a coexisting order which competes with superconductivity. Recently, there has been an escalating amount of evidence that suggests the presence of charge ordering (CO) phenomena in underdoped cuprates coming from different probes and materials. Quantum oscillations [26,115], Hall resistance [25], and nuclear magnetic resonance (NMR) [116] measurements on Y-based cuprates point to Fermi surface reconstruction and electronic ordering induced by the application of high magnetic fields.

Figure 5.1(a) summarizes the quantum oscillations experiments where underdoped Y-based systems show a small Fermi surface, while measurements on the Tl-based overdoped cuprates show a large Fermi surface [117]. These measurements have been interpreted as evidence for Fermi surface reconstruction in the underdoped cuprates. A natural origin for reconstruction is band-folding induced by the presence of an ordered potential. Therefore, these experiments indirectly suggest the presence of CO
in underdoped cuprates. Further support for Fermi surface reconstruction comes from measurements of the Hall coefficient, from which the sign of the charge carriers can be inferred. For samples near $x = 1/8$ doping, a change of the Hall sign from hole-like to electron-like is observed upon cooling [25]. These results have been interpreted in the following way. At high temperatures the band structure is characterized by large hole-like barrels, similar to what is observed in overdoped samples. Upon lowering of temperature a CO onsets, which results in folding of the band structure. Depending on details of the CO this folding can result in the formation of electron pockets, which would then explain the change in the sign of the Hall coefficient at low temperatures. Of course the measurements mentioned above do not provide direct evidence for charge ordering.

A first hint into the presence of CO came from NMR measurements, which can be sensitive to the electronic states through the hyperfine interaction. Those experiments were performed on ortho-II $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ samples, whose structure leads to two different Cu-sites in the CuO$_2$ plane. Naturally, these two sites result in two distinct lines in the NMR spectrum. In the presence of magnetic fields, lowering of temperature causes one of these lines to split, which suggests the presence of an additional charge modulation in real space [116]. The temperature onset of this apparent charge ordering coincided with the temperature where the Hall coefficient changes signs (see Fig. 5.1(b)) suggesting a connection between the two. Still, the experiments described above are performed in the presence of high-magnetic fields, which raises the question of whether CO is relevant to the zero-field cuprate phase diagram. Furthermore, none of the above experiments can actually provide the periodicity of the inferred CO.

More recently, x-ray scattering experiments, which can be directly sensitive to charge ordering, have discovered that in samples with the hole concentration near $x = 1/8$ there is a competing charge organization with an incommensurate ordering vector ($\approx 3.3a^*$ periodicity) in highly ordered Y-based cuprates [15, 16] (see Fig. 5.1 (c-d)). Additionally, in La-based cuprates, a suppression of $T_c$ near $x = 1/8$ doping
Figure 5.1: (a) Schematic of the high-$T_c$ cuprate phase diagram as a function of nominal hole doping ($p$) denoting the electronic structure on the overdoped and underdoped side, measured by quantum oscillation experiments at high magnetic fields. The superconducting region at zero magnetic field is schematically represented by a dashed boundary. Circles represent the relative size of Fermi surface orbits observed in quantum oscillation experiments. A small Fermi surface for underdoped samples was interpreted as a consequence of order-induced Fermi surface reconstruction. The figure is reproduced from [117]. (b) Phase diagram of underdoped YBa$_2$Cu$_3$O$_{y}$. The charge ordering temperature $T_{charge}$ (defined as the onset of the Cu2F line splitting in NMR experiments; blue open circles) coincides with $T_0$ (brown plus signs), the temperature at which the Hall constant $R_H$ changes its sign. $T_0$ is considered as the onset of the Fermi surface reconstruction [118]. The continuous line represents the superconducting transition temperature $T_c$. The dashed line indicates the speculative nature of the extrapolation of the field-induced charge order. The magnetic transition temperatures ($T_{spin}$) are from muon-spin-rotation ($\mu$SR) data (green stars). The figure is reproduced from [116]. (c) X-ray diffraction evidence for charge ordering in YBa$_2$Cu$_3$O$_{6.67}$. Scan along $(h,0,0.5)$ for 2K and 0, 17T magnetic fields. Here the incommensurate charge order at $h \approx 0.3$ appears reflected from the $h = 2$ Bragg peak at $h \approx 1.7$ (d) Temperature dependence for the charge order peak for different magnetic fields showing that it competes with superconductivity. Figures (c-d) are reproduced from [16].
(hole/Cu) coinciding with the organization of charge into stripe-like patterns with four lattice constants \((4a^*)\) periodicity, already provided early evidence for a CO which competes with superconductivity \([13, 119]\) at zero-magnetic field. These experiments raise the question of whether each family of cuprates has its own charge organization pattern or whether there is a universal charge ordering mechanism common to all underdoped cuprates [though crystalline structures in each compound may modify details of the resulting ordering patterns \([120, 121]\)]. If there is a connection between the observed COs in different compounds, the next important issue is to understand the mechanism by which this phenomenon competes or is intertwined with high-\(T_c\) superconductivity. The answer to these questions will help determine the relation of CO to quantum oscillation experiments at high magnetic fields in Y-based cuprates \([26, 115]\), or to the field-induced CO behavior observed in nuclear magnetic resonance (NMR) experiments \([116]\). Moreover, identifying the portions of the cuprate Fermi surface involved in the CO would determine its connection to the pseudogap phase, which is characterized by anti-nodal gapping.

To address these questions, we have carried out STM spectroscopy and resonant elastic x-ray scattering (REXS) measurements on underdoped Bi-2212 samples. Bi-2212 system is the only material system among the cuprates for which there is detailed spectroscopic information on the Fermi surface and the occupied electronic states as a function temperature and doping from angle-resolved photoemission spectroscopy (ARPES) performed over the last two decades \([122–124]\). Yet, ARPES measurements have not shown any evidence of band folding associated with CO along the Cu-O bond direction in this system \([40, 123, 125]\). STM studies have long reported evidence of spatial modulation of electronic states in Bi-based cuprates \([29, 37, 126–128, 128–130]\), but evidence for CO in these experiments is often obfuscated by the disorder-induced energy-dispersive quasiparticle interference (QPI) effect \([29, 30, 131]\). Analysis of STM conductance maps over a range of energies has been used to provide evidence for fluctuating charge organization in Bi-2212 below \(T^*\), with strongest enhancement near 1/8 doping – the same doping range where charge organizations have been seen in
Y- and La-based cuprates [29]. However, it remains a challenge to clearly separate signatures of CO from those of QPI in STM experiments, and more importantly, to corroborate the surface-sensitive measurements with bulk sensitive experiments. Here we provide high-resolution energy-revolved STM spectroscopy experiments that clearly distinguish between QPI and CO features as a function of doping and temperature. Remarkably, this CO signature and its competing nature are also detected in our temperature-dependent REXS measurements, similar to the recently observed charge density wave (CDW) in Y-based cuprates [15, 132, 133]. Altogether, the considerable similarities between CO phenomena in underdoped Bi-2212 and in Y- and La-based systems suggest a universal CO organization competing with superconductivity in the cuprates. Furthermore, by providing spectroscopic information about both occupied and unoccupied electronic states from STM measurements, we not only explain the absence of CO signatures in ARPES studies, but also show a possible understanding of how CO impacts quantum oscillation and other experiments in high magnetic fields [25, 26, 115, 116].

5.1 Charge Ordering in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

Figure 5.2A shows the geometry of the combined experimental approach for examining CO in underdoped Bi-2212 samples, where we contrast the discrete Fourier transform (DFT) of STM conductance maps with bulk scattering results from REXS. A typical example of an STM conductance map is shown in Fig. 5.2B for a UD45 (underdoped Bi-2212, $T_c = 45$ K) sample at 30 K. The DFT of the conductance map (Fig. 5.2C-D) shows a strong peak of wavevector $q = (\pm \delta, 0)2\pi/a^*$ and $(0, \pm \delta)2\pi/b^*$, and $\delta \approx 0.3$, along the Cu-O bond directions, corresponding to the real space modulations in Fig. 5.2B. Figure 5.2E-F shows the results from REXS measurements (incident photon energy of $931.5$ eV, resonant with the Cu $L_3$-edge) on the same sample, as a function of the component of momentum transfer along $\pm a^*$ directions, respectively (see Fig. 5.2A and section 5.3.1 for more details). Remarkably, the low temperature
Figure 5.2: (A) REXS experiments were performed with vertically polarized photons ($\sigma$) in a horizontal scattering geometry and yield momentum space information corresponding to the real space modulations seen in real space by STM (front panel in A), or, more directly, to the DFT of the STM real space data (back panel in A). We use the tetragonal crystal structure where $a^* = b^* \approx 3.8$ Å represent the nearest neighbor Cu-Cu distance. (B) STM conductance map (15 meV, normalized to its spatial average) on a UD45 sample measured at 30 K showing real space modulations of the local electronic density of states. Inset shows the direction of the Cu-O-Cu bond direction relative to the measurement. White bar represents 140 Å. (C) DFT of the conductance map in (B), where the corners of the image represent the atomic Bragg peaks at ($\pm 2\pi/a^*$, 0) and (0, $\pm 2\pi/b^*$). The DFT is normalized to its average value and the color scale represents the power spectral density (PSD). The $\delta = 0.3$ feature (marked by the blue arrow), corresponds to the real space modulations seen in (B). (D) Line-cut of the energy-averaged (0 to 50 meV) DFT along the Cu-O bond direction showing a clear peak at $\delta = 0.30$. Dashed line represents fit to a Lorentzian plus a background (see appendix C). (E) REXS $\delta$-scans (see section 5.3.1) for positive (E) and negative (F) $\delta$ at low (blue) and high (red) temperatures, showing a clear enhancement near $\delta = 0.3$ at low temperatures.
REXS measurements (Fig. 5.2E-F) show weak peaks at the same incommensurate wavevector ($\delta \approx 0.3$) as those in the DFT of the STM conductance maps (Fig. 5.2C-D). Insets of Fig. 5.2E-F show the background subtracted 10 K data, where the dashed line represent a Lorentzian fit to the data (see section 5.3.1 for details of the analysis). Our REXS results establish, for the first time, that the STM modulations on the surface of Bi-2212 sample are in fact due to a CO that can also be detected in the bulk.

5.2 Energy Evolution of Modulations

The weak intensity of the CO peak in our REXS measurements and their broad widths (full width at half maximum $2\Gamma = 0.05\text{rlu}; \approx 5$ periods of CO modulation), suggest a rather short-range or fluctuating order. However, the REXS measurements, being energy integrated, cannot differentiate between elastic and quasi-elastic scattering. To determine whether the CO is static or fluctuating, we examine the energy dependence of the STM conductance maps. In doing so, we expect to differentiate between CO effects, which are expected to have an energy-independent wavevector, from those related to QPI, which are expected to disperse with energy. However, great care must be taken when analyzing energy-static modulations with the STM, since they are susceptible to the so-called setpoint effect.

5.2.1 Setpoint Effect

In STM, a differential conductance map at a pre-set current $I_S$ and pre-set bias $V_S$ is given by

$$\frac{dI}{dV}(\vec{r}, z, \omega = eV) = \frac{eI_s N(\vec{r}, \omega)}{\int_0^{eV_S} N(\vec{r}, \omega) d\omega}$$ (5.2.1)

where $N(\vec{r}, \omega)$ represents the electronic density of states at the spatial position $\vec{r}$ and energy $\omega$. The denominator in Eq. 5.2.1 corresponds to the local density of states integrated within the Fermi energy and the set-point bias and represents what
is known as the STM set-point effect. Since $N(\vec{r}, \omega)$ is expected to vary locally, the denominator of Eq. 5.2.1 is also expected to vary locally. In most cases the spatial dependence of $N(\vec{r}, \omega)$ follows the topograph and the effects of the set-point mirror in the atomic Bragg peaks. However, if strong modulations with an arbitrary wavevector exist at a specific energy $\omega = \omega_1$ lying within the set-point bias, then these modulations could show up in the experimentally measured $dI/dV(\vec{r}, z, \omega = eV)$ for a wide range of energies through the denominator of Eq. 5.2.1. In other words, a modulation of the real density of states of the material at $\omega_1$ could appear at energies $\omega_2 \neq \omega_1$ in the $dI/dV$ measurement. Since the denominator of Eq. 5.2.1 is controlled by the set-point bias $V_s$, we can experimentally probe the effect of the set point on the measured charge ordering signal.

Figure 5.3A-C shows the $E-\delta$ structure of the charge ordering obtained directly from the DFTs for a UD35 sample measured at 30 K, for different set-point biases. The central difference among the different data sets is the non-dispersive feature near $\delta = 0.3$. At $V_s = +200$ mV there are three branches of non-dispersive modulations near $\delta = 0.3$: $E > +75$ mV, $E < -50$ mV and $0 < E < 50$ mV. At $V_s = +400$ mV the high energy branches become weaker, suggesting that they are systematics of the measurement. Notice, however, that the low-energy branch ($0 < E < 50$ mV) seems unaltered by the change in $V_s$, indicating that it represents a real modulation of $N(\vec{r}, \omega)$. Since the low-energy branch is only present above the chemical potential, it should not influence $\int_0^{eV_s} N(\vec{r}, \omega)d\omega$ for $V_s < 0$. As a control experiment, in Fig. 5.3C we plot the same data measured with $V_s = -300$ mV. The observation of only the low-energy $0 < E < 50$ mV, with no shadows, confirms that the non-dispersive $\delta = 0.3$ modulations exist only above the Fermi energy within $0 < E < 50$ mV. Since it is expected that features associated with set-point effect systematics to be weaker than real modulations of $N(\vec{r}, \omega)$, we further normalize each energy-specific real space conductance map to its spatially averaged value prior to the DFT operation. Figures 5.3D-E, produced through this analysis, clearly show that the low energy branch is
Figure 5.3: (A-C) $E$-$\delta$ structure of the LDOS modulations along the Cu-O bond direction obtained directly from the DFT of the conductance maps. (D-F) similar to A-C but with the real-space conductance maps normalized to the spatially averaged energy spectrum. (G-I) Z-maps constructed from Eq. 5.2.2. The Z-map construction was reflected about zero-energy to illustrate its loss of information regarding particle-hole symmetry.
the dominant feature and therefore reinforces our identification of this feature as real and the other branches as systematics.

It is important to also note that the denominator in Eq. 5.3 can be removed by another post-processing analysis which has been widely used in the STM literature, the so-called Z-map, or Z-ratio. It is constructed as a ratio of positive and negative conductance maps, therefore canceling the denominator which contains the shadow signals.

\[ Z(\vec{r}, \omega) = \frac{\frac{dI}{dV}(\vec{r}, \omega = +eV)}{\frac{dI}{dV}(\vec{r}, \omega = -eV)} \]  

(5.2.2)

Indeed, Figs. 5.3G-I show that all the high energy branches disappear in the Z-map. Unfortunately, it can also be seen that the Z-map analysis is highly detrimental to the finer features observed in the raw data. For example, quite obviously, the information regarding particle-hole symmetry is lost in this analysis. Altogether, Fig. 5.3 shows that the \( \delta = 0.3 \) feature is a low-energy particle-hole asymmetric feature, absent at negative energies, and therefore must be measured with a choice of negative set-point bias. All the measurements shown below were performed with \( V_s = -300 \text{ mV} \).

### 5.2.2 Doping Dependence

Figure 5.4 shows the energy evolution of the features in the DFT of the conductance maps, along the Cu-O bond direction, measured at 30 K for a range of doping, from optimally doped (OP91) to strongly underdoped (UD15) samples. In the optimally doped sample (Fig. 5.2A) at temperatures well below \( T_c \), the energy-wavevector structure along the Cu-O bond direction shows no sign of CO. Instead, it shows an energy-dispersing particle-hole symmetric wavevector originating from disorder-induced scattering interference of superconducting Bogoliubov-de Gennes quasiparticles (BdG-QPI) \[29, 37, 130, 134\]. This particle-hole symmetry is the hallmark of superconducting quasiparticles. Reducing the doping towards the underdoped regime (Fig. 5.4B-G), we find that the BdG-QPI features are systematically weakened, while a separate non-dispersive modulation with a relatively sharp wavevector appears and
Figure 5.4: (A-G) Energy-momentum structure of the modulations seen in STM along the Cu-O bond direction, extracted from line cuts along the \((2\pi/a^*, 0)\) direction of the DFTs measured at 30 K for different doping levels (see appendix C for details of the samples). (H) \(\delta\) location of the CO feature as a function of doping, extracted from energy integrated \(\delta\) cuts (see appendix C). The error bars in (H) represent the half width at half maximum of the extracted peaks.

strengthens. This wavevector (see for example \(\delta = 0.3\) in Fig. 5.4E-G correspond to the CO wavevector we find in the REXS measurements (Fig. 5.2E-F).

To better visualize the particle-hole asymmetry of the charge modulation in Bi-2212, in Fig. 5.5A we show the intensity of the \(E-\delta\) structure in the DFT, integrated over positive ([0 to 50] meV blue curves) and negative ([0 to \(-50\)] meV red curves) energies, as a function of momentum for all the different samples. Depending on the momentum, the data contains information from both BdG-QPI and CO modulations. Remarkably, all samples show a striking particle-hole asymmetry only in the momentum range around \(\delta = 0.3\) for UD15, UD35, UD45 and \(\delta = 0.25\) for UD52, UD61, UD73, corresponding to the charge ordering phenomena. The optimally doped sample, OP91, displays particle-hole symmetry over the entire momentum range, expected from the BdG-QPI. A blow-up of the data around the critical momenta for all the samples is shown in Fig. 5.5B.
Energy cuts of the intensity of the $E\delta$ structure for two constant momenta $\delta = 0.2$ and $\delta = 0.30$ (0.25). Curves were normalized to the maximum of the two curves.

Figure 5.5C displays energy cuts of the intensity of the $E\delta$ structure for two constant momenta $\delta = 0.2$, corresponding to a BdG-QPI wavevector and $\delta = 0.30$ (0.25) corresponding to the critical charge ordering wavevector. For $\delta = 0.2$, the data show a particle-hole symmetry for positive and negative energies as expected from BdG-QPI, whereas for the critical CO wavevector, the data show a clear asymmetry indicating that the CO exist above the Fermi energy in all these samples.

The momentum widths of this CO peak ($\approx 0.04$ rlu), which agree well with our REXS measurements, are larger than those recently observed in the Y-based cuprates [15]. Our energy resolved STM conductance maps, further show that these CO modulations only appear over a range of energies (0 to 50 meV) above the chemical potential, a behavior not expected in a conventional CDW order. Despite being broad in energy, we find the intensity of the CO feature to be centered at approximately +20 meV above the chemical potential at all doping levels, thereby indicating that CO is likely not static but rather fluctuating. The particle-hole asymmetry of the CO
feature in the STM data clearly distinguishes it from the BdG-QPI signals and more importantly explains the absence of such CO features in the ARPES studies.

The CO wavevectors extracted from our STM measurements show distinct similarities to other families of the cuprates. Figure 5.4H shows that for a hole concentration of $x < 0.1$, the incommensurate CO wavevector $\delta \approx 0.3$ matches the CDW observed in the Y-based cuprates, whereas for $x > 0.1$, the nearly commensurate wavevector $\delta \approx 0.25$ is very similar to that found in the stripe phase of La-based cuprates. Though an incommensurate $\delta$ and its decrease with doping are expected from a Fermi surface nesting scenario, the narrow doping range over which the jump in $\delta$ occurs in Bi-2212 may be an indication of possible competition between two different stable forms of CO in the cuprates. More broadly though, the fact that CO in Bi-2212, in a range of doping without any structural distortion, can be either similar to Y-based or La-based cuprates demonstrates our key point that CO is a ubiquitous phenomenon to all underdoped cuprates.

5.3 Temperature Dependence

Further evidence which connects measurements on Bi-2212 to other cuprates and probes the interplay between CO and superconductivity comes from examining the temperature dependence of the REXS and STM data.

5.3.1 REXS

The REXS experiments reported here were performed with photon energies near the Cu-$L_3$ absorption edge (931.5 eV), which is resonant to the $2p_{3/2} \rightarrow 3d$ transitions, at the UE46-PGM1 beam line of the Helmholtz-Zentrum Berlin at BESSY-II. To maximize intensity, vertically polarized photons in a horizontal scattering geometry were used (see Fig. 5.2A). The 2-circle diffractometer was equipped with a continuous flow He cryostat reaching a base temperature of 10 K. The $\delta$ values reported here
Figure 5.6: For each temperature, theta scans were performed ten times and averaged to obtain a better signal-to-noise ratio. Each curve is shifted by a constant to account for a temperature dependent offset of the background.

represent the component of momentum-transfer parallel to the Cu-O planes, obtained from theta scans at fixed detector angle 167°.

Figure 5.6 shows the temperature-dependent enhancement near $\delta = 0.29$. It can already be seen in the raw data that this peak evolves most rapidly for temperatures between 100 K and 200 K. Due to the small amplitude of the signal, it is critical to properly characterize the background in the rocking scans. Because the background can be dependent on the position of the beam on the sample, extra caution was taken during the temperature dependent measurements. The sample position was adjusted at each temperature in order to correct for thermal drift and therefore maintain the beam position on the sample constant throughout all temperatures. Nevertheless, due to small changes in the background as a function of temperature, the fitting procedure outlined in Fig. 5.7 is used to extract the CO peak from the background. A fourth-order polynomial fit is performed on the tails ($\delta < 0.22$ and $\delta > 0.37$) and subtracted from the total signal in order to isolate the CO peak.
Figure 5.7: Background is fitted to a fourth-order polynomial for $\delta < 0.22$ and $\delta > 0.37$. A Lorentzian function is fitted to the data after background subtraction. Notice the small kink in the raw data above $\delta = 0.22$ signaling the presence of the peak on top of the smooth background.

Figure 5.8A displays the background subtracted REXS data for the UD45 sample at different temperatures, showing a peak in the intensity at the CO wavevector ($\delta \approx 0.30$). Fitting the peaks to Lorentzians we are able to extract intensity as a function of temperature. The result in Fig. 5.8B displays very similar behaviors between the REXS data from this Bi-2212 sample and resonant x-ray scattering experiments on underdoped Y-based cuprates [15, 132, 133]. In both systems, CO onsets at relatively high temperatures and peaks near $T_c$, thereby demonstrating that the appearance of superconductivity suppresses the propensity towards charge organization.

5.3.2 STM

A similar suppression of CO with the onset of superconductivity can be observed in the temperature dependence of the energy-wavevector structure of our STM data, as shown in Fig. 5.9 for a UD75 sample. The CO signature above the chemical potential near $\delta \approx 0.25$ for this sample, which is very strong at temperatures just above $T_c$
Figure 5.8: (A) Background subtracted REXS $\delta$-scans (for positive $\delta$) for a UD45 sample at selected temperature, showing the evolution of the CO peak near $\delta = 0.3$. The lines are Lorentzian fits to the data. (B) The REXS intensity extracted from the peak maxima in (A) as a function of temperature. The vertical dashed line corresponds to $T_c = 45$ K.
Figure 5.9: (A-D) Energy-momentum structure of the modulations seen in STM along the Cu-O bond direction, extracted from line cuts along the \((2\pi/a^*, 0)\) direction of the DFTs for a UD75 sample measured at selected temperatures. The data show the opposite temperature dependence between the particle-hole symmetric BdG-QPI and the particle-hole asymmetric CO. (E) Schematic layout of the Fermi surface in Bi-2212 UD75 sample. The green and white segments represent the Fermi arc as determined by ARPES below and above \(T_c\), respectively [19] (see appendix C). The vertical lines (also reproduced horizontally in A-D) correspond to QPI wavevectors connecting the Fermi surface (consistent with ARPES [18], see appendix C) at different regions.

(Fig. 5.9A), is nearly absent when the sample is cooled to roughly \(0.15T_c\) (Fig. 5.9D). Instead, at low temperatures, as Fig. 5.9D shows, the STM data for this weakly underdoped sample recovers the particle-hole-symmetric dispersing features that are due to BdG-QPI, consistent with d-wave superconducting gap [135].

Figure 5.10A shows the intensity of the \(E-\delta\) structure measured on UD75, integrated over positive ([0 to 50] meV blue curves) and negative ([0 to −50] meV red curves) energies, as a function of momentum for different temperatures. It is clear that particle-hole asymmetry is strongest in the momentum range around \(\delta = 0.25\) corresponding to the charge ordering phenomena. Figure 5.10C displays energy cuts of the intensity of the \(E-\delta\) structure for \(\delta = 0.2\), corresponding to a BdG-QPI wavevector and \(\delta = 0.25\) corresponding to the CO wavevector. For \(\delta = 0.2\) below \(T_c\), the data show a particle-hole symmetry for positive and negative energies as expected from BdG-QPI, whereas for \(\delta = 0.25\), the data show a clear temperature evolution from particle-hole symmetry at low temperatures (10 K) to particle-hole asymmetry above \(T_c\) (80 K). The temperature evolution shown in Fig. 5.10 is strikingly similar to the doping evolution (at constant temperature) seen in Fig. 5.5. Altogether the data in Figs. 5.9 and 5.10 not only clearly show superconductivity wins over CO, but it
Figure 5.10: A $E$-$\delta$ structure in the DFT, integrated over positive ([0 to 50] meV blue curves) and negative ([0 to $-50$] meV red curves) energies, as a function of momentum for a UD75 sample for different temperatures. (B) Same as in A but in a narrower range around $\delta = 0.25$. All the curves in A and B are normalized to their local maximum value near $\delta = 0.25$. (C) Energy cuts of the intensity of the $E$-$\delta$ structure for two constant momenta $\delta = 0.2$ and $\delta = 0.25$. Curves were normalized to maximum of the two curves.

also provides key information about this competition in momentum space, which we discuss next.

Previous analyses of impurity-induced QPI data at low temperatures, such as that in Fig. 5.9D, associated the observed dispersing wavevectors in DFTs along the Cu-O bond direction with the scattering of BdG quasiparticles between points on the Fermi surface. Figure 5.9E shows a schematic Fermi surface for a Bi-2212 UD75 sample together with the different QPI wavevectors connecting different segments of the Fermi surface, starting from near the antinodes at large energies (small $\delta$) to points near the nodes at low energies (large $\delta$) [37, 130, 134, 135]. Contrasting the
high and low temperature STM data shows that the CO wavevector dominates the high-temperature data in a region of energy-wavevector space that is associated with quasiparticle scattering away from the anti-node at low temperatures (Fig. 5.9). This finding demonstrates that the formation of the CO, which is favored with increasing temperature, influences the Fermi arcs where the d-wave superconductivity resides.

5.4 Summary

Our spectroscopic evidence that CO competes with superconductivity for spectral weight on the Fermi arcs imply that this phenomenon is secondary to the formation of the pseudogap phase, which gaps the anti-nodal portion of Fermi surface in underdoped cuprates. Furthermore, based on this finding, we expect that the suppression of the gap near the d-wave nodes with a magnetic field would enhance charge ordering in a similar fashion as temperature. This observation provides a natural explanation for how magnetic fields, which are modest in magnitude when compared to anti-nodal pseudogap energy scale, can result in the Fermi surface reconstruction observed in experiments performed in the presence of magnetic field [25,26,115,116]. While much remains to be understood about the underlying mechanism of charge ordering, its universality across cuprate families demonstrated here establishes it as a critical component for understanding the unconventional electronic properties and superconductivity of high-$T_c$ cuprates.
Chapter 6

Detection of Electronic Nematicity
Using the STM: A Cautionary Tale

The charge ordering in the underdoped cuprates discussed in chapter 5 requires that the underlying lattice translational symmetry be broken. Notice, however, that stripe order breaks not only translational but also rotational symmetry due its unidirectionality. Indeed, there also exists the possibility that rotational symmetry is broken without the loss of translational symmetry breaking, and such states are called nematic.\(^1\) In particular, electronic nematic phases, where electronic states undergo a spontaneous four-fold \(C_4\) to two-fold \(C_2\) symmetry breaking, have been proposed to occur in various correlated electron systems such as cuprates, iron-based superconductors, and heavy fermion materials [32,131,137–140]. Additionally, nematicity was recently claimed to have been detected in STM conductance maps of the pseudogap states of Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\). This chapter is dedicated to a careful analysis of how STM images periodic structures and how the tip geometry influences such imaging. For this purpose, we are challenged to revisit the usual assumptions made when analyzing tunneling data (see chapter 2), and find that Eq. 2.1.3, is no longer adequate in the context of rotational symmetry breaking. Hopefully this chapter exemplifies the need to always be questioning one’s assumptions, no matter how well established they

\(^1\)The name is borrowed from the field of liquid crystals [136].
may appear to be. This chapter is based on a paper I coauthored which appeared in Physical Review B in 2013 [22].

Below we show, through model calculations and experimental measurements on three correlated electron materials (CeCoIn$_5$, Bi-2212, and URu$_2$Si$_2$), that a tunneling interference effect within an STM junction composed of a realistic tip (with some spatial anisotropy) can result in an artificial energy-dependent symmetry breaking of the STM conductance maps. This phenomenon can occur even when the STM topograph taken with the same tip appears to be symmetric. We demonstrate that previously reported two-fold symmetric conductance maps in high-$T_c$ cuprates [33, 141] are not evidence for rotational symmetry breaking ($C_4$ to $C_2$) originating from a nematic phase in these materials, but are rather due to the interference effect within an STM junction. In Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, systematic measurements with different tips on the same area of the sample, are also used to clearly demonstrate the lack of nematic order, without relying on any pseudogap-specific assumptions about the tunneling process. Nevertheless, the interference effect within the STM junction can be used as a sensitive tool to detect changes in the quasiparticle band structure as a function of energy.

6.1 Previous Studies of Rotational Symmetry Breaking in Correlated Systems

Due to possible twined domain boundaries, STM (a local probe) has been proposed as the method of choice for the detection of nematic order. Indeed, rotational symmetry breaking has been vastly probed by STM studies over the last five years [33, 141–147]. These results can be coarsely classified into two kinds: those which observed domain boundaries, and those which did not. Of the former there are many examples in the literature, such as the structural [143] and electronic smectic [141] orderings in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, and electronic nematic ordering in iron-based superconductors [142, 147]. As it must be with any experiment that aims to detect
any kind of symmetry breaking, not only rotational, great care must be devoted into making sure that any observed symmetry breaking signal originates solely from the sample. Figure 6.1 shows an example of a boundary between domains of orthogonal nematicity as imaged by the STM [148]. Quite clearly, since the same tip is used across the boundary, the difference between the domains must be inherent to the sample under study. The rule of thumb is simple: the observation of a domain boundary implies that the observed symmetry breaking is not the result of an anisotropic tip apex geometry.

Nevertheless, the absence of an observed domain boundary, does not rule out electronic nematicity. In fact, Lawler et al. [33], and Mesaros et al. [141] in a subsequent study, explored this possibility and interpreted the rotational symmetry breaking in the STM data as evidence for an electronic nematic state inside the pseudogap phase.
of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. Below we decompose their interpretation and develop a better understanding of the spatial structure of tunneling matrix element in Eq. 2.1.1.\(^2\)

6.2 Spatial Structure of SI-STM

The naïve expectation has been that the influence of the STM tip’s geometric structure is limited to inducing an easy-to-detect anisotropy in STM topographs or to influence energy-resolved STM differential conductance ($dI/dV$) maps in an energy independent manner. We start by considering how STM probes the electronic structure of a sample’s surface.

Most discussions of STM data assume a metallic tip (energy-independent density of states), and approximate the STM differential conductance $dI/dV$ (at small bias) as the spatial convolution ($\ast$) of the tip ($\rho_t$) and sample ($\rho_s$) densities of states (DOS) [39]:

$$\frac{dI}{dV}(eV, \vec{r}) \propto \rho_t \ast \rho_s(eV) \quad (6.2.1)$$

with $\rho_s(eV) = \sum_s |\psi_s|^2 \delta(E_s - E_f - eV)$. Then under the usual assumption of an isotropic tip, the conductance maps are simply proportional to the local DOS of the sample.

Within this model of STM measurements the topograph is constructed from integrating such maps between the Fermi level up to the tip-sample bias. In many studies, the topograph is presented as a visualization of structural features (step edges, point defects, atomic structures) and the $dI/dV$ as direct imaging of the DOS. Based on this, Lawler et al. assumed that the absence of rotational symmetry breaking in the topograph implied an isotropic tip. If true, this interpretation implies that the symmetry breaking observed as a function of energy in the conductance maps must be

\[^2\]The rest of this chapter is recommended to any researcher in the field of STM. The following requires no more than a good understanding of quantum mechanics at the undergraduate level.
evidence for electronic nematicity. This interpretation of the topography is of course not internally consistent. Purely from an experimental stand, it should be noted that if there is symmetry breaking in the $dI/dV$ signal, and the topograph is simply the height response to the current ($I = \int (dI/dV) dV$), then it should be alarming to see a $C_4$ symmetric topograph.

6.2.1 Bardeen Tunneling

In Bardeen’s formalism [38,39] the tunneling current is determined by

$$I = \frac{2\pi e}{\hbar} \sum_{s,t} f(E_s)[1 - f(E_t + eV)]|M_{st}|^2 \delta(E_s - E_t)$$  \hspace{1cm} (6.2.2)$$

where $s(t)$ indexes the sample (tip), $f(E)$ is the Fermi-Dirac distribution, and $M_{st}$ is a matrix element between the sample and tip states. The spatial structure of the STM image is therefore contained in $M_{st}$, which Bardeen [38] showed to be

$$M_{st} = \frac{\hbar^2}{2m} \oint d\mathbf{S} \cdot (\psi_s^* \nabla \psi_t - \psi_t \nabla \psi_s^*)$$  \hspace{1cm} (6.2.3)$$

where $\mathbf{S}$ is any closed surface in the vacuum separating the tip and the sample. We choose the surface of the sample to be the $z = 0$ plane. Then the tip is above at coordinates $(x_t, y_t, z_t)$, and $\mathbf{S}$ can be the $0 < z < z_t$ plane. Manipulation of Eq. (6.2.3) shows that $M_{st}$ resembles a probability current through the $z$ surface:

$$M_{st}(x_t, y_t, z_t) = \frac{\hbar^2}{2m} \int \left(\psi_s^*(x, y, z) \frac{\partial \psi_t(x - x_t, y - y_t, z - z_t)}{\partial z} - \psi_t(x - x_t, y - y_t, z - z_t) \frac{\partial \psi_s^*(x, y, z)}{\partial z}\right) dx dy$$  \hspace{1cm} (6.2.4)$$

It can now be seen explicitly that the matrix element is dependent on the position of the tip. Equation (6.2.4) describes the spatial structure of the STM measurement.
and it can be written in a simplified way:

\[
M_{st}(x_t, y_t, z_t) = \frac{\hbar^2}{2m} \left( \psi_s^* \frac{\partial \psi_t}{\partial z} - \psi_t \frac{\partial \psi_s^*}{\partial z} \right),
\]  

(6.2.5)

where the * operation denotes convolution in the \( x \) and \( y \) coordinates, and \( M_{st}(x_t, y_t, z_t) \) is a function of the tip coordinates.

### 6.2.2 Sample and Tip Wave Functions

#### Sample

According to Tersoff and Hamann [39] the sample wave function is written as

\[
\psi_{s, \vec{k}}(\vec{r}) = \sum_{\vec{G}} a_{\vec{G}} \exp[i\vec{\kappa}_G \cdot \vec{r} - (\kappa^2 + |\vec{\kappa}_G|^2)^{\frac{1}{2}} z] \]  

(6.2.6)

\[
\vec{\kappa}_G = \vec{k} + \vec{G} \]  

(6.2.7)

\[
\kappa = \frac{(2m\phi)^{\frac{1}{2}}}{\hbar} \]  

(6.2.8)

The \( z \)-dependence depends on the work function \( \phi \) and on \( \vec{G} \). For large \( \vec{G} \) the penetration of the corresponding Bloch waves into the vacuum decreases exponentially. Therefore we restrict the sum in Eq. (6.2.6) to the three highest order terms: \( \vec{G} = 0, \vec{G} = \vec{G}_x, \) and \( \vec{G} = \vec{G}_y, \) where without loss of generality we have taken the simplest case of a square lattice defined by reciprocal lattice vectors \( \vec{G}_x \) and \( \vec{G}_y \). These three highest order terms also represent the simplest wave function which can produce a square lattice in Eq. (6.2.6). Here we have taken the values \( a_0 = 1, \) and \( a_{\vec{G}_x} = a_{\vec{G}_y} = 2e^{\frac{i\pi}{4}}. \) Though these coefficients determine the spatial phase of the periodic lattice structure, different relative values have been tested and do affect our conclusions. The results of the present study can also be easily expanded to other Bravais lattices, or other long-range periodic structures, by appropriate choice of the reciprocal space vector basis.
Tip

First we consider an ideal tip, where the characteristic scale of its wave function is much smaller than the period of $\psi_s$. Then $\psi_t$ can be modeled as an infinitely sharp delta function, and Eq. (6.2.6), together with Eq. (6.2.5), yield $M_{st} \propto |\psi_s|^2$ and consequently $dI/dV \propto \rho_s$. This is the usual STM assumption that the differential conductance is proportional to the local density of states of the sample. However, Tersoff and Hamann [39] showed that an infinitely sharp tip is not necessary to obtain atomic resolution with the STM. We extend their results to accommodate for anisotropic tips. Considering the typical separation between sample and tip ($\approx 5\, \text{Å}$) we model the tip as an s-wave:

$$\psi_t = e^{i\alpha} e^{-\frac{\Gamma}{2}\sqrt{x^2+y^2+(z-z_t)^2}}, \quad (6.2.9)$$

where $\alpha$ is the phase of this wave function and $\Gamma$ determines its penetration into the vacuum. We find that the simplest choice to model an anisotropic tip is to write its wave function as a combination of four s-waves with their centers separated by $2 \times \delta x$, and $2 \times \delta y$:

$$\psi_t = e^{-\frac{\Gamma}{2}\sqrt{(x-\delta x)^2+y^2+(z-z_t)^2}} + e^{-\frac{\Gamma}{2}\sqrt{(x+\delta x)^2+y^2+(z-z_t)^2}} + (x \leftrightarrow y) \quad (6.2.10)$$

We have chosen this particular functional form for $\psi_t$ because of its simplicity, though any other choice of anisotropic wave function in the $x$-$y$ plane suffices to produce the apparent rotational symmetry breaking described below.

---

3Even if $\psi_t$ is broad (several lattice constants), the STM can still measure with atomic resolution [39].
We now demonstrate the effect of the tip geometry on STM measurements, by simulating the conductance maps using Bardeen’s matrix element (Eq. (6.2.5) above) with a two-fold symmetric tip structure, characterized by orthogonal lengths $\delta x = 0.2$, $\delta y = 0.9$ (lattice constant set to unity). We assume that the sample has a $C_4$ symmetric electronic structure with a generic parabolic band structure Fig. 6.2(a), which is isotropic in the $k_x-k_y$ plane. Calculations of the STM topographic image (at $eV = 3.95t$) and conductance maps at two different energies of this four-fold symmetric sample with elongated tip wave function are shown in Fig. 6.2(b-d). While the STM conductance maps can show apparent asymmetry in the $x-y$ plane Fig. 6.2(c), the topograph appears to be remarkably four-fold symmetric Fig. 6.2(b). Clearly, the summation of $dI/dV$ maps over an appropriate range of energies can lead to a four-fold symmetric topograph. This finding demonstrates that a four-fold symmetric topograph cannot be used as an accurate method to characterize the STM tip geometry, as it is often assumed (for example see Ref. [33]).

An anisotropic tip would naturally induce an apparent breaking of four-fold symmetry in measurements of the electronic structure of a four-fold symmetric sample, as the conductance maps demonstrate. However, the energy dependence of the $x-y$ asymmetry (which can change sign, see below), or its absence for some energies (Fig. 6.2(d)), points to a previously overlooked interference effect of STM measurements. Examining Eq. (6.2.5) we realize that the periodic corrugation along the $x$ and $y$ directions in the conductance maps are determined by the interference (see Fig. 6.2(h) for schematic) between the sample’s quasiparticle states $\psi_{s,\mathbf{k}}$ with momentum $\mathbf{k}$ together with those of the tip (characterized in our two-fold symmetric tip by $\delta x$ and $\delta y$). Previous studies of the influence of asymmetric tips [149–151] have overlooked the interference within the STM junction by using the approximation in Eq. (6.2.1) which ignores the phase information ($e^{i\mathbf{k}\cdot\mathbf{r}}$, see Eq. (6.2.6)) of the sample wave functions that are relevant in the evaluation of Eq. (6.2.5). Additionally, studies of quantum interference effects in tunneling junctions [152–155] have not considered
Figure 6.2: (a) Parabolic band structure \( E = E_0 + tk^2 \), with \( t = (50/e^2) \) and \( E_0 = 0.59t \) used to generate (b), (c) and (d). (b) Simulated topography at \( eV = E = 3.95t \) imaged by the tip in the lower inset. The inset of the tip represents the simulated \(|\psi_t|^2\) and is plotted on the same spatial scale as the lattice. (c) Simulated differential conductance at \( E = 3.8t \) showing rotational symmetry breaking with the same tip as in (b). (d) Simulated differential conductance at \( E = 2.3t \) showing no rotational symmetry breaking with the same tip as in (b). (e-g) represent the intensity (normalized to the maximum) of the two orthogonal Bragg peaks generated by the DFTs of (b), (c), and (d), respectively. (h) One-dimensional schematic representation of the interference between the wavefunction of a double tip with a quasiparticle state of momentum \( \vec{k} \). Reproduced from [22].
the effects of geometrically asymmetric tips on the measurement of long-range periodic structures by the STM. In contrast, our model calculations clearly show that the electronic structure of a four-fold symmetric square lattice probed by a real STM tip can be two-fold symmetric depending on the momentum $\vec{k}$ (consequently energy) of the quasiparticles probed.

For a more detailed analysis of the energy-dependence of this asymmetry in STM conductance maps, and to make a connection to experimental measurements, we quantify the calculated STM conductance maps with the two-dimensional asymmetry parameter that is commonly used in the context of nematic ordering [32]:

$$O_N(E) = \frac{X(E) - Y(E)}{X(E) + Y(E)}$$  \hspace{1cm} (6.2.11)

where $X(E)$ and $Y(E)$ are the energy dependent amplitudes of the two Bragg peaks along the orthogonal directions obtained from discrete Fourier transformation (DFT), as indicated in Fig. 6.3(a). A map with $O_N = 0$ corresponds to a four-fold symmetric image, whereas $O_N = 1$ indicates an image with zero corrugation along either...
the $x$ or $y$ direction (as expected for example for one-dimensional stripes). Figure 6.3(b) shows $O_N(E)$ for different tip configurations. Despite the simplicity of the model band structure, $O_N(E)$ shows a significant energy dependence over the entire bandwidth and even a sign change. This illustrates the sensitivity of this tip-induced interference effect to the band structure. Although the magnitude of $O_N(E)$ can only be understood by a detailed knowledge of $\psi_L$, its energy dependence acts as a detector of changes in the momentum structure of the quasiparticle states.

### 6.3 Experimental Evidence for Tip-dependent Rotational Symmetry Breaking

Our model calculation suggests that materials with changes in their electronic band structure as a function of energy (such as a rapid change of band dispersion) are likely to be good candidates for exhibiting the interference effect associated with asymmetric tips. A good material candidate for such a study is the heavy fermion compound CeCoIn$_5$, which crystalizes in the tetragonal crystal structure, ensuring the four-fold symmetry of its electronic states. Recent STM studies on CeCoIn$_5$ have demonstrated that the electronic structure of this compound exhibits the development of a hybridization gap and associated heavy bands near the Fermi energy at low temperatures [20]. Figure 6.4 shows a topograph (a) of CeCoIn$_5$, a DFT of a conductance map on the same area (b) together with the STM spectrum as a function of energy (c), which demonstrates the presence of a hybridization gap in this compound near the Fermi energy. Also shown in Fig. 6.4 is the intensity of the Bragg peaks in the conductance maps as a function of energy (d) and the asymmetry parameter $O_N(E)$ (e) introduced above.

Approaching the energy window near the Fermi level, where we expect strong changes in the band structure of CeCoIn$_5$ due to hybridization of $spd$- and $f$-like electrons, we find a strong $C_4$-symmetry breaking of the STM conductance maps (Fig. 6.4(d,e)). Both the Bragg peaks and $O_N(E)$ show an energy-dependent asym-
Figure 6.4: (a) Topograph of CeCoIn$_5$ (setpoint condition at $-200$ mV and 1.6 nA) showing a square lattice. For enhanced contrast the derivative of the data is shown. (b) DFT of conductance ($dI/dV$) map taken at $-52$ meV over the same FOV as (a) showing strong Bragg peaks representing the square lattice. Inset shows an enlargement of the bottom right Bragg peak. (c) Tunneling spectrum averaged over the area in (a). (d) Energy dependence of the Bragg peak intensity obtained via the DFT operation. (e) Asymmetry parameter calculated via Eq. (6.2.11). Inset of (e) represents the asymmetry parameter of the topograph acquired simultaneously to the conductance maps. Reproduced from [22].
metric behavior in tandem with the features of the STM spectrum. The apparent breaking of $C_4$ symmetry in this experiment is not associated with nematic order in CeCoIn$_5$ but rather probes the strong momentum dependence of the band structure of this compound near the Fermi level. In fact, it is remarkable that $O_N(E)$ is sensitive to the most subtle features in the spectra as a function of energy (see dashed lines in Fig. 6.4(c)), which are associated with changes in the electronic momentum structure as previously detected in the quasiparticle interference of this compound [20].

Further evidence that the asymmetry between $X$ and $Y$ detected in the conductance maps of CeCoIn$_5$ is associated with interference in the STM junction can be found by repeating the same experiment with slightly different tips (created by interacting with the surface, see Appendix D) over the same field of view (FOV) or equivalent areas of the same cleaved sample. As expected from our model calculations (Fig. 6.3(b)) different tips have different sensitivity to the momentum structure of the electronic structure of the sample, and depending on their geometry exhibit different degrees of $C_4$-symmetry breaking in the acquired conductance maps. As Fig. 6.5(a) shows, the energy dependence of the asymmetry parameter in the conductance maps, $O_N(E)$, is a very strong function of the tip and not always correlated with the presence, or the degree of, Bragg peak asymmetry in the STM topographs of the same area.

We turn our attention next to the claims that STM measurements of underdoped Bi-2212 samples break $C_4$ symmetry and exhibit nematic order [33, 141]. As shown in Fig. 6.5(b) measurements on such a sample exhibit very similar characteristics to those of CeCoIn$_5$, where changes in the spectrum associated with the pseudogap coincide with apparent asymmetry and a non-zero $O_N(E)$ in this energy window. Not only this correlation is very characteristic of the tip-induced symmetry breaking originating from interference effects within the STM junction, we also find that $O_N(E)$ displays a strong sensitivity to the tip structure when probing the exact same FOV with slightly different tips. Remarkably, tips that show very similar, nearly $x$-$y$ symmetric, topographs can show very different energy dependences for $O_N(E)$,
Figure 6.5: (a) $O_N(E)$ measured on CeCoIn$_5$ with different tips at 20 K. (b) $O_N(E)$ measured on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ ($T_c = 35$ K) at 30 K over the same FOV with different tip configurations. (c) Open symbols represent $O_N(E)$ measured on URu$_2$Si$_2$ above $T_{HO}$ (20 K) and below (15 K) over the same FOV with the same tip. Measurements on a second FOV with different tip configurations (closed symbols) were carried out below $T_{HO}$ (15 K). For comparison purposes, the average tunneling spectra are displayed (dashed curves) for the respective materials (for URu$_2$Si$_2$ the average spectrum at 10 K is displayed). The insets represent the asymmetry parameter of the respective individual topographs acquired simultaneously to the conductance maps. Reproduced from [22].
and even exhibit opposite signs for the effect on the same exact area of the sample. Clearly, such behavior is more consistent with the tip-dependent interference in the STM junction, associated with changes in the momenta of electronic states within the pseudogap, rather than any nematic order. Consistent with this view, and with previous experiments [33, 141], no domain boundaries between regions of different nematic order parameter have ever been found despite the large areas used for STM studies.

Before we conclude, we present experiments on one more materials system, the results of which demonstrate that the interference within the STM junction and the associated asymmetry parameter can in fact be used to probe the onset of sudden changes in electronic band structures of materials. We have carried out temperature dependent experiments on the heavy fermion URu$_2$Si$_2$, which shows a sharp second order phase transition in the so-called ”hidden order state” below $T_{HO} = 17.5$ K, the nature of which continues to be a mystery [21, 50, 60]. Experiments on this compound are also consistent with the asymmetry parameter picking up changes in the electronic states at low temperatures through the tip-dependent interference. However, contrasting measurements below and above the $T_{HO}$, over the same FOV, and with the same tip (open symbols in Fig. 6.5(c)), shows that the signals in $O_N(E)$ change from a peak-like shape to a smooth curve, directly reflecting the change in the band structure as the hidden order phase transition is crossed. At temperatures just below the transition, when the changes in the electronic states are difficult to detect in the STM spectra, we find that $O_N(E)$ is extremely sensitive to the changes that occur in the electronic structure of this material below $T_{HO}$.

6.4 Summary

Overall, the systematic measurements on three different materials (with three different characteristic gap energy scales, 30 meV for CeCoIn$_5$, 4 meV for URu$_2$Si$_2$, and 100 meV for Bi-2212), demonstrate the strong sensitivity of the asymmetry parame-
ter $O_N(E)$ to different tip configurations, and, specifically, how it can change sign for measurements over the same FOV. From these results, we conclude that $O_N(E)$ is not a measure of the symmetry breaking of the electronic states of the sample, rather it is the result of the interference effect which is evident in the elementary model of tunneling from a realistic tip discussed in here. Although STM can in principle detect the onset of nematic order, we have demonstrated that symmetry analyses of conductance maps can be dominated by the energy-dependence of the band structure of the sample rather than nematic order. Perhaps the only experimentally reliable approach to detect rotational symmetry breaking order with the STM would be to image the presence of domain boundaries, as discusses above. Alternatively rotation of the STM tip by an appropriate angle ($90^\circ$ in the case of $C_4$ symmetry) while maintaining the same location on the sample could be developed to discount the role of the tip geometry. Regardless, the interference within the STM junction with realistically anisotropic tips described above shows that such measurements are a sensitive probe of the changes in the quasiparticle states of the sample as a function of energy, even when such changes might not be apparent in STM spectra.
Chapter 7

Conclusion

As is often the case in scientific endeavors, answers often lead to more questions. Below, I discuss how the experiments described in this thesis relate to the main questions in the field of unconventional superconductivity, and elaborate on possible future research directions.

7.1 Heavy Fermions

In the case of the heavy fermions, we demonstrated how STM spectroscopy can be sensitive to the composite nature of quasiparticles which originate from the formation of a coherent Kondo lattice. Our combined experiments and model calculations provided a basic understanding of the tunneling process on heavy-fermion compounds which allowed us to detect signatures of quantum criticality in the temperature evolution of the tunneling spectrum. However, the specific details of this strong scattering have yet to be measured. Under the paradigm that the identification of fluctuations that can take the role of the pairing glue can lead to a theory of unconventional superconductivity, it becomes imperative to understand the nature of the fluctuations responsible for the temperature-energy scaling observed in CeCoIn$_5$. For example, what is momentum structure of these quantum critical fluctuations? Is the structure of the fluctuations simply originating from the proximity to the antiferromagnetic
ground state, or do they have a different momentum structure which is more specific to the quantum critical point?

Nevertheless, the basic understanding of the high-temperature properties of CeCoIn$_5$ described in chapter 3 paved the way for mili-Kelvin measurements, with and without high magnetic fields, which directly probe the symmetry of the superconducting order parameter in CeCoIn$_5$. The results of these measurements have now been published and show the d-wave nature of the superconducting order parameter in these compounds [23]. Though this result adds to the list of similarities between the unconventional superconductors described in this thesis, the complex multi-band, three-dimensional nature of the CeCoIn$_5$ band structure makes its comparison to the cuprates difficult. It is open to debate whether CeCoIn$_5$ is also a multi-gap system. If so, at what temperatures do these different gaps open? Do they all share the same gap symmetry?

A natural extension of these experiments will be to explore the relation between fluctuations and superconductivity. Doping of Cd at the In sites can be used as a tuning parameter between superconductivity and antiferromagnetism. Preliminary measurements above $T_c$ show that the presence of Cd can shift the energy position of the spectral peak near zero-energy (the one that shows quantum critical behavior) in a spatially inhomogenous fashion. If the quantum critical fluctuations are mediating the superconducting pairing, it will be important to perform similar measurement below $T_c$ and determine if there is a spatial correlation between peak-position (or peak-width) and the superconducting gap.

Regarding URu$_2$Si$_2$, the first order of business remains to understand the hidden order. Recently, torque magnetometry measurements have shown evidence for rotational-symmetry breaking inside the hidden order phase [139]. However, this apparent nematic signal has only been detected on small samples. It has been suggested that twin-domain structures are responsible for this dependence on sample size. Based on these reports we have performed REXS measurements on URu$_2$Si$_2$, with photon energies resonant to the U $M$-edge. Initial results on samples of differ-
ent sizes suggest a spatial correlation between rotational symmetry breaking and the parasitic commensurate antiferromagnetism [156]. The only certainty is that further experiments are needed to uncover this now 27-year old mystery.

7.2 Cuprates

The combined STM-REXS approach to study charge ordering (CO) on Bi-2212 yielded an unprecedented agreement between bulk- and surface-sensitive techniques, and allowed us to show the universality of this CO to different cuprate families. Our spectroscopic measurements presented in chapter 5 show evidence that CO competes with superconductivity on the Fermi arcs. Still, the relation between charge order and pseudogap is not fully understood. The apparent location of the CO-associated scattering on Bi-2212, coming from the end of the Fermi arcs, suggest that the pseudogap nucleates CO. Whether they are the same phenomenon remains to be determined. One possibility is that the pseudogap is the gap which originates from mixing \( \vec{k} \) and \( \vec{k} + \vec{Q} \) states, where \( \vec{Q} \) is the CO wavevector. However, the STM measurements displayed in chapter 5 show that charge ordering is a low-energy phenomenon (\( \sim 20 \text{ meV} \)), when compared to the pseudogap (\( \sim 200 \text{ meV} \)) which suggest a different microscopic origin.

The relation between stripes and the charge ordering observed in YBCO also remains a matter of debate. The results in chapter 5 enter right in the middle of this debate. One possibility is that the propensity toward charge ordering is a universal property of high-\( T_c \) superconductors, and the choice of wavevectors is simply dependent on details of the crystal structure of the specific materials. Support for this scenario is found in the RXS measurements on YBCO, which show the presence of the incommensurate charge order around 1/8 doping, where stripes are strongest in La-based cuprates. Such intertwinement is also seen in our STM data, which shows a jump as a function of doping in the CO periodicity from incommensurate at low dopings to commensurate (stripe-like) at higher dopings (see Fig. 5.4).
Another possibility is that the discontinuity near 0.11 doping is related to either a competition between CO and stripes or to a pinning effect. In such case, we would need to consider three distinct phenomena: incommensurate CDW, stripes, and superconductivity. Though this cannot be ruled out at the moment, the remarkable similarity between the STM data above $T_c$ on UD35 ($\delta = 0.3$) and UD75 ($\delta = 0.25$) suggest they are different manifestations of the same phenomenon. From an experimental stand point it will be important to confirm the doping dependence of the $\delta$ wavevector with REXS measurements. However, the remarkable agreement between the STM and REXS measurements on the UD45 sample indicate that the doping dependence in the STM observations are bulk related.

From a theoretical perspective, the energy of the charge ordering above the chemical potential represents a major challenge. On a basic level, we need to understand how charge ordering would couple to the single-particle spectral function. Naïvely one expects that a fluctuating order would appear strongest at energies that are on resonance with the time scale of the fluctuations. However, it is possible that the relation of the charge order to other phenomena (e.g. antiferromagnetic fluctuations) enhances charge ordering above the chemical potential. Unfortunately, ARPES is not capable of measuring unoccupied states, leaving open the possibility of a more complex cuprate band structure in which additional bands exist above the chemical potential.

Finally, the results presented in chapter 5 represent a significant step toward the unification of zero magnetic field results to measurements in the presence of high magnetic fields. The energy scale of the charge ordering, as well as its location on the Fermi surface, provide a path to understand the presence of quantum oscillations at moderately low values of magnetic field. However, extension of the current STM and REXS measurements to high-magnetic fields, will be necessary to clarify this connection.
Appendix A

Appendix to Chapter 3: CeCoIn$_5$

A.1 The Cleavage Planes in Ce-115 Compounds

Cleaving of the three different Ce-115 compounds CeCoIn$_5$, CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$, and CeRhIn$_5$, revealed identical sets of cleavage planes. In all cases, multiple surfaces were obtained after cleaving with similar sub-unit cell step heights and surface topographies. Figure A.1 shows the multiple surfaces and their relative step heights in CeRhIn$_5$ and compares the exposed layers to the bulk crystal structure. The exposed surfaces A, B, and C are identified as Ce-In, Rh, and In$_2$, respectively in correspondence with CeCoIn$_5$ (Fig. 3.5).

Figure A.2 displays a topographic image of the A surface in CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ showing the dopant Hg atoms which replace the surface In atoms. Figure A.1(a) shows the topography of the area on which the conductance maps of Fig. 3.7(a) (of the main text) were measured. In all samples the surfaces B (or B) and C (or C) were exposed with equal probabilities whereas, within the limited statistics, surface A (or A) was obtained with a slightly lower probability. In some cases, insulating or unstable surfaces were obtained which immediately destroyed the STM tip and terminated the experiment. In principle, breaking of the two different chemical bonds between the different layers would result in four exposed surfaces, namely, Ce-In, In$_2$ on Co, Co,
Figure A.1: STM topography of the different exposed surfaces in CeRhIn$_5$. (a) The atomic surface A corresponding to surface A of CeCoIn$_5$. (b) The reconstructed surface C corresponding to surface C of CeCoIn$_5$. Note the unidirectional electronic structure on the reconstructed surface which follows structural defects and step edges. (c) Relative sub-unit cell step heights within the different layers. (d) A line cut through the different surfaces (solid line in (c)) showing the relative step heights compared to the bulk crystal structure.
Figure A.2: Topographic image of the A surface in CeCo(In_{0.9985}Hg_{0.0015})_5 showing the dopant Hg atoms which replace the surface In atoms.

and In$_2$ on Ce-In. Within the limited statistics, the absence of the second In$_2$ surface (on Ce-In) might be associated with the observation of unstable insulating surfaces.

A.2 Spectra on the Stoichiometric Compound

Spectroscopic measurements were performed on CeCoIn$_5$ and, to enhance the QPI signal, on CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$. Spectra on both samples revealed similar results, further verifying the negligible effect of 0.15% Hg doping to the transport properties. Fig. A.3 displays temperature dependent spectra measured on surface A.
A.3 Comparison of the QPI Bands with the LDA Band Structure.

A theoretical calculation of QPI from the full bulk band structure is required to understand the full details of our QPI measurements. However, in the absence of such calculations, one can still make progress understanding the QPI patterns by considering the two-dimensional QPI pattern observed in our experiments at the surface of this material as a 2D projection of the possible scattering within the different \( k_z \) planes of the 3D Brillouin zone. We can make progress by combining this idea,
Figure A.4: (a) Quasiparticle interference pattern in CeCo(In$_{0.9985}$Hg$_{0.0015}$)$_5$ displaying two concentric square like patterns. Arrows indicate the magnitude $q$ of the outer quasiparticle band. (b) LDA calculation of the (135 sheet) Fermi surface in CeCoIn$_5$ displaying four cylindrical sheets at the corners of the Brillouin zone. (c) Cut of the Fermi surface in the Z-plane illustrating the sheets which are connected by the scattering wave vector $q$ (black arrows).

with the fact that the most intense QPI signals will be dominated by scattering between points on the surfaces of constant energy in $\vec{k}$-space with the highest density of states. Furthermore, one would expect that the most prominent features of the QPI signal measured at a surface would be related to wavevectors connecting nearly parallel contour (of constant energy) sheets. Following this approach, the square-like shape of the quasiparticle scattering wavevectors ($q$ in Fig. A.4(a)) can be understood as a result of the inter-band scattering of quasiparticles between the two conduction bands centered at the Brillouin zone corners (Points A in Fig. A.4(b,c)) as calculated by LDA for both CeRhIn$_5$ and CeCoIn$_5$ (Fig. A.4(b,c)) [85].

Figure A.4(c) displays a cut of the LDA Fermi surface in the Z-plane of the Brillouin zone for CeCoIn$_5$ \(^1\) together with the magnitude of the QPI wavevector $q$ (black arrows), which matches the inter-band separation of the two square-like bands (black arrows in Fig. A.4(c)). While the Fermi surface exhibits multiple sheets, scattering is expected to be strongly enhanced between these two square-like bands owing to their two dimensional nature (Fig. A.4(b)). The other features of the QPI with smaller

\(^1\)Private communication, 2012.
Figure A.5: Transition from a small to large Fermi surface. The crossing between the solid red (QPI band) and the dashed black (Fermi energy) lines define the QPI Fermi wavevector.

wavevectors require more detailed analysis since they can originate from several combinations which connect different Fermi surface sheets.

### A.3.1 Transition from Small to Large Fermi Surface

Figure A.5 shows the QPI band structure in CeCo(In_{0.9985}Hg_{0.0015})_{5} at 70 K and 20 K. At 70 K the QPI band crosses the Fermi energy at a wave vector \( k_{F}^{70} \approx 0.52 \text{ rlu} \) (rlu: reciprocal lattice units). Heavy fermion hybridization at low temperatures alters the band structure splitting the band and forming two heavy fermion bands. At 20 K
the lower heavy fermion QPI band, due to this hybridization, cuts the Fermi surface at a smaller wave vector $k_F^{20} \approx 0.40$ rlu. Owing to the fact that the QPI wavevectors are scattering vectors, therefore, can represent either direct or Umklapp scattering. In the latter case, decreasing QPI wavevector corresponds to an enlarging Fermi surface. Such a scenario is also consistent with the scattering analysis of the previous section where the wavevector $q$ is an Umklapp scattering connecting the Fermi sheets across different Brillouin zones (Fig. A.4(c)).

### A.4 $f$-Width at Zero Temperature

From the calculation outlined in Sec. 3.1.1, even in the absence of any lifetime broadening $\gamma_f$, the peaks in the simulated spectra for large values of $t_f/t_c$ still exhibit a finite width. This is caused by the finite dispersion of the $f$-band (unrenormalized $f$ bandwidth of 8 meV, see Fig. 3.2(b)) and the finite value of $t_f/t_c$. The simulation presented in Fig. A.6 addresses this point for an infinitesimally small $\gamma_f$. Therefore at zero temperature and for infinitesimally small scattering, the STM measurements such as that in Fig. 3.6(a) would still have a finite width. The zero temperature intercept extracted from such data in Fig. 3.9(a) is likely the results of such behavior.

### A.5 Energy-Temperature Scaling

Information on the lifetime of heavy quasiparticles can be obtained by analyzing the widths of the sharp spectroscopic features in the lineshapes of Fig. 3.6(b). In order to isolate the heavy quasiparticle peak from the rather smooth background, we fit a second order polynomial to the data outside the bias range of $\pm 50$ meV (Fig. A.7. This range of bias lies outside the hybridization energy scale where the density of states reflects the bare light electronic bands. Fig. A.8 displays the background (polynomial) subtracted spectra $(dI/dV)_S$ for the different temperatures. The clear double peak structure near the Fermi energy, reflecting the heavy electronic states, is apparent. In
addition to this double peak structure, a much broader and a weakly temperature dependent shoulder, near $-20 \text{meV}$, is also visible in the data, which could be related to crystal field excitations. To extract the linewidth of the sharp quasiparticle peak near the Fermi energy, the spectra are fitted to three Gaussian peaks centered near $\approx -20$, 1, and 18 meV. The extracted linewidth of the central peak near the Fermi energy, representing the inverse heavy quasiparticle lifetime, is displayed in Fig. 3.9(a) of the main text. The scaling in Fig. 3.9(b) are obtained from the data after subtracting the smooth background, following similar procedure such as those in measurements of dynamical susceptibility [44,88].

Figure A.9 shows a plot of $(dI/dV)_S \propto k_B T^\alpha$ as a function of $(E/k_B T)^\beta$ for different values of $\alpha$ and $\beta$. Clearly the plots show that the collapse of the data at different temperatures to a single curve occurs only for $\alpha = 0.53$ and $\beta = 1$. To get an estimate of the goodness of the collapse we compute the variance $\chi^2$ of the data at different temperatures (after interpolating the data at each temperature to the same number
Figure A.7: Spectroscopic lineshapes of Fig.3.6(b) (solid lines) together with a second order polynomial fit to the bias range lying outside ±50 meV (dashed lines).

Figure A.8: Background subtracted spectra for different temperatures (blue) together with a fit of three Gaussian peaks to the data (red line). The green lines represent the individual Gaussian fit.
Figure A.9: Energy-temperature scaling of the spectra of Fig. 3.6(b) of the main text within a narrow energy window near the Fermi energy scaled with a \((k_B T)^{0.5}\), b \((k_B T)\), and c \((k_B T)^2\), for different values of the critical exponent \(\alpha\). Insets show the \(\chi^2/N\) as a function of \(\alpha\) for the three different cases.

of data points \(N = 40\) with respect to each other as a function of \(\alpha\),

\[
\chi^2 = \sum_{x=1}^{N} \sum_{T,T'} \frac{[y_T(x) - y_{T'}(x)]^2}{y_{T'}(x)}, \tag{A.5.1}
\]

where \(x = (E/k_B T)^\beta\) and \(y_T = (dI/dV)_S \times k_B T^\alpha\). The insets show the extracted \(\chi^2/N\) as a function of \(\alpha\) for the three different values of \(\beta\).

In Fig. A.10 we plot a map of \(\chi^2/N\) as a function of both \(\alpha\) and \(\beta\). Clearly the map shows that the smallest value of \(\chi^2/N\), corresponding to the best collapse of the data, is achieved for \(\alpha = 0.53 \pm 0.03\) and \(\beta = 1.0 \pm 0.05\).
Figure A.10: (a) A map of $\chi^2/N$ as a function of both $\alpha$ and $\beta$. (b) Zoom in of the low $\chi^2/N$ region in (a)
Appendix B

Appendix to Chapter 4: URu$_2$Si$_2$

We performed the tunneling measurements in a home-built variable-temperature scanning tunneling microscope that operates in the temperature range from 6 to 180 K. Lower temperature (2 and 4 K) measurements were performed on a low temperature scanning tunneling microscope. The single crystal URu$_2$Si$_2$ samples used for this study were grown in an optical floating-zone furnace. Small, flat crystals were oriented along the crystallographic axes and cut into sizes suitable for scanning tunneling microscopy measurements ($\approx 2 \times 2 \times 0.2 \text{ mm}^3$). The samples were cold cleaved on a surface perpendicular to the c axis at $T \approx 10$ K in ultrahigh vacuum and transferred in situ to the microscope head. Differential conductance ($dI/dV$) measurements were performed using standard lock-in techniques. The relative variation in $dI/dV(V)$ at a single point does not depend on the height of the tip and is therefore assumed to be representative of the local electronic density of states (DOS) within an overall normalization.

B.1 Identifying the Cleavage Planes

Multiple surfaces have been obtained after cleaving (Fig. B.1 and Fig. 4.2). In $\approx 55\%$ of the cases, the topography is as shown in Fig. B.1A. This 300-Å image of the surface (termed surface A) displays a square lattice ($a \approx 4.1$ Å) that corresponds to
Figure B.1: (A) Constant current topographic image (100 mV, 50 pA) over a 300-Å area of the atomic surface (surface A), showing atomic terraces. The inset shows the magnification of the atomically ordered surface. (B) Constant current topographic image (100 mV, 80 pA) over a 1000-Å area of the reconstructed surface (surface B). The inset shows the magnification of a 100-Å area showing the reconstruction. In both panels step heights are \( \approx 4.8 \text{ Å} \), corresponding to half the unit cell. The red lines show the locations of horizontal cuts through the data.

either the U or Si spacing [50]. The Ru layer has a smaller interatomic spacing because it is rotated 45 with respect to the U layer (see Fig. 4.4B). The step size between equivalent surfaces \( \approx 4.8 \text{ Å} \) corresponds to half the unit cell. In approximately 45% of the cases, the topography is as shown in Fig. B.1B. The surfaces in this 1000-Å image show a cigar-like reconstruction (Inset) with a width of two lattice constants \( \approx 8.2 \text{ Å} \), surface B). The step height between the reconstructed surfaces \( \approx 4.8 \text{ Å} \) is also equivalent to half the unit cell.

Averaged spectroscopic \( dI/dV \) measurements on the different surfaces at \( T = 4 \text{ K} \) are shown in Fig. B.2. The spectra on the reconstructed surfaces do not necessarily resemble that of the bulk.
Figure B.2: Averaged $dI/dV$ measurements on the different observed surfaces. The spectra on surface B strongly depend on the location. In between the cigars the spectra shows a gap-like feature similar to that of surface C. On top of the cigars the spectra show a resonance-like feature. The spectra are offset by 4 nS for clarity.
Figure B.3: Averaged $dI/dV$ at 18 (Blue) and 6.6 K (Green). Above the hidden order temperature, the data are fitted to a Fano line shape and a V-shaped background (Dashed Lines). Below the hidden order temperature, the data are fitted with the same function multiplied by a BCS-like gap (Dotted Line). The red solid lines represent the fit to the data above (sum of dashed lines) and below (sum of dashed lines multiplied by the dotted line) the hidden order temperature.

B.2 Fitting the $dI/dV$ spectra

Fig. B.3 illustrates our fitting procedure for the electronic DOS shown in Fig. 4.3. The high temperature data (above $T_{HO}$) were fitted to the sum of a Fano line shape and a V-like background (Dashed Lines in Fig. B.3). The background is obtained from a phenomenological fit to the highest temperature data (120 K) consisting of a linear spectrum with different slopes for hole and electron tunneling. The lower temperature data (below $T_{HO}$) were fitted to the same function multiplied by an asymmetric (BCS)-like gap function (dotted line). The fitting functions were convolved with the Fermi function appropriate for the temperature. The results of the fits are shown as red lines both below and above the hidden order. The extracted hidden order gap magnitude is plotted in Fig. 4.5C.
Figure B.4: (A) The experimental data below $T_{HO}$ divided by the 18 K data showing the evolution of a gap in the DOS. (B) The same data as in A all thermally broadened to 18 K, which clearly demonstrates that the gap evolves with temperature more rapidly than simple thermal broadening.

**B.3 Temperature Evolution of the Hidden Order Gap**

To clarify the temperature dependence of the hidden order gap, and show that it evolves more rapidly than simple thermal broadening, we thermally broaden the data below $T_{HO}$ all to 18 K. The divided raw and the artificially broadened gaps are shown in Fig. B.4. Though the spectra (Fig. B.4B) are smeared out due to the artificial broadening, they still show the opening of a gap already visible at 15 K. This confirms that the gap evolves with temperature rather than filling up due to thermal broadening.

**B.4 Normalization Independence of the Onset Temperature**

We see from the measured spectra that the hidden order gap is not seen in the raw spectra by $T = 18$ K. Accordingly, the spectra were normalized by the 18-K curve. To further verify that our results are independent of this choice of normalization tem-
Figure B.5: The averaged $dI/dV$ for $T < 40$ K divided by the $T = 40$ K data. The data show the development of a gap near the Fermi energy below 18 K. The spectra also display the residue of the asymmetric Fano line shape.

Plotted in Fig. B.5 are the averaged spectra of Fig. 4.3B below $T = 40$ K divided with the 40-K spectrum, which shows that the hidden order gap indeed opens below 18 K. Since the Kondo-Fano resonance has somewhat broadened at 40 K relative to 18 K, an additional background is produced by this choice of normalization temperature. However, the hidden order gap can be clearly distinguished from this weak background.
Appendix C

Appendix to Chapter 5: Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

C.1 Data Acquisition and Analysis

The STM measurements were carried out on a homebuilt variable temperature ultra-high vacuum scanning tunneling microscope. The conductance maps are measured using standard lock-in techniques and always using the same set-point bias of $-300$ mV. This value of set-point bias was carefully chosen to avoid systematics originating from the so-called set-point effect (see section 5.2.1). We typically chose a lock-in modulation of 3 mV for all measurements taken below 60 K and a set-point current between 150 and 200 pA. Measurements at 80 K were performed with a lock-in modulation of 4 mV (still much lower than thermal broadening) and currents between 60 and 100 pA. This was necessary due to the intrinsic instabilities of the tunneling junction on Bi-2212 at these high temperatures.

The conductance maps were taken on a square area equivalent of 20 b-axis supermodulations on a $256 \times 256$ pixel grid. We reject signals in the conductance maps that are two standard deviations away from the average of the map. At these pixels, we use the average value of the map. However, at the typical quality of the maps acquired for this work, less than 0.1% of pixels are rejected. Prior to carrying out the
discrete Fourier transform (DFT), each conductance map is corrected for picometer-scale drifts by using the algorithm outlined by Lawler et al. [33]. We use this drift correction to achieve the highest momentum resolution. However, even in the absence of the drift correction procedure, the typical deviations are smaller than the momentum-width associated to the charge ordering (CO) peak or other errors due to tip geometries.

Prior to performing the DFT of a conductance map, we normalize the maps by their mean to eliminate any dependence on junction impedance and to allow a direct comparison of the modulations strength for different energies (also see Fig. 5.3 and Sec. 5.2.1). After carrying out the discrete Fourier transforms (DFT), we use the mirror symmetry (relative to the a-axis of the crystal) to further suppress the influence of random tip geometries (which might have a preferential direction) on our measurements. Still, variations in the sharpness of the tip between different measurements can lead to large differences in the intensity of the CO feature in the DFTs. However, since we are interested only in the relative strength between the CO and BdG-QPI features, each energy-wavevector \((E-\delta)\) plot is normalized to its average intensity in the area encompassed by \(-75 \text{meV} < E < 75 \text{meV}\) and \((\delta^*-0.15) < \delta < (\delta^*+0.05)\), where \(\delta^*\) is the location of the CO feature (e.g. \(\delta^*=0.3\) for UD35). This choice of normalization area contains both CO and QPI features and allows a direct comparison of the interplay between CO and superconductivity for measurements done on different samples and at different temperatures. All the \(E-\delta\) plots of the modulations along the Cu-O bond direction displayed in chapter 5 are produced by the procedure outline above.

## C.2 Samples

To achieve low doping levels (UD15, UD35, and UD45) the Bi-2212 samples were doped with Dy. To verify that the doping evolution seen in Fig. 5.4 of the main text is not affected by the presence of absence of Dy, we have taken the UD45 sample and
Figure C.1: The energy integrated (0 to 50 meV) δ-cut (blue crosses) is fitted to a smooth step-like background (green) plus a Lorentzian function (red). Curves are offset for clarity.

Oxygenated it at high pressure, resulting in the UD75 sample. Comparing the $E$-δ structure at 30 K between UD73 (no Dy, Fig. 5.4F) and UD75 (with Dy, Fig. 5.9C) shows that the presence of Dy has no influence on our STM measurements. Furthermore, notice that the same sample can show a CO feature with $\delta = 0.30$ (UD45) or $\delta = 0.25$ (UD75) depending solely on its oxygen content.

### C.3 Doping Dependence of the CO δ-value

Figure 5.4H of the main text displays a sudden jump in the δ-value of the CO: $\delta \approx 0.30$ for UD45 and $\delta \approx 0.25$ for UD52. This jump can already be seen directly in analysis presented in Fig. 5.5 A-B. For each sample the energy integrated δ-dependent curves are fit to a Lorentzian function plus a step like background. An example of this fitting procedure is illustrated in Fig. C.1, for a UD45 sample. The δ values of the CO plotted in Fig. 5.4H corresponds to the location of the Lorentzian peak from the fit and the error bar is the half width at half maximum.
C.4 Regions of the Fermi Surface Associated with Charge Order

Figure C.2 shows a schematic Fermi surface for a Bi-2212 UD75 sample. For simplicity, the hole barrels are modeled as circles, with their radii adjusted to match the nodes as determined by ARPES [18]. The green arc near the node represents the segment of the Fermi surface below $T_c$ terminated where a deviation (kink) in the energy gap is seen in ARPES measurements [19]. The white arc near the node represents the Fermi arc above $T_c$ corresponding to zero gap regions, as seen by ARPES [19].

Following this construction, the anti-nodal BdG-QPI scattering at high energies is expected to correspond to $\delta = 0.15$ (see blue line in Fig. C.2). This corresponds approximately to the lowest value of $\delta \approx 0.12$ detected in our STM measurements around $\pm 45$ meV. Contrasting these measurements to high energies we find that the $\delta$-value associated with CO connects regions of the Fermi surface lying on the Fermi arcs of the d-wave order parameter (see red line in Fig. C.2).
Appendix D

Appendix to Chapter 6: Tip-changing Procedures

D.1 CeCoIn$_5$ and URu$_2$Si$_2$

The tip is offset from the measurement area and the configuration of its apex is modified by moving the tip toward the surface until we see a saturation in the tunneling current (beyond the limits of our pre-amplifier). This we call a controlled poke onto the surface. We have determined the optimal voltage applied to the scanner piezo empirically. Because of the metallic nature of the CeCoIn$_5$ and URu$_2$Si$_2$ surfaces, this controlled poke does not compromise the stability of the tunneling junction, nor does it modify the poking site beyond a few tens of angstroms. The change in the tip apex configuration is confirmed by subsequent topographic measurements showing a change in the relative intensities of the Bragg peaks.

D.2 Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

Contact between the tip and the Bi-2212 sample can results in an unstable tunneling junction and the possible destruction of the approached area, thus decreeing the poking procedure used in URu$_2$Si$_2$ and CeCoIn$_5$ unusable. To circumvent this
problem we developed a method to change the configuration of the tip apex which preserves the stability of the tunneling junction and allows subsequent measurements on the same area. Scanning over large areas ($\approx 5000 \text{ Å}$), it is possible to find small spots ($\approx 1 \text{ Å}$) over which the tunneling junction is highly unstable. By scanning over them at lower bias set points ($\approx 20 \text{ mV}$) while maintaining a large tunneling current ($\approx 300 \text{ pA}$), the tip sample separation is decreased and the tip is more susceptible to changes in its apex configuration. Such a tip changing event is characterized by a single spike in the tunneling current. The change in the tip apex configuration is confirmed by subsequent topographic measurements.

**D.3 Effects on Spectra**

The average spectrum for each of the measurements in Fig. 6.5 of the main text is displayed in Figs. D.1, D.2, and D.3. Notice that the measurements on URu$_2$Si$_2$ displayed in Fig. 6.5(c) of the main text were taken just below $T_{HO}$ (15 K), where the effects of the hidden order gap on the spectrum are small [21] (see Fig. D.2(b)) but where the sensitivity of $O_N(E)$ to the hidden order is strong (Fig. D.2(a)). For comparison we show similar measurements taken at 4.2 K where the hidden order gap is fully developed.

Small variations between measurements are expected since the different tip-geometries should yield different tunneling matrix elements. However, the relative small variance over the different measurements indicates that tunneling spectra is mostly unchanged by the tip-changing procedures used here and that the large variance seen in the $O_N(E)$ curves displayed in Fig. 6.5 is likely due to different tip geometries.
Figure D.1: Average spectra (lower panels) from the $dI/dV$ measurements used to generate the corresponding $O_N(E)$ curves in Fig. 6.5(a) (reproduced in the upper panel). The spectra were normalized to their integral over a range of voltages ($-60 < V < 0$). The insets represent the asymmetry parameter of the respective individual topographs acquired simultaneously to the conductance maps.
Figure D.2: (b) Average spectra from the $dI/dV$ measurements used to generate the corresponding $O_N(E)$ curves in Fig. 6.5(c) (reproduced in (a)). (c) $O_N(E)$ measured on URu$_2$Si$_2$ below $T_HO$ (4.2 K) over the same FOV with the different tips. (d) Average spectra from the $dI/dV$ measurements used to generate the corresponding $O_N(E)$ curves in (c). The insets represent the asymmetry parameter of the respective individual topographs acquired simultaneously to the conductance maps.
Figure D.3: Average spectra (lower panels) from the $dI/dV$ measurements used to generate the corresponding $O_N(E)$ curves in Fig. 6.5(b) (reproduced in the upper panel). The spectra were normalized to the their integral over a range of voltages ($-100 < V < 0$). The insets represent the asymmetry parameter of the respective individual topographs acquired simultaneously to the conductance maps.
Appendix E

Prior Presentation

Some of the work presented in this thesis has been previously presented publicly at scholarly meetings, as listed below.

- 10th International Conference on Spectroscopies in Novel Superconductors, Berkeley, CA, USA, June 24-28, 2013 – Oral Presentation
- Gordon Research Seminar and Conference on Superconductivity, Les Diablerets, Switzerland, May 11-17, 2013 – Poster Presentation
- APS March Meeting, Baltimore, MA, USA, March 18-22, 2013 – Oral Presentation
- International Conference on Material and Mechanism of Superconductivity (M2S), Washington DC, USA, July 29 - August 3, 2012 – Poster Presentation
- APS March Meeting, Boston, MA, USA, February 27-March 2, 2012 – Oral Presentation
- Gordon Research Conference on Superconductivity, Waterville Valley, NH, USA, June 5-10, 2011 – Poster Presentation
- APS March Meeting, Dallas, TX, USA, March 21-25, 2011 – Oral Presentation
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