CHARGE FLUCTUATIONS OF THE STRANGE METAL IN SPACE AND TIME

BY

ALI ABDULLAH HUSAIN

DISSEETATION

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Doctoral Committee:

Assistant Professor Fahad Mahmood, Chair
Professor Peter Abbamonte, Director of Research
Professor Anthony J. Leggett
Assistant Professor Bryce Gadway
Abstract

The strange metal is an enigma within the field of many-body quantum physics, as it defies the standard Fermi liquid theory of metals due to the absence of well-defined, electron-like quasiparticles. It has been presumed that strange metal behavior arises due to strong correlations between electrons that are not present in ordinary Fermi liquids, but the exact nature of these correlations is unknown. To this end, this thesis aims to address the fundamental question: What, precisely, is so strongly correlated about charge in the strange metal?

This question is tackled by experimentally measuring the dynamic charge response function $\chi''(\mathbf{q}, \omega)$, which directly encodes charge correlations in momentum and energy, using the technique of Momentum-resolved Electron Energy-loss Spectroscopy (M-EELS). In particular, two prototypical members of the cuprate and ruthenate strange metal families are studied: $\text{Bi}_2\text{Sr}_{1.9}\text{Ca}_{1.0}\text{Cu}_2\text{O}_{8+x}$ (Bi-2212) and $\text{Sr}_2\text{RuO}_4$.

By studying Bi-2212 at optimal doping, it is found that the charge response of the strange metal is characterized by a broad continuum of fluctuations that are momentum and energy independent over a large range of parameter space, unlike Fermi liquid charge correlations which exhibit propagating density waves of charge with well defined energy and momentum (i.e. plasmons). We argue that, in essence, the charge correlations of the strange metal are highly localized in both space and time, unlike the Fermi Liquid where they are localized in momentum and energy instead.

To understand how charge correlations change as one leaves the strange metal regime, the M-EELS response of Bi-2212 is mapped out as a function of doping and temperature. At high temperature, it is found that the continuum is largely doping independent. However,
upon cooling, very large changes in spectral weight are observed over a range of energy scales nearly two orders of magnitude larger than the thermal scale $k_B T$. Moreover, this change in spectral weight undergoes a sign reversal as a function of doping, with spectral weight enhancement on the underdoped side, suppression in the overdoped regime, and no change at optimal doping. These changes in spectral weight are completely unlike the case of the Fermi liquid, where doping only acts to rigidly shift the plasmon energy and no significant changes occur as a function of temperature.

Finally, we venture further and ask whether strange metal and Fermi liquid charge correlations can simultaneously coexist in a material. To explore this possibility, we measured the M-EELS response of Sr$_2$RuO$_4$, a material which exhibits strange and bad metal behavior at high temperature, but transitions to a well-defined Fermi liquid at low temperature. Surprisingly, in the strange metal regime, Sr$_2$RuO$_4$ exhibits both a broad continuum similar to Bi-2212 and a propagating Fermi liquid collective mode at low-energies and momentum. Upon cooling, low-energy spectral weight is suppressed in the strange metal continuum and the Fermi liquid collective mode velocity is strongly renormalized. These findings confirm the strange metal and Fermi liquid can coexist and demonstrate that Sr$_2$RuO$_4$ exhibits charge correlations with strange metal character at high energies and short length scales and Fermi liquid character at low energies and long wavelengths.
Look into that creation which is around you. You will see nothing out of proportion in the creation of the All-Merciful. So, cast your eye again. Do you see any rifts? Then cast your eye again and again, and each time the eye will come back to you dazzled, humbled and aweary by the depth of what it has seen. (Quran: Al-Mulk 3-4)
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Chapter 1

Outline of this thesis

In this thesis, I aim to address the fundamental question of what makes some metals “strange” and strongly correlated, while others are “normal” and weakly correlated. Understanding correlations is most directly done by measuring correlation functions on the appropriate time- and length-scales of the system. Accordingly, I argue that Momentum-resolved Electron Energy-Loss Spectroscopy (M-EELS) is the right tool to use because it measures charge correlations and therefore put it to use to address the nature of the strange metal. This introduction will describe the importance of understanding strange metals, and subsequently will outline the work I will present in this thesis.

1.1 Importance of the strange metal

Despite nearly a century of research into the quantum theory of solids, physicists have not found more conductive or economical substitutes for traditional metals like copper, silver, and gold. It may seem, therefore, that studying strange or bad metals, which are poor conductors and quite expensive, is a manifest waste of time and resources. Admittedly, in the grand scheme of things, this line of thinking is not completely wrong, but there is more to strange metals than their poor conductivity.

Despite appearances, studying strange metals does have a clear and tangible motivation. Curiously, strange metals appear in close conjunction with the highest temperature superconductors known to man at atmospheric pressure, the cuprates and iron pnictides, along with a host of other seemingly unrelated material families including ruthenates, or-
ganic molecular solids, and f-electron heavy-fermion compounds. Laying at the heart of all of these systems, the strangeness of the strange metal manifests itself through violations of decades of common sense developed from the Fermi liquid theory of metals. In particular, strange metals typically exhibit anomalous scaling in their resistivity, thermal conductivity, optical conductivity, spin susceptibility, photoemission spectra, electronic Raman susceptibility, and more. Individually, any one of these anomalous properties can be explained away by finely-tuned material parameters, but the amount of fine tuning needed to explain all strange properties in aggregate is at odds with the apparent ubiquity of the strange metal across very different material systems. Thus, it is conjectured that the strange metal is its own state of matter distinct from the good, Fermi-liquid metals, and has unique instabilities towards high-temperature superconductivity, magnetism, spin liquids, and other exotic phases. Should one be able to understand the strange metal, the hope is that these instabilities can ultimately be tamed and manipulated by clever engineering.

From a broader perspective, the strange metal is also seen as the prototypical problem to solve for making progress in understanding many-body quantum systems. While the Fermi liquid is characterized by low-energy physics where electrons are renormalized but effectively weakly-correlated, electrons in the strange metal are thought to be much more “strongly correlated”, thus precluding an effectively non-interacting description. It should be emphasized that this comparison between the strange metal and Fermi liquid is a hand-waving one, and one of the purposes of this thesis is to make this comparison precise by measuring the charge correlation function of the strange metal directly.

1.2 Overview of this dissertation

In Chapter 2, this thesis will introduce some of the foundations for understanding many-body quantum systems, emphasizing the importance of response functions. From there, Chapter 3 will discuss some theoretical and experimental aspects of Fermi liquids and strange metals.
The goal of this chapter is to present aspects of the strange metal that deviate from Fermi liquid theory and what big picture questions remain open on the topic.

From there, the theory of inelastic electron scattering in the form of Momentum-resolved Electron Energy-Loss Spectroscopy (M-EELS) will be introduced in Chapter 4. First, the purpose and role of scattering experiments in condensed matter will be presented with emphasis on the need for inelastic electron scattering. Then, the derivation and interpretation of the M-EELS cross-section and sum rules will be discussed, especially in the context of well-understood material systems and models. Finally, open questions on the theoretical foundations of M-EELS will be presented.

In Chapter 5, we will present the experimental implementation of M-EELS at UIUC. This chapter will first discuss the overall setup of the instrument, design of the M-EELS spectrometer and tuning of the electron beam. Subsequently, sample alignment and data analysis procedures will be shown. The chapter will conclude with a roadmap for next-generation M-EELS instruments.

The remainder of this thesis (Chapters 6 and 7) will cover M-EELS results on two well-known material systems that exhibit strange metal behavior: the Bismuth-based high-$T_c$ cuprate $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{Ca}_{1.0}\text{Cu}_2\text{O}_{8+x}$ (Bi-2212) and ruthenate $\text{Sr}_2\text{RuO}_4$. Broadly speaking, these chapters will answer the following three questions:

1. How do the charge correlations of the strange metal compare to the Fermi liquid?

2. How do strange metal charge correlations change as one leaves the phase?

3. Are the charge correlations of the strange metal and Fermi liquid mutually exclusive, or can they simultaneously coexist?

In Chapter 6, which addresses questions #1 and #2 above, M-EELS results on the Bi-2212 are presented. The chapter will begin with a brief synopsis of strange metal behavior in the cuprates and their overall phenomenology. From there, M-EELS results deep in the
strange metal regime of the cuprate Bi-2212 at optimal doping and 300 K will be shown. The measured charge correlations suggest that strange metals are defined by a featureless of continuum of non-propagating charge excitations, unlike the propagating plasmon collective mode of the Fermi liquid. We argue then that the answer to question #1 above is that the strange metal exhibits charge fluctuations localized in time and space, unlike the Fermi liquid where they have well-defined energy and momentum instead.

Chapter 6 will continue on to study the doping and temperature dependence of the strange metal continuum in order to address question #2. At room temperature the strange metal continuum is found to be unchanged with doping. Upon cooling however, large changes in spectral weight occur at low temperature with a sign-reversal at optimal doping. In specific, spectral weight below 0.5 eV at low temperatures is shown to be strongly enhanced when underdoped, suppressed when overdoped, and unchanged at optimal doping. This phenomenology maps out a fan-like strange metal region in the cuprate phase diagram, and is entirely different from the Fermi liquid, where doping rigidly shifts the plasmon energy and temperature plays essentially no role. Chapter 6 will then conclude by connecting this spectral weight transfer to other properties of the cuprates and with a discussion of the possible theoretical origins of the strange metal continuum.

Finally, in Chapter 7, we explore the possibility for coexisting Fermi liquid and strange metal excitations in Sr$_2$RuO$_4$, a ruthenate which behaves as a high-temperature strange metal and low-temperature Fermi liquid. We begin by summarizing the general phenomenology of Sr$_2$RuO$_4$, particularly in terms of the so-called “Hund’s metal”. From there, M-EELS results on Sr$_2$RuO$_4$ will be presented within the strange metal regime at 300 K. The M-EELS results indeed show that a strange metal continuum dominates up to high energies (about 1.2 eV) and over 90% of the Brillouin zone, similar to Bi-2212. Surprisingly, however, a coherent, dispersing Fermi-liquid collective mode is observed at low energies and long wavelengths. Upon cooling below the nominal Fermi liquid coherence temperature, the strange metal response undergoes spectral weight suppression and the Fermi liquid mode exhibits
a large renormalization of its dispersion, with a 40% reduction in mode velocity. Thus, question #3 can be answered in the affirmative, as our M-EELS results show that Sr$_2$RuO$_4$ hosts coexisting strange metal and Fermi liquid excitations, with the strange metal continuum dominating at high energies and short wavelengths, and the Fermi liquid mode at low energies and long wavelengths. We then conclude Chapter 7 with a discussion of promising future research directions for linking the strange metal and Fermi liquid in the context of the ruthenates.

1.3 Personal contributions and collaborations

Unless otherwise noted, all the M-EELS data presented in this thesis have been acquired and analyzed by myself with the help of my labmates Matteo Mitrano, Melinda Rak, Samantha Rubeck, Sean Vig, and Anshul Kogar. Optical measurements of the dielectric function for enforcing the f-sum rule on M-EELS data was provided by the groups of Dirk van der Marel (Bi-2212 and Sr$_2$RuO$_4$) and Erik van Heumen (Bi-2201).

Single crystals of Bi$_{2+1}$Sr$_{1.0}$Ca$_{1.0}$Cu$_2$O$_{8+x}$ were grown and characterized by John Schneeloch and Ruidan Zhong from the group of Genda Gu at Brookhaven National Laboratory. Overdoped crystals of the single layer cuprate Bi$_2$Sr$_2$CuO$_{8+x}$ with $T_c = 12$ K with lead-doping (to suppress the superlattice) were grown by the group of Erik van Heumen at the University of Amsterdam. Crystals of Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ were grown by Chanchal Sow and Fumihiro Nakamura respectively from the group of Yoshiteru Maeno at Kyoto University. Crystals of single crystal graphite were purchased from Naturally Graphite™ who obtained them from natural graphite mines in Tanzania and New York.

Theoretical support for understanding M-EELS results on the cuprates at various stages and levels was provided by Bruno Uchoa, Chandra Varma, Philip Phillips, Jan Zaanen, and Nigel Goldenfeld. Work on Sr$_2$RuO$_4$ was also done with valuable theoretical insight from Antoine Georges, Manuel Zingl, and Hugo Strand. Scanning Transmission Electron
Microscopy EELS (STEM-EELS) experiments on Bi-2212 were done by Katia Marche and Christian Dwyer at Arizona State University. STEM-EELS sample preparation and measurements on Sr$_2$RuO$_4$ were done by myself, Hongbin Yang, and Philip Batson using the Nion UltraSTEM Scanning Transmission Electron Microscope at Rutgers University.

1.4 Resulting publications

The work described in this dissertation has resulted in the publications and in-progress manuscripts listed below.

- On the use of M-EELS in condensed matter physics and its cross-section in the presence of strong dynamical scattering


- Sum rules and polarizability for reflection M-EELS of layered two-dimensional systems

  B. Uchoa, A. A. Husain, M. Mitrano, M. S. Rak et al., Response function of momentum-resolved electron spectroscopy in layered systems (in preparation)

- Charge correlations of the strange metal, as measured in the cuprates


  A. A. Husain, M. Mitrano, M. S. Rak, S. I. Rubeck et al., Crossover of Charge Fluctuations across the Strange Metal Phase Diagram, Phys. Rev. X 9, 041062 (2019)
• Demonstration of coexisting strange metal and Fermi liquid collective charge excitations in Sr$_2$RuO$_4$

**A. A. Husain**, M. Mitrano, M. S. Rak, S. I. Rubeck, et al., Coexisting Fermi Liquid and Strange Metal Excitations in Sr$_2$RuO$_4$, (to be submitted)
Chapter 2

Introduction

In this chapter we will give a high-level overview of the quantum many-body problem from the experimental point of view. We will see that quantum many-body physics is the study of approximately good quantum numbers, as the true good quantum numbers are, in general, too complicated to extract. We will then discuss how one experimentally measures these approximate quantum numbers through the lens of response and correlation functions. Finally, we discuss how one particular response function, the charge density response $\chi(q, \omega)$, allows one to directly address the question of what makes the strange metal so strongly correlated.

2.1 Overview of the quantum many-body problem

One of the central disconnects between textbook physics and reality is the simple fact that textbook objects are small and real-life objects are big. Not only are they big in size, but, more importantly, the number of internal components is enormous. To make matters worse, the threshold for being considered “big” is fairly low, with anything larger than two being too big for exact solutions in either classical and quantum mechanics, and exact quantum computational methods having trouble beyond about 50. How, then, can we ever hope to make progress in solving, at the quantum level, for the properties of something like a copper wire, which has over $10^{23}$ atoms? This is the realm of quantum many-body physics, and the remedy lies in changing our standards of what constitutes a “solution”.

In few-body quantum systems, one solves for the behavior of the system through its wavefunctions, starting from the ground state $\psi_0(x_1, \ldots, x_n)$ to the excited states $\psi_i(x_1, \ldots, x_n)$. 
These wavefunctions are obtained by diagonalizing the Hamiltonian $H$ which exactly determine the system’s static and dynamical behavior. Importantly, one can radically reduce the complexity of these wavefunctions by representing them with a discrete set of good quantum numbers that encapsulate their most important properties. For a free particle, this is simply the momentum $k$, while in an atom this could be the atomic shell number $n$ and total angular momentum quantum numbers $j, m_j$. Basic properties of few-body systems, such as their optical absorption spectra or magnetic behavior, can be calculated by introducing an interaction term in the Hamiltonian and studying the resulting coupling between states of different quantum numbers.

On the other hand, in many-body systems, the full wavefunctions are incredibly complicated because of the enormous number of particles involved. Even if one had a large enough computer to store these many-body wavefunctions, one would much rather have a simplified set of good quantum numbers to make sense of the system. Unfortunately, even these good quantum numbers are too complicated to describe exactly in many-body systems. Thus, the principal challenge of understanding many-body systems is the sheer complexity of their good quantum numbers. This complexity is schematically compared with the case of few-body systems in Fig. 2.1.

However, all is not lost for understanding many-body physics. Progress can still be made by giving up on the true quantum numbers and instead asking how well the many-body eigenstates are described by approximate quantum numbers. For the sake of simplicity, these approximate quantum numbers are usually taken to be those of free particles, such as the free electron’s momentum $k$ and spin $\sigma$. From this perspective, we can roughly classify weakly-interacting many-body states as states with true quantum numbers that are well approximated by those of free particles, while strongly-interacting states are states with quantum numbers that are not well approximated as such.

More formally, consider the creation and annihilation operators for a free-particle state $a_n^\dagger$ and $a_n$. This free particle state has quantum numbers $\mathbf{n}$. For example, these operators
Figure 2.1: **Comparison of few-body and many-body quantum systems.** (a) A few-body system, such as an atom, is characterized by discrete eigenstates with quantum numbers \((A, B, C, D)\) which each have their own subset of quantum numbers \((a_i, b_i, c_i, d_i)\). These could be, for example, the total angular momentum \(J\) and its substates \(m_j\). Because these are good quantum numbers, each state is long-lived (i.e. sharp in energy), and typically eigenstates are separated on experimentally accessible energy ranges between 0.1 to 10 eV. (b) Many-body systems are characterized by an enormous number of eigenstates resulting in a congested continuum of states separated by extremely small energies of order \(10^{-23}\) eV. Some of these eigenstates can be grossly labeled by approximate quantum numbers \((\tilde{A}, \tilde{B}, \tilde{C}, \tilde{D})\), while others have quantum numbers that are simply unknown (denoted by question marks).
could create an electron with wavefunction $e^{ikx}$ and spin up, in which case $\mathbf{n} = (k, \uparrow)$. Now, let $|i\rangle$ denote an arbitrary many-body eigenstate. Then, the question of how well $|i\rangle$ is approximated by quantum numbers $\mathbf{n}$ is captured by the following expression.

$$S_{ii}(\mathbf{n}, \mathbf{n}) \equiv \langle i|a_\mathbf{n}^\dagger a_\mathbf{n}|i\rangle$$

(2.1)

If there exists some subset of true quantum numbers for the state $|i\rangle$ that are well-approximated by a free-particle state with quantum numbers $\mathbf{n}$, then $S_{ii}(\mathbf{n}, \mathbf{n})$ will be large. If there is no such subset, then $S_{ii}(\mathbf{n}, \mathbf{n}) \approx 0$, and $\mathbf{n}$ is a bad approximation for any of the true quantum numbers. This quantity, $S_{ii}(\mathbf{n}, \mathbf{n})$, is a type of correlation function, which are the primary quantities of interest in many-body systems, rather than the complicated true quantum numbers themselves. Moreover, as we will see next, these correlation functions are not simply theoretical constructs, but form a powerful language for expressing what is measured in actual experiments on many-body systems.

### 2.2 What is measured in (ideal) experiments?

We will now show that, under quite general conditions, the result of an experiment can be related to a correlation function. With the added assumption of thermal equilibrium, these experimentally measured correlation functions can be connected to a response function. These response functions embody how the system responds to a sudden fluctuation and thus allows one to explore the excited states of a system in analogy to the classical case of hitting a bell to discover its resonant frequencies.

Let us first describe the measurement process. At their core, experiments in condensed matter (and many other fields of physics) are done in three conceptually separate steps. First, the experimentalist carefully prepares the initial state of some probe system $|i\rangle$ so that it is in a state of some definite quantum number (e.g. momentum, spin, electric field, photon number). Then, the second step is to let the probe interact with the system of
Figure 2.2: The measurement procedure. (a) In a typical experiment, the experimentalist prepares a probe system in a definite state \(|i\rangle\). This probe state then interacts with the target system \(|\psi\rangle\) through some interaction Hamiltonian \(H_{\text{int.}} = \mathbf{j} \cdot \mathbf{A}\), where \(\mathbf{j}\) acts on the target system and \(\mathbf{A}\) acts on the probe. Once the interaction is complete, the probe’s final state is measured. (b) By measuring the probe’s final state repeatedly, one is able to reconstruct the reduced density matrix of the probe after interaction. Typically, the diagonal components are measured, rather than the off-diagonal elements. Peaks in these matrix elements reveal the excited states of the target system.

Important information is gained by examining how the transition rate \(S(i \rightarrow f)\) varies with final state \(|f\rangle\) and with external parameters applied to \(|\psi\rangle\) (e.g., temperature, magnetic field). For example, a resonance in \(S(i \rightarrow f)\) may indicate that the system has an order parameter \(\langle \hat{O} \rangle\) with symmetry such that \(\langle f | \hat{O} | i \rangle \neq 0\). Similarly, how \(S(i \rightarrow f)\) changes with temperature might signify a phase transition.

Static experiments (also called DC or elastic experiments) focus on the time-independent properties of the (thermodynamic) ground state of the system \(|\psi\rangle\). For comparison, inelastic (or dynamic) experiments probe the pathways for transitions of the ground state \(|\psi\rangle\) into its excited states \(|\psi_n\rangle\). Let us give two concrete examples: resistivity and inelastic electron scattering. Abstractly speaking, in a measurement of resistivity, one applies an external electric field \(\mathbf{E}\) between two disconnected wires in a state of zero current \(|0\rangle\). Then, one
inserts a material and measures the final state current of the two wires $|\mathbf{j}\rangle$ to obtain $S(0 \rightarrow \mathbf{j}) \approx \delta(\mathbf{j} - \mathbf{j}_0)$ which ultimately gives the resistivity $\rho = E/j_0$. For inelastic electron scattering, one prepares a free electron in state of definite momentum $|\mathbf{k}_i\rangle$, allows it hit a sample, then measures its final momentum $|\mathbf{k}_f\rangle$, with a scattering rate $S(\mathbf{k}_i \rightarrow \mathbf{k}_f)$. Transitions between free-electron states with the same energy tell us about the static properties of the system, while transitions into different energies ($k_i \neq k_f$) reveal possible fluctuations into excited states.

To quantitatively describe the transition rates and what they imply, we need to know the form of the interaction Hamiltonian $\mathcal{H}_1$ between the probe and system that acts in addition to the system’s usual Hamiltonian $\mathcal{H}_0$. The time evolution of the combined probe-system state in the interaction picture can then be described by equation 2.2.

$$U(t) \equiv \mathcal{T} \left[ e^{-\frac{i}{\hbar} \int dt \mathcal{H}_1(t)} - 1 - \frac{i}{\hbar} \int_{t_0}^{t_1} dt \mathcal{H}_1(t) + \mathcal{O}(\mathcal{H}_1^2) \right]$$ (2.2)

Because the goal here is to measure properties of the system, not the probe, it is imperative that the interaction can be treated perturbatively. If the interaction is too strong for a perturbative treatment, then we are no longer measuring the properties of the original Hamiltonian $\mathcal{H}_0$, but the properties of the (presumably) less interesting Hamiltonian $\mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_1$. It should be noted however, that a perturbative interaction need not mean that the linear contribution of $\mathcal{H}_1$ in $U(t)$ is dominant, but instead means that only a finite number of terms in the expansion are needed.

Furthermore, for an ideal probe, the interaction Hamiltonian has a tensor product form of $\mathcal{H}_1 = g(t) \mathbf{j} \otimes \mathbf{A}$, where $\mathbf{j}$ is an operator that only acts on states of the system, $\mathbf{A}$ only acts on the states of the probe, and $g(t)$ is the explicit time-dependence of the interaction. This separable form allows the uninteresting dynamics of the probe under $\mathbf{A}$ to be divided out from the resulting measurement, leaving only the interesting dynamics of the target system under $\mathbf{j}$. If instead $\mathcal{H}_1 = \sum_i g(t) \mathbf{j}_i \otimes \mathbf{A}_i$, then the probe and system become “too entangled”,

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generically resulting in a measurement that is an incoherent sum of different processes that are difficult to disentangle without further information.

Retaining just the linear term in equation 2.2, and noting that $\mathcal{H}_1(t) = e^{i\mathcal{H}_0 t/\hbar} \mathcal{H}_1 e^{-i\mathcal{H}_0 t/\hbar}$ when written out fully, the probability of a transition to an excited state $|f\rangle |j\rangle$ is:

$$\langle j|\langle f|U(t)|\psi\rangle|i\rangle \approx -\frac{i}{\hbar} \left( \int_{t_0}^{t_1} dt e^{i(\omega_f - \omega)t} g(t) \right) \langle j|A|i\rangle \langle f|j|\psi\rangle,$$  \hspace{1cm} (2.3)

where $\omega \equiv \omega_j - \omega_i$. If the interaction occurs over much longer timescales than the transitions of interest, then the integral can be replaced by a $\delta(\omega_f - \omega)$. In an actual experiment, we are typically only able to measure the transition rate of the probe going into the final state $|j\rangle$, while the system’s final state $|f\rangle$ is left unmeasured. Thus, a partial trace must be taken over the system states, giving the famous Golden rule in equation 2.4.

$$R(i \rightarrow j) \approx \frac{2\pi}{\hbar} |\langle j|A|i\rangle|^2 \sum_f |\langle f|j|\psi\rangle|^2 \delta(\omega_f - \omega)$$  \hspace{1cm} (2.4)

For an ideal probe, the matrix element $\langle j|A|i\rangle$ is exactly known and can be divided out, leaving just

$$\sum_f |\langle f|j|\psi\rangle|^2 \delta(\omega_f - \omega) \equiv \langle j(\omega)|j(0)\rangle \leftrightarrow S(\omega).$$  \hspace{1cm} (2.5)

Where $S(\omega)$ is a dynamic correlation function (also referred to as a spectral function).

Thus, we have shown that ideal experiments measure correlation functions, which are the primary quantity of interest in studying many-body systems. Figure 2.2 summarizes the above derivation more schematically. Equation 2.4 can easily be generalized to the case of a thermal state as well, as the transition rates for different starting system states $|\psi\rangle$ can be summed classically with a Boltzmann weight $e^{-\beta \hbar \omega}$.

Although we have mathematically shown that experiments measure correlation functions, these functions can be much more intuitively understood by recasting them in terms of
response functions. These response functions are also mathematically identical to retarded many-body Green functions, which can be calculated through diagrammatic field theoretic approaches, making them also convenient for comparing experiments to theory.

To define a response function, consider the following scenario. Let us start again with our system’s Hamiltonian $H_0$, but now consider a sudden fluctuation $\mathcal{H} = H_0 - g(t)j$. For intuitive purposes, imagine $j$ to be the current density operator, although it could be any Hermitian operator in principle. Then, what we are considering is the sudden appearance of a current fluctuation in the system. We can then ask, what time-dependent current $\langle j(t) \rangle$ do we expect in response to this sudden current fluctuation?

Noting that, within the interaction picture, $j(t) = e^{iH_0 t/\hbar}j e^{-iH_0 t/\hbar}$, and thus $\langle j(t) \rangle = \langle \psi(t_0) | e^{i\mathcal{H}_1 (t-t_0)/\hbar}j(t) e^{-i\mathcal{H}_1 (t-t_0)/\hbar} | \psi(t_0) \rangle$, we can again expand each time evolution operator to first order as $e^{-i\mathcal{H}_1 t/\hbar} \approx 1 - \frac{i}{\hbar} \int \mathcal{H}_1(t)$. Performing this expansion gives:

$$\langle j(t) \rangle = \langle \psi | j(t) | \psi \rangle - \frac{i}{\hbar} \int_{t_0}^{t} d\tau g(\tau) \theta(\tau-t_0) \langle \psi | [j(t),j(\tau)] | \psi \rangle$$ (2.6)

Where $|\psi\rangle = |\psi(t_0)\rangle$. Without loss of generality, we can set $t_0 = -\infty$ and can redefine $\tau \rightarrow t-\tau$. Also note that $\langle \psi(t_0) | j(t_1) j(t_2) | \psi(t_0) \rangle = \langle \psi(t_2) | j(t_1-t_2) j(0) | \psi(t_2) \rangle$ so that we can rewrite the above expression as:

$$\langle j(t) \rangle = \langle \psi | j(t) | \psi \rangle - \frac{i}{\hbar} \int_{-\infty}^{\infty} d\tau g(t-\tau) \langle \psi | [j(\tau),j(0)] | \psi \rangle$$ (2.7)

$$= \langle j(t) \rangle_{\text{equil.}} + \int_{-\infty}^{\infty} d\tau g(t-\tau) \frac{-i}{\hbar} \theta(\tau) \langle \psi | [j(\tau),j(0)] | \psi \rangle$$ (2.8)

The first term in 2.8 denotes the contribution to the current coming from the pre-existing equilibrium current, which is usually uninteresting, while the second term is a convolution integral of the response function $\chi(\tau)$ and the time-dependence of the fluctuation $g(t)$. The
interpretation of $\chi(\tau)$ is simple. Taking current as an example, if the system is perturbed by a current fluctuation spike at $t = 0$, the resulting current at a later time $t = \tau$ is given by the response function (also known as the susceptibility) $\chi(\tau)$. This situation is formally identical to the simple classical cases of hitting a bell with a hammer, dropping a rock in a pond, or the impulse response of a passive electrical circuit.

The response function can then be connected back to the experimentally measured correlation function by taking the Fourier transform of equation 2.8

$$\langle j(\omega) \rangle = \langle j(\omega) \rangle_{\text{equil}} + g(\omega)\chi(\omega). \hspace{1cm} (2.9)$$

Noting that the Fourier transform of a step function is $\theta(\omega) = \frac{1}{2} \delta(\omega) - \frac{i}{2\pi\omega}$, the imaginary part of the susceptibility $\chi''(\omega)$ is given by

$$\chi''(\omega) = \frac{1}{2\hbar} \langle [j(\omega), j(0)] \rangle. \hspace{1cm} (2.10)$$

Then, assuming the system was in thermal equilibrium before the fluctuation, detailed balance mandates that $S(\omega) = \langle j(\omega)j(0) \rangle = e^{-\beta\hbar\omega} \langle j(-\omega)j(0) \rangle = e^{-\beta\hbar\omega} S(-\omega)$. Which finally gives the fluctuation-dissipation theorem below.

$$\chi''(\omega) = \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega})S(\omega) \hspace{1cm} (2.11)$$

The above derivation and convention follows that of [1], but another common convention in field theory approaches to many-body physics differs by a few constant prefactors for $S(\omega)$ [2], giving the relation below.

$$\chi''(\omega) = -\pi(1 - e^{-\beta\hbar\omega})S(\omega) \hspace{1cm} (2.12)$$

Thus, the correlation function measured by an ideal experiment can be directly related to the response function of a system to a perturbation. In other
words, if this experiment couples to an operator $j$, then the system undergoes a sudden fluctuation in $j$ and the resulting time-dependent $\langle j(t) \rangle$ is measured by the experimentalist’s probe. A cartoon representation of this idea is presented in Figure 2.3. Using the language of quantum numbers introduced in at the beginning of this chapter, the experimentalist’s probe creates a perturbation that takes the form of a free-particle-like state with quantum number(s) $j$, and then observes how that perturbation decays in time due to the free-particle quantum number(s) being only an approximation for the true many-body ones. If some portion of the system does resemble a free-particle eigenstate of $j$, this perturbation will be long-lived and/or oscillatory, otherwise it will rapidly decay.

An important generalization of response and correlation functions is to study their non-local structure. So far, we have focused on perturbations that varied temporally, but not spatially. If the perturbation is instead localized in time and space (i.e. $\delta(t)\delta(r)$), then the response function also varies spatially as well $\chi \to \chi(r,t)$. The result is that the response function exhibits propagating wave dynamics similar to throwing a rock in a pond, as shown in Figure 2.4.

Naturally, the above discussion of response functions can be performed to arbitrary order in perturbation theory with any operators of interest. For a higher-order response function of order $n$, there are generally $n$ frequencies (or times) involved $\chi^{(n)}(\omega_1, \ldots, \omega_n)$. In practice, it is very rare to go beyond third-order perturbation theory except in highly non-linear optical measurements. The primary reason for this is the difficulty of isolating the (typically much weaker) higher-order responses from lower order ones.

It is also worth mentioning at this point that the information content of $\chi''(\omega)$ and $\chi'(\omega)$ is redundant due to the appearance of a step function in $\chi(t)$. This step function means that $\chi(t)$ can be understood to have equal and opposite even and odd contributions, of which the Fourier transform of the even part gives $\chi'(\omega)$ while that of the odd part gives $\chi''(\omega)$. Thus, if one has either $\chi''(\omega)$ or $\chi'(\omega)$, the other can be obtained by taking the inverse Fourier transform, multiplying by the sign function $\text{sgn}(t)$, and a final forward Fourier transform.
Figure 2.3: **Measurement and correlation functions.** (a) Response functions quantify the system's response to a sudden fluctuation in the Hamiltonian $\mathcal{H}(t) = \mathcal{H}_0 + \delta(t)\mathbf{j}$. (b) Resulting response function to the perturbation in (a) as function of time. Notice that the response function is causal, meaning it is strictly zero before the perturbation (as one would expect) and obeys the Kramers-Kronig relations. (c) Dissipative part of the response function in the frequency domain $\chi''(\omega)$ showing peaks at the resonant frequencies of the system at $\omega_1, \omega_2$. (d) Fluctuation in a *thermal* Hamiltonian at finite temperature. Note now that there are thermal fluctuations besides the perturbation, unlike in (a). (e) Correlation function $S(t)$ showing how correlations of the system decay as fluctuations become more separated in time. This correlation function $S(t)$ is not causal, unlike $\chi(t)$. (f) Dynamic correlation function $S(\omega)$ in the frequency domain. Note that peaks appear at the same frequency positions as in (c), but with different intensities due to the Boltzmann factor inherent to thermal systems.
Figure 2.4: **Real-space response functions.** Response function of a system with a gapped, quadratic-dispersing mode (i.e. a 3D Fermi liquid plasmon) **(a)** Before the perturbation occurs \((t < 0)\), the response function is identically zero over all space, as one would expect. **(b)** Immediately when the perturbation arrives \((t = 0)\), the response function is strongly peaked at the perturbation’s position but is largely zero everywhere else. This structure represents the fact that the response of the system has a characteristic velocity \(v\). For \(r/t \gg v\), the system does not “see” the perturbation yet. **(c)** After some time comparable to the intrinsic time dynamics of the system \((t \approx \tau)\), non-trivial spatial structure is visible in the response function in the form of oscillations. **(d)** After longer times \((t \gg \tau)\), the spatial structure of the response function is largely damped and most of the response has dissipated into other channels, leaving only the slowest modes remaining.
This procedure is shown in the equation below.

\[
\chi(t) = \frac{1}{2} (\chi(t) + \chi(-t)) + \frac{1}{2} (\chi(t) - \chi(-t)) = \mathcal{F}^{-1}[\chi'(\omega)] = \mathcal{F}^{-1}[\chi''(\omega)]
\]

The transform between \(\chi'(\omega)\) and \(\chi''(\omega)\) can also be done in one step with the Hilbert transform, and is more commonly known in spectroscopy as the Kramers-Kronig transformation. The procedure for implementing the Kramers-Kronig transformation is shown below in Equation 2.14.

\[
i\chi''(\omega) \xrightarrow{\mathcal{F}^{-1}} \frac{1}{2} (\chi(t) - \chi(-t)) \xrightarrow{\times \text{sgn}(t)} \frac{1}{2} (\chi(t) + \chi(-t)) \xrightarrow{\mathcal{F}} \chi'(\omega)
\]

More information about the mathematical properties of correlation and response functions can be found in [3]. One can understand the real part of the response function \(\chi'(\omega)\) as quantifying phase shifts, while the imaginary part \(\chi''(\omega)\) represents dissipation. As most experiments measure absolute intensities rather than phase, the imaginary part \(\chi''(\omega)\) is what is usually measured.

We end this section by presenting a reference list of commonly measured correlation/response functions in Table 2.1 for the reader’s benefit. A more complete version of the table is available in Appendix A.1. As Tables 2.1 and A.1 show, many distinct experimental techniques measure the same response function but over different parameter regimes. In addition, there is an inherent tradeoff between measuring more sophisticated/informative response functions and experimental flexibility. Thus, “simple” measurements, such as resistivity or magnetometry, are often the most informative in practice due to their ability to be performed in extreme conditions reliably and accurately.
<table>
<thead>
<tr>
<th>Correlation/Response Function</th>
<th>Energy Scales</th>
<th>Momentum Resolved?</th>
<th>Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current-Current</td>
<td>DC to keV</td>
<td>No</td>
<td>Resistivity, Optical Reflectivity (FTIR), Ellipsometry, Time-domain THz, XAS/XES/EXAFS/etc.</td>
</tr>
<tr>
<td>Spin-Spin</td>
<td>DC to eV</td>
<td>Yes</td>
<td>SQUID Magnetometry, NMR, Mössbauer Spectroscopy, Muon Spin-Resonance, Magnetic Inelastic Neutron Scattering, Resonant Inelastic X-ray Scattering,</td>
</tr>
<tr>
<td>Nuclear position-position</td>
<td>DC to 100 meV</td>
<td>Yes</td>
<td>Neutron Diffraction, Inelastic Neutron Scattering</td>
</tr>
<tr>
<td>Electron density-density</td>
<td>meV to keV</td>
<td>Yes</td>
<td>X-ray Diffraction, Inelastic X-ray Scattering</td>
</tr>
<tr>
<td>Fermion Occupation Number Density</td>
<td>0.5 meV to eV</td>
<td>Yes</td>
<td>ARPES, X-ray Photoemission, Spectroscopic STM, X-ray Compton Scattering</td>
</tr>
<tr>
<td>Higher-order current-current</td>
<td>DC to eV</td>
<td>No</td>
<td>Raman Scattering, Second-Harmonic Generation, Resonant Inelastic X-ray, Other nonlinear optical spectroscopies</td>
</tr>
<tr>
<td>Charge density-density</td>
<td>DC, meV to keV</td>
<td>Yes</td>
<td>Electron Diffraction, M-EELS</td>
</tr>
</tbody>
</table>

Table 2.1: Table of common experimental techniques and their response functions: List of techniques that are measured in condensed matter systems along with their energy scales, possibility for momentum resolution, and experimental manifestations. A more detailed table with many more techniques is presented in Appendix A.1.
2.3 Quantifying interactions in a solid

Because there are hundreds of techniques for studying condensed matter systems, from simple resistivity with a multimeter to billion-dollar free-electron laser-based spectroscopies, it is easy to get lost in the forest of possible experiments. To make progress in understanding the Fermi liquid and strange metal, it is useful to take a step back and think about what we want to know in the first place.

The many-body Hamiltonian for a system of charges is given by

\[ H = \hat{T} + \hat{V} = \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i,j} \int d\mathbf{r}_i d\mathbf{r}_j \frac{\hat{\rho}_i(\mathbf{r}_i)\hat{\rho}_i(\mathbf{r}_i)}{|\mathbf{r}_j - \mathbf{r}_j|}. \] (2.15)

Then, from a high-level point of view, the two most basic questions to ask about a many-body system are:

1. **What are the electrons doing in this system (i.e. what is the structure of \( \hat{T} \))?**

2. **How are the electrons interacting (i.e. what is the structure of \( \hat{V} \))?**

The first question concerns the behavior of electrons in a system at a single-particle level. Because the most important quantum numbers for a fermion in a solid are its momentum, spin, energy, and orbital character, obtaining the complete distribution of electrons in terms of these quantum numbers (i.e. \( n(\mathbf{k}, \sigma, E, l) \), or the related Green function \( G = -i\langle Tc_{\mathbf{k},i}^\dagger c_{\mathbf{k},i} \rangle \)) provides an answer to this question. Once this distribution is known, one can examine the structure of \( \hat{T} \) by integrating over \( n(\mathbf{k}, \sigma, E, l) \) in the regions of parameter space of interest.

With some important caveats, this fermion distribution function can be measured to a certain degree by Angle-resolved Photoemission Spectroscopy (ARPES) [4]. With knowledge of \( n \) in hand, fundamental aspects about the many-body system at the single-particle level are revealed, such as the presence or lack of a gap, nature and shape of the Fermi surface, band structure, and degree of quasiparticle coherence.
On the other hand, with regards to question #2, the interactions between electrons are emphatically not encoded within the distribution function \( n(k, \sigma, E, l) \). Nonetheless, one signature of strong interactions, as we will discuss later, is to broaden and reduce the spectral weight of the sharp quasiparticle peaks found in \( n \). Thus, while techniques which measure quantities related to \( n(k, \sigma, E, l) \), such as ARPES or STM, can signal when strong interactions are at play, they simply cannot tell us the actual nature of those interactions directly. Instead, we can guess that a measurement of a quantity like \( \langle \hat{\rho}(r_i)\hat{\rho}(r_j) \rangle \) will give us the insight we need into the structure of \( \hat{V} \) to address the nature of interactions in solids.

To quantify the effective interaction between charges in a many-body system, consider the following thought experiment. We introduce a test charge fluctuation into our system \( \delta \rho_{\text{ext}}(r', t) \), and ask, what kind of effective electric potential is produced and how does that compare to the bare Coulomb potential of a free electron?

In a solid, the charges of the system will act to screen (or sometimes anti-screen) the charge fluctuation in a manner that depends on their distance from the fluctuation and the time after its appearance (see e.g., Figure 2.4). The sum of the bare external charge fluctuation \( \delta \rho_{\text{ext}} \) along with the induced change in the system’s charge density \( \delta \rho_{\text{ind}} \) will give rise to a new effective Coulomb interaction in terms of the total charge fluctuation \( \delta \rho_{\text{tot}} = \delta \rho_{\text{ext}} + \delta \rho_{\text{ind}} \). We will see that this effective interaction is simply a non-local, quantum version of the dielectric function of ordinary electromagnetism \( \epsilon(q, \omega) \).

We can work through this thought experiment using the language of response functions developed in the last section. First, assume that the system’s response to the charge fluctuation is neither sufficiently fast nor localized enough for the fluctuating magnetic field to play a significant role\(^1\). Then, the interaction Hamiltonian of the external test charge and the system is

\(^1\)In other words, the relevant energy and momentum scales of interest are such that \( \omega/q \ll c \).
\[ \mathcal{H}_1 = \int \int d\mathbf{r} d\mathbf{r}' \frac{\delta \rho_{\text{ext}}(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') = \int d\mathbf{r} \left( \int d\mathbf{r}' \frac{\delta \rho_{\text{ext}}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \right) \rho(\mathbf{r}). \quad (2.16) \]

Where \( V_{\text{ext}}(\mathbf{r}, t) \) is the external scalar potential induced by the external charge fluctuation (not an operator), while \( \rho(\mathbf{r}) \equiv \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i) \) is the charge density operator. Then, repeating the same procedure as in equation 2.8, we can approximate the change in the system’s charge density in terms of the external potential due to the external charge fluctuation \( V_{\text{ext}} \) and the system’s inherent charge susceptibility \( \chi(\mathbf{r}, \mathbf{r}', \tau) \) by

\[ \langle \delta \rho(\mathbf{r}, t) \rangle_{\text{ind}} = \int \int d\tau d\mathbf{r}' V_{\text{ext}}(\mathbf{r}', t - \tau) \frac{-i}{\hbar} \theta(\tau) \langle \psi | [\rho(\mathbf{r}, \tau), \rho(\mathbf{r}', 0)] | \psi \rangle. \quad (2.17) \]

We then assume we are interested in length scales that are larger than the size of the atomic bond lengths, in which case we can invoke translational symmetry to give \( \chi(\mathbf{r}, \mathbf{r}', \tau) = \chi(\mathbf{r} - \mathbf{r}', \tau) \). This assumption means we are ignoring the structure of the “local-field” so that the absolute location of the charge fluctuation is irrelevant and the response only depends on the distance from it. As an explicit example, consider ordinary table salt (NaCl). What we are doing is making the assumption that placing the charge fluctuation on the Na\(^+\) site will produce the same response as if the fluctuation were located on the Cl\(^-\) site. This assumption is invalid if we look at the response on length scales comparable to the Na-Cl bond length, but for larger distances we assume the response is the same\(^2\).

This assumption of translation symmetry means that the space-time Fourier transform of the induced response \( \langle \delta \rho(\mathbf{q}, \omega) \rangle_{\text{ind}} \) is simply given by

\[ \langle \delta \rho(\mathbf{q}, \omega) \rangle_{\text{ind}} = V_{\text{ext}}(\mathbf{q}, \omega) \chi(\mathbf{q}, \omega). \quad (2.18) \]

\(^2\)Sometimes \( \chi(\mathbf{r} - \mathbf{r}', \tau) \) and \( \chi(\mathbf{r}, \mathbf{r}', \tau) \) are respectively called the “macroscopic” and “microscopic” response functions to emphasize the (approximate) restoration of translation symmetry at large macroscopic length scales in crystals.
Without loss of generality, we can also take $\delta \rho(r', t)_{\text{ext}} = \delta(r') \delta(t)$ such that $\delta \rho(q, \omega)_{\text{ext}} = 1$. Then the expression for the external potential can be simplified to give $V_{\text{ext}}(q, \omega) = \frac{4\pi e^2}{q^2} = V(q)$, where $V(q)$ is the bare Coulomb potential from a point charge and absorbs the units of charge from the densities. We then have an expression for the total charge density resulting from the external charge fluctuation

$$
\langle \delta \rho(q, \omega) \rangle_{\text{tot}} = \langle \delta \rho(q, \omega) \rangle_{\text{ext}} + \langle \delta \rho(q, \omega) \rangle_{\text{ind}} = 1 + V(q)\chi(q, \omega).
$$

(2.19)

Now we are ready to express the net effective potential produced by the initial charge fluctuation. Recall that the dielectric function relates the externally applied electric field to the net electric field $E_{\text{tot}}(q, \omega) = \frac{1}{\epsilon(q, \omega)} E_{\text{ext}}(q, \omega)$. Because we are ignoring magnetic contributions, all the relevant electric fields can be represented as a gradients of their respective electric potential $E(q, \omega) = i q \phi(q, \omega)$. Furthermore, by using Poisson’s equation we can relate the potential to the charge density via $\phi(q, \omega) = \frac{4\pi e^2}{q^2} \rho(q, \omega)$. Thus, we can state

$$
V_{\text{tot}}(q, \omega) = \frac{1}{\epsilon(q, \omega)} V_{\text{ext}}(q, \omega) = V(q) \langle \delta \rho(q, \omega) \rangle_{\text{tot}}
$$

(2.20a)

$$
\implies \frac{1}{\epsilon(q, \omega)} = 1 + V(q)\chi(q, \omega).
$$

(2.20b)

In other words, the effective potential that one charge sees from another charge is dressed by a factor of $\epsilon^{-1}(q, \omega)$ compared to the bare Coulomb potential $V(q)$. Therefore, a measurement of the charge response function $\chi(q, \omega)$, precisely quantifies the nature of charge interactions in a solid. In addition, because the dynamic charge response is directly related to the charge correlation function $S(q, \omega)$, $\chi''(q, \omega)$ also provides a direct measure of the nature and degree of charge correlations in a material. We should therefore expect a grossly different $\chi(q, \omega)$ (or $S(q, \omega)$) in a strongly-correlated material compared to a weakly-correlated one.

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3We are using CGS units so that the externally applied electric field $E_{\text{ext}}$ is identical to the displacement field $D$. 

25
In general, the many-body nature of the system gives rise to numerous resonances in the effective interaction $V_{\text{tot}}(r - r', \omega)$ that are not present in the bare Coulomb interaction. Just as poles in the single-particle Green function (or sharp peaks in $n(k, \sigma, E, l)$) signify fermion quasiparticles, poles of $\epsilon^{-1}(q, \omega)$ can be understood as collective excitations with boson statistics\(^4\). One can see this by noting that $\epsilon^{-1}(q, \omega)$ is defined as $E_{\text{tot}}(q, \omega) = \frac{1}{\epsilon(q, \omega)} E_{\text{ext}}(q, \omega)$, so a pole in $\epsilon^{-1}(q, \omega)$ indicates the system will produce an electric field $E_{\text{tot}}(q, \omega)$ spontaneously due to vanishingly small perturbations. The approach often taken by field theories of condensed matter is to approximate interactions between electrons in a solid through an effective photon which arises from a pole in $\epsilon^{-1}(q, \omega)$. There are numerous flavors of such collective excitations including the plasmon, phonon, exciton, bipolaron, holon, CDW amplitudon, magnetoplasmon, Josephson plasmon, demon\(^5\), and more. In BCS superconductors and many charge-density wave materials, it is the phonon resonance in the effective interaction that gives rise to superconductivity and insulating behavior respectively [8, 9]. Similarly, in so-called “excitonic”-insulators, the effective interaction via a plasmon-exciton hybrid mode leads way to an exciton condensate [10]. As we will see in the next few sections, the primary collective mode of the (charged) Fermi liquid is the plasmon. A summary of these collective modes and their related energy scales is shown in Figure 2.5

It is worth mentioning that another commonly used quantity in describing effective interactions is the polarizability $\Pi(q, \omega)$, also known as the screened susceptibility $\chi_{\text{sc}}(q, \omega)$. $\Pi(q, \omega)$ relates the induced potential $V_{\text{ind}}$ to the total potential $V_{\text{tot}}$, which is different than $\chi(q, \omega)$ which relates the external potential $V_{\text{ext}}$ to the total potential $V_{\text{tot}}$. In other words, while we would use $\chi$ to represent the system’s response to an external bare electron, we

---

\(^4\)They are bosons because the underlying charge density operator is a real scalar involving two fermion operators.

\(^5\)Just as a phonon is essentially a plasmon of the charged nuclei that becomes gapless/acoustic due to screening by electrons, the “demon” was predicted [5] to be an acoustic plasmon in a system of heavy and light electron bands where the latter screens the former. While phonons are guaranteed to be well-defined because nuclei cannot scatter and turn into electrons, a heavy electron band can certainly scatter into a lighter band. Thus, it is likely that demons generally do not exist, although the experimental search continues [6, 7].
Figure 2.5: **Energy scales and collective modes in condensed matter.** (a) Typical energy scales for various interactions in condensed matter systems adapted from [11, 12]. (b) Each type of interaction in (a) gives rise to different collective modes with widely varying energy scales. Collective mode energy scales in this figure are largely based on [13].

would use Π to represent the response of the system to a fictitious pre-screened electron. Recall from ordinary electromagnetism in solids that the total electric field in a material can be separated into the external field $E_{\text{ext}} = D$ and an induced polarization density $P$ such that $E_{\text{ext}} = E_{\text{tot}} + P$. In the linear-response regime, the polarization density is linearly proportional to $E_{\text{ext}}$, so let us define $\Pi(q, \omega)$ in such a way that $P = -V(q)\Pi(q, \omega)E_{\text{ext}}$. Recalling once more that $E_{\text{ext}} = \epsilon(q, \omega)$, we then have the relations

$$\epsilon(q, \omega) = 1 + V(q)\Pi(q, \omega)$$

$$\chi(q, \omega) = \frac{\Pi(q, \omega)}{1 - V(q)\Pi(q, \omega)} = \Pi (1 + VII + VII\Pi + \ldots )$$

---

6Note that in nonlinear optics it is common to denote $V(q)\Pi(q, \omega)$ as a current susceptibility $\chi(\omega)$ which should be distinguished from the charge susceptibility $\chi(q, \omega)$ used here [1].
The final expansion in Equation 2.22 is a Dyson series of the total charge susceptibility $\chi$ in terms of the polarizability $\Pi$. The diagrammatic interpretation of this series is that $\Pi$ represents the irreducible polarizability, while $\chi$ is the reducible polarizability [2, 14]. This is analogous to the relationship between the fermion Green function $G(k, \omega)$ and the self-energy $\Sigma(k, \omega)$ commonly used in the description of Angle-resolved Photoemission Spectroscopy (ARPES) [4]. Another understanding of that statement is that $\Pi$ represents the response of the system with short-range interactions, and by adding in the long-range Coulomb interaction $V(q)$ one gets the true response $\chi$ [15]. Because $\Pi$ involves short-ranged (or screened) interactions, it is also more convenient to calculate perturbatively in a consistent manner [16]. We will revisit this approach in Chapter 3 when we discuss the Random-Phase Approximation (RPA).

As a last technical note for this section, it should be kept in mind that collective modes no longer show up as poles in $\Pi$ as they did in $\epsilon^{-1}$ and $\chi$, but rather appear as zeros. A more opaque, but technically more accurate, description of $\Pi$ is that $\Pi$ is the response function to an external voltage, while $\chi$ is the response function to an external charge [15]. The external voltage is controllable externally only in the long-wavelength limit $q \to 0$ (e.g. through the use of macroscopic capacitors or wire leads), while the latter is controllable through the use of electron scattering at arbitrary momentum. Thus, experimentally, only $\chi(q, \omega)$ is directly measurable at non-zero momentum.
Chapter 3

The Fermi liquid and the strange metal

In this chapter we will take a look at Landau’s theory of the Fermi liquid and see how it can be used to understand the behavior of metals. This theory is based on an adiabatic connection between a non-interacting and interacting system of fermions, and postulates that the end result of interactions is the formation of well-defined fermionic quasiparticles that are infinitely long-lived at zero temperature. Using this general idea, we will describe the extension of Fermi liquid theory to charged fermions and introduce the concept of screening. We will then move on to discuss the strange metal, which is a “non-Fermi” liquid in the sense that quasiparticles are very short-lived or absent altogether. As there is no accepted theory of the strange metal, we will provide an experimental and theoretical overview of its properties with emphasis on the transport and spectroscopic signatures of ill-defined quasiparticles. We will end this chapter by posing four well-defined questions about the strange metal, three of which we will explicitly answer in Chapters 6 and 7.

3.1 Theoretical basis of Fermi liquid theory

For a non-interacting system of fermions (i.e. a Fermi gas), one is able to construct the ground state by simply populating single-particle energy levels from the lowest level up. As fermions obey Pauli exclusion, each level will be filled by $2S+1$ fermions until all $N$ fermions are accounted for. The total energy of the ground state is then given by the energy of each level times its occupation number $E = \sum_{k,\sigma} E_{k,\sigma} n_{k,\sigma}$. The extension of this procedure to excited states with energy $E'$ is quite straightforward as well, one simply changes the
occupation of the different single-particle levels to \( n_{k,\sigma}' \) by shifting fermions around different single-particle levels.

The ability to explicitly write down the ground state and construct all excited states through a fermion occupation function is very powerful, and we would like to keep a similar framework in the presence of interactions. The approach originally taken by Landau [17] for Helium-3, and extended to charged systems by Silin [18], was to argue that if the energy spectrum of the interacting system exhibits Fermi statistics (at least for some small energy window), one can argue by adiabaticity that the energy levels of the interacting Fermi liquid system are connected to those of the non-interacting Fermi gas. Accordingly, one can then write the energy of the interacting system as a functional of a fermion occupation function \( n_{k,\sigma} \) for “quasi”-particles in the interacting system, rather than the original bare particles.

It should be emphasized that the preservation of Fermi statistics in the interacting system is not something Fermi liquid theory proves, but rather takes as a condition for its own validity. Even in Landau’s original work it was recognized that starting with particles obeying Fermi statistics is an insufficient condition for ending up with a system with states that obeys Fermi statistics. As an example, deuterium as a whole is a fermion, but in the interacting state forms \( D_2 \) molecules with Bose statistics. Moreover, the Fermi liquid also exhibits collective modes (e.g. the plasmon in a charge Fermi liquid of electrons), which are boson states without a non-interacting counterpart, so clearly not all interacting states are adiabatically connected to the Fermi gas. Thus, Fermi liquid theory is by no means a description for all systems (or even all energy scales), but was also never intended to be such a catch-all description in the first place\(^1\). We will return to the (non)applicability of Fermi liquid theory later in this section.

Let us now write a general expression for the energy of an excited state \( \delta E \) of the interacting system in terms of the change in occupation relative to the ground state \( \delta n(k, \sigma) \).

\(^1\)In many ways, Fermi liquid theory is almost unreasonably effective in describing the properties of solids, as it was never envisioned to do so at the outset.
Unlike the non-interacting case, the total energy is not the sum of the individual energies of each quasiparticle but must include interactions, which to first order take the following form.

$$\delta E = \sum_{k,\sigma} \epsilon_{k,\sigma} \delta n_{k,\sigma} + \frac{1}{2} \sum_{k,k',\sigma,\sigma'} f(k, k', \sigma, \sigma') \delta n_{k,\sigma} \delta n_{k',\sigma'} + \ldots$$  (3.1)

Where $f(k, k', \sigma, \sigma')$ is known as the Landau function and represents interactions between quasiparticles. One can then write the energy cost of creating a quasiparticle with momentum $k$ and spin $\sigma$ as

$$\tilde{\epsilon}_{k,\sigma} \equiv \frac{\delta E}{\delta n_{k,\sigma}} = \epsilon_{k,\sigma} + \sum_{k',\sigma'} f(k, k', \sigma, \sigma') \delta n_{k',\sigma'} = \epsilon_{k,\sigma} + \Sigma(k, \sigma)$$  (3.2)

One can then identify $\epsilon_{k,\sigma}$ as the energy cost of the quasiparticle relative to the ground state, while the second term $\Sigma(k, \sigma)$, known as the self-energy, represents the energetic impact of the introduced quasiparticle on the rest of the system. For an isotropic Fermi surface, one can approximate this energy $\tilde{\epsilon}_{k,\sigma}$ to linear order in momentum near the Fermi surface $k_F$ by defining a renormalized Fermi velocity

$$\tilde{\epsilon}_{k,\sigma} \approx v_F (k - k_F)$$  (3.3)

$$v_F = \frac{\hbar k_F}{m} + \Sigma'(k_F).$$  (3.4)

It is also common to equivalently define an effective mass $m^*$ such that $v_F = \hbar k_F / m^*$, where $m^*$ is written in terms of $\Sigma'(k_F)$ or an integral over the Landau function.

One can make quite a bit of progress in predicting the experimental signatures of the Fermi liquid by utilizing the basic Landau functional to construct a semi-classical Boltzmann transport equation for quasiparticles along with using a Fermi-Dirac distribution for quasiparticle energies. One can also do this procedure “microscopically” with many-body
perturbation theory by realizing that \( f(k, k', \sigma, \sigma') \) is a functional derivative of a partition function [14, 15]. A brief table of the Fermi liquid scaling laws as one might observe for various experiments is shown in table 3.1. We will not go into these calculations here, but will instead focus on one key feature of the Fermi liquid which is the scaling of the quasiparticle lifetime with temperature as \( T^{-2} \).

One can compute the lifetime \( \tau \) of a quasiparticle with momentum \( k \) near the Fermi surface at a temperature \( T \) due to scattering from another quasiparticle by the use of Fermi’s golden rule. If this scattering is only dependent on momentum transfer (e.g. the Coulomb interaction), then temperature only comes in through the occupation of initial and final states, which follow the Fermi distribution. At finite temperature \( T \), the volume of available states for a single quasiparticle in momentum-space goes as \( T/E_F \). Therefore, the total scattering rate, which requires two unoccupied final states for a scattering event to occur, goes as \( \tau^{-1} = (T/E_F)^2 \).

One can repeat the above argument for an electron at a finite energy \( \omega \) away from the Fermi surface and obtains a lifetime of the form \( \tau^{-1}(\omega) \propto \omega^2 + (b \pi k_B T)^2 \), where \( b = 2 \) for a conventional Fermi liquid and in general depends on the nature of the scattering mechanism [19]. This quadratic scaling of the scattering rate between electrons is often taken as the essential definition of a Fermi liquid, as it means that quasiparticles are long-lived near the Fermi surface and become true many-body good quantum numbers when \( T = 0 \). In practice, such Fermi liquid scaling is very rarely ever observed directly [13, 20, 21, 22], and so it is common to attribute a resistivity that scales as \( T^2 \) as a clear signature that a system is a Fermi liquid, although, strictly speaking, resistivity is not a measure of quasiparticle lifetime and so this attribution should be done with caution [23].

\(^2\)In fact, one can make the same argument for the \( T^{-2} \) scaling of quasiparticle lifetime even in the absence of momentum being a good quantum number (i.e. a disordered Fermi liquid). We use the concept of a Fermi surface and momentum space because we will focus on crystalline systems.
Measurement | Approximate Fermi Liquid Scaling
--- | ---
Heat Capacity  | \( C \propto T \)
Magnetometry/NMR  | \( \chi_s = \text{const.} \)
Resistivity  | \( \rho \propto T^2 \)
ARPES  | \( \Sigma''(\omega) \propto \omega^2 + (2\pi k_B T)^2 \)
Optical Reflectivity  | \( \sigma \propto (-i\omega + \omega_0^{-1}(\omega^2 + (b\pi k_B T)^2))^{-1} \)

Table 3.1: **Fermi liquid scaling of common experimental observables:** These scalings can be found in various references, such as [20, 24].

### 3.1.1 Screening and charge response of a Fermi liquid

The form of the Landau energy functional of equation 3.2 is only meaningful if \( f(k, k', \sigma, \sigma') \) is a well-behaved function. This is clearly true to the case of (non-superfluid) Fermi liquid Helium-3 where the predominant interactions are short-ranged [15, 25], but is less clear in the case of charged electrons. If one were to take the naive approach and use the bare Coulomb interaction \( V(q) = \frac{4\pi e^2}{q^2} \) in the definition of \( f \), divergences near \( q = |k - k'| = 0 \), would render Fermi liquid theory meaningless. However, even charged systems are overall neutral, which means the bare Coulomb interaction is screened and ultimately well-behaved at long wavelengths. **Thus, any theory of a Fermi liquid in a metal must account for screening of the long-ranged Coulomb interaction to achieve self-consistent and sensible results.** Fermi liquid theory on its own however, does not provide a unique way to incorporate screening into the theory, so another procedure must be used.

The now standard approach to account for screening in a Fermi liquid is the Random-Phase Approximation (RPA) [15]. Roughly speaking, in the RPA one treats the long-ranged Coulomb interaction between electrons to all orders (small \( q \)), but assumes that short-ranged interactions (large \( q \)) in the screened polarizability \( \Pi(\mathbf{q}, \omega) \) are weak and given by first-order perturbation theory [14]. The RPA becomes exact in the limit of high electron density, where short range effects (e.g., the intrinsically inhomogeneous crystal lattice) can be ignored because the screening cloud surrounding each electron is infinitely small. Schematically speaking then, within the RPA, one can write a form for the Fermi liquid Landau function

\[ f(k, k', \sigma, \sigma') \approx \frac{\sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (k - k')} \Pi(\mathbf{q}, \omega)}{1 - \sum_{\mathbf{q}} e^{i\mathbf{q} \cdot (k - k')} \Pi(\mathbf{q}, \omega)} \]
that is free of divergences by separating out the divergent Coulomb contribution (which will be canceled out by screening) from the total interaction function as

\[
f_{\text{total}}(k, k') = \frac{4\pi e^2}{q^2} + f(k, k').
\] (3.5)

The first-order contribution to \(\Pi(q, \omega)\) is the only term retained in the RPA, and it is given by the density response of the non-interacting electron Fermi gas. In this case, the action of the density operator can be written exactly as

\[
\hat{\rho}(r, t) = e^{i\mathcal{H}_0 t} a^\dagger(r) a(r) e^{-i\mathcal{H}_0 t}
\] (3.6)

\[
= \sum_{k, k'} e^{i\mathcal{H}_0 t} a^\dagger(k) a(k') e^{i(k-k') \cdot r} e^{-i\mathcal{H}_0 t}
\] (3.7)

\[
= \sum_{k, k'} (1 - n_k) n_{k'} e^{i(k-k') \cdot r} e^{i(\epsilon_k - \epsilon_{k'}) t}.
\] (3.8)

Because the free electron gas is translation-invariant, the full polarizability \(\Pi(r', r, t', t)\), given by \(\Pi(r', r, t', t) = -\frac{i}{\hbar} \langle [\rho(r', t'), \rho(r, t)] \rangle_{\text{sc}}\), can be written as \(\Pi(r, t)\) which gives

\[
\Pi(r, t) = -\frac{i}{\hbar} \langle [\rho(r, t), \rho(0, 0)] \rangle_{\text{sc}}
\] (3.9)

\[
= -\frac{i}{\hbar} \sum_{k, k'} (1 - n_k) n_{k'} e^{i(k-k') \cdot r} e^{i(\epsilon_k - \epsilon_{k'}) t} \theta(t) - (1 - n_k) n_{k'} e^{i(k-k') \cdot r} e^{-i(\epsilon_k - \epsilon_{k'}) t} \theta(-t)
\] (3.10)

\[
= -\frac{i}{\hbar} \sum_{k, k'} (n_{k'} - n_k) e^{i(k-k') \cdot r} e^{i(\epsilon_k - \epsilon_{k'}) t} \text{sgn}(t).
\] (3.11)

Moving to Fourier space, one then obtains the Lindhard response function \(\Pi(q, \omega)\)
\[ \Pi(q, \omega) = \sum_k \frac{n_k - n_{k+q}}{\omega - (\epsilon_{k+q} - \epsilon_k) + i\eta}, \]  

(3.12)

where a convergence factor of \( i\eta \) is used to keep \( \Pi \) analytic on the upper half of the complex \( \omega \)-plane. The interpretation of the Lindhard \( \Pi(q, \omega) \) is simple, one approximates the polarizability as a sum over all the possible electron-hole pairs across the Fermi surface separated by momentum \( q \) and energy difference \( \omega \). In other words, the RPA form for the polarizability is the joint density of states for two-particle excitations\(^3\). One can readily apply RPA in the solid-state by using the band structure form for \( \epsilon_k \), rather than the free electron form, which accounts for the ionic crystal potential. An example calculation of the RPA \( \Pi(q, \omega) \) for a three-dimensional system of electrons with a parabolic dispersion is shown in Figure 3.1.

After calculating the RPA form of \( \Pi \), one can obtain the total dynamic charge susceptibility \( \chi \) using the relation

\[ \chi(q, \omega) = \frac{\Pi(q, \omega)}{1 - V(q)\Pi(q, \omega)}. \]  

(3.13)

As shown in Figure 3.1a, the screened response function \( \Pi \) is dominated by incoherent and broad multiparticle excitations, whose distribution in energy and momentum depends on the shape of the Fermi surface. On the other hand, Figure 3.1b shows that the action of the long-ranged Coulomb interaction in equation 3.13 results in a qualitatively different charge susceptibility \( \chi \), which is dominated by a sharp collective mode at frequency

\[ \omega_p = \sqrt{\frac{4\pi e^2 N}{m}}, \]  

(3.14)

\(^3\)Because the RPA only considers a single electron-hole pair in the calculation of \( \Pi \), the sharp edge of the Fermi surface gives rise to sharp cutoffs in \( \Pi \), as two-particle excitations are forbidden as soon as \( q \) and/or \( \omega \) lies outside a kinematically allowed region. In reality, these sharp features in \( \Pi \) are smoothed out by considering higher-order multipair excitations [26] beyond RPA, so they should not be taken too seriously. Nonetheless, the general structure of \( \Pi \) still reflects the shape of the Fermi surface even beyond the RPA.
Figure 3.1: **Dynamic charge susceptibility within the Random-Phase Approximation.** *(a)* Imaginary part of the polarizability $\Pi''(q, \omega)$ for a 3D, spherical Fermi surface with quadratic dispersion within the RPA. The key feature to notice is the presence of a dispersing particle-hole continuum, whose shape is given by the Fermi surface. *(b)* Resulting density response function $\chi''(q, \omega)$ from the RPA polarizability in (a) using equation 3.12. Unlike the polarizability which was dominated by particle-hole pairs, the charge response has a gapped, dispersing collective mode known as the plasmon. This mode was well-defined energy and momentum until it reaches the particle-hole continuum where it subsequently decays into particle-hole pairs (i.e. Landau damping).
known as the plasmon [5, 15]. Here \( N \) is the electron density of the system, and for most metals the plasmon has an energy in the range of 1 to 13 eV, much larger than the thermal energy scale \( k_B T \). In general, the combined momentum dependence of the Coulomb interaction and Fermi surface, as encoded in \( \Pi \), act to give the plasmon a dispersive nature (i.e. \( \omega_p \) is a non-trivial function of momentum), and one expects the plasmon to stay well-defined until it becomes kinematically allowed to decay into particle-hole excitations\(^4\). In fact, a dispersive plasmon is a generic feature one can expect from a Fermi liquid (even beyond the RPA), as the simple existence of a Fermi surface sets a length scale \( k_f^{-1} \) and momentum-dependent energy scale \( \omega = v_f q \) for the system. For energies below \( v_f q \), quasiparticle excitations are possible, but they are kinematically suppressed for energies significantly larger than \( v_f q \).

If we then look at the space-time Fourier transform of density response \( \chi(r, t) \), which tells us the fate of a charge fluctuation in the system, it is therefore a generic property of the Fermi liquid that charge fluctuations propagate spatially with well-defined energy on length scales larger than \( k_f^{-1} \).

Because \( \chi''(q, \omega) \) encodes the charge correlations of the system, we can now provide justification for the notion that electrons in a Fermi liquid are “weakly-correlated”. Since the vast majority of the spectral weight of \( \chi''(q, \omega) \) sits at the plasma frequency \( \omega_p \), quasiparticles with energy much lower than \( \omega_p \) do not see the bare charge of one another due to screening. Therefore, as far as correlations due to charge are concerned, quasiparticles are essentially uncorrelated. We can then conclude that Fermi liquid theory, which aims to describe the low-energy physics, is an effective theory of weakly-correlated electron-like quasiparticles even in charged systems. Said differently, the Fermi liquid is indeed strongly-correlated, but all of those correlations are bundled up on energy-scales near the (very large) plasma frequency and therefore permit a weakly-correlated low-energy effective description.

\(^4\)This decay does not occur abruptly as RPA might suggest, but is smooth when one considers higher-order processes, interband transitions, local-field effects, etc. [27].
3.1.2 Metals beyond the Fermi liquid

A key feature of the Fermi liquid is the existence of a Fermi surface and excitations which are long-lived fermionic quasiparticles. In the important case of charged quantum liquids, screening of charge permits an effective description of metals in terms of Fermi liquid theory just as in the neutral case. One may then ask, in what ways can the Fermi liquid give way to another phase of matter or simply fail to be descriptive?

Because the fundamental basis of a Fermi liquid is the existence of fermionic quasiparticles, the most apparent instability of the Fermi liquid is to the formation of bosonic bound states. If quasiparticles living on a Fermi surface are allowed to form bosonic bound states, the Pauli degeneracy pressure holding the Fermi surface together collapses. This instability, which was already pointed out by Landau in his original work [17], is most obvious in the BCS theory of superconductivity, but underlies phase transitions to other phases such as the charge-density wave, excitonic insulator, and Luttinger liquid.

Nonetheless, one of the most useful aspects of Fermi liquid theory is the ability to understand its own instabilities. As an example, BCS superconductivity can be worked out by considering a particular superposition of quasiparticle states in the presence of an attractive interaction, or equivalently by defining an order parameter built of two time-reversed quasiparticle states. The simple fact that a quasiparticle-based approach works at all to describe superconductors is very powerful, as one can work out an enormous amount of superconductor phenomenology within a picture that is ultimately based on the Fermi liquid. Likewise, one can build similar frameworks for the charge-density wave, Luttinger liquid, etc. More generally, a rigorous framework for understanding different types of instabilities of the Fermi liquid is possible through a perturbative renormalization group treatment [28].

A major challenge appears when one wishes to study metallic states that are not well-described in terms of Fermi liquid theory because the quasiparticle lifetime is too short for
the concept to be meaningfully applied\(^5\) (i.e. \(\tau^{-1} \geq \omega\) so the quasiparticle occupation is a bad quantum number). Not only would one have to build a new framework to describe such a metallic state, but the nature of its phase transitions could in principle be entirely different than the those of the Fermi liquid. Far from being a simple curiosity, this strange metallic state comes hand-in-hand with the highest superconducting transition temperatures on record at ambient pressure, along with a host of other exotic strongly-correlated phases. In the next section, we will look deeper at the strange metal with an eye for addressing the question: “what is so strongly-correlated in the strange metal compared to the Fermi liquid?”.

### 3.2 The strange metal

Departures from Fermi liquid behavior in the form of a strange metallic state have now been observed in a wide variety of different systems, ranging from organic molecular solids to transition metal oxides and heavy-fermion systems [23, 30, 31, 32, 33, 34, 35]. As shown in Figure 3.2, the strange metal regime\(^6\) of these material families tends to occupy a distinct region of the phase diagram, and is almost always in close proximity to other exotic strongly-correlated phases such as high-temperature superconductivity, charge order, antiferromagnetism, spin liquids, nematic order, and more. At first sight, all these systems would seem to have very little in common besides being “strongly-correlated” in their own unique ways. However, the anomalous metallic state of these systems do share a common lack of well-defined quasiparticles, suggesting that the strange metal may be a more generic state of matter. In this section we will focus on two core aspects of the strange metal: its apparently non-quasiparticle transport, and the lack of quasiparticle peaks in spectroscopy. We will

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\(^5\)This challenge is solvable in the special case of one-dimensional systems by bosonization as in the Luttinger liquid [29]. At its core, this success builds on the fact that one-dimension is special because particles cannot slip past one another, thus making spin-statistics “trivial” and the distinction between boson and fermion ill-defined. As a result, extensions into two- and three-dimensional systems have not been nearly as successful.

\(^6\)We will differentiate the terms “strange” metal and “bad” metal in section 3.2.3.
3.2 Signatures of the strange metal: transport

As its name implies, the strange metal conducts electricity, but does so in a fashion that precludes a simple description in terms of quasiparticles. Accordingly, this lack of well-defined quasiparticles generally manifests itself in two general sets of measurements: transport and spectroscopy (see Figure 3.3). Let us first discuss transport signatures of the strange metal, focusing mainly on resistivity as a function of temperature due to resistivity being widely measured across material families. What we will see is that the scaling of resistivity with temperature for many strange metal families deviates from the expected Fermi liquid scaling,

then discuss current theoretical attempts to describe the strange metal and conclude with important open questions about the strange metal that demand experimental attention.
Figure 3.3: **Transport and spectroscopic signatures of the strange metal.** Strange metal behavior is manifested in transport in two forms, (a) an anomalous scaling of resistivity with temperature [39] and (b) as a violation and total irreverence for the Mott-Ioffe-Regel bound on resistivity [40]. The primary spectroscopic signature of the strange metal is the general lack of quasiparticle peaks in ARPES. In the case of the strange metal cuprates near optimal doping ($T_c = 92$ K), no quasiparticle peak is visible until the compound becomes superconducting at low temperature [41]. (d) Similarly, in the case of Sr$_2$RuO$_4$, quasiparticle peaks vanish as one increases the temperature [42].

Typically with a distinct linear-in-T form. More generally, and perhaps more profoundly, the absolute magnitude of the resistance of strange metal families are orders of magnitude larger than Fermi liquid metals, with no sign of resistivity saturation at the so-called Mott-Ioffe-Regel (MIR) bound, even up to the melting point.

Transport measurements are performed on very long, macroscopic times and lengths compared to actual electron dynamics and therefore only probe the properties of the thermodynamic ground state. To make any inferences about deviations from the Fermi liquid which are reflected primarily in the lifetime of quasiparticles excitations on microscopic scales, one must perform transport measurements as a function of some external parameter. In the case of resistivity, temperature is often the first experimental knob, and inferences about quasiparticle scattering rates $\tau^{-1}(\omega)$ are often argued on the basis of converting the temperature into an energy scale $k_B T \leftrightarrow \omega$.

To heuristically understand the resistivity of a metal, it is common to use a Drude form

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\[ \rho = \sigma_0^{-1} = \frac{m^*}{ne^2} \tau^{-1} \propto \text{(Eff. Carrier Density)}^{-1} \times \tau^{-1}, \tag{3.15} \]

where \( n \) is the carrier density, \( m^* \) is the effective mass, and \( \tau \) the relaxation time for current. In principle, the \( \tau \) that appears in the resistivity is not the same as the quasiparticle lifetime \( \tau_{QP} \), because the direction of momentum relaxation matters for the decay of current but not for the quasiparticle lifetime. Thus, implicit in the discussion to follow is the assumption of momentum-independent scattering, in which case both the current and quasiparticle scattering rates are identical.

For a “good” metal, such as copper or aluminum, electron-phonon and electron-electron scattering are the dominant contributors to the resistivity. The former has the Bloch-Gruneisen form and dominates for temperatures above some fraction of the Debye temperature going as \( \rho_{ep} \sim T^5 \) for \( T < 0.2 \cdot T_{\text{Debye}} \) and as \( \rho_{ep} \sim T \) for \( T > 0.2 \cdot T_{\text{Debye}} \). Electron-electron scattering dominates at low temperature and goes as \( \rho_{ee} \sim T^2 \), originating in the Fermi liquid quasiparticle lifetime of \( \Sigma'' \sim \omega^2 + k_B T^2 \). Thus, there is no reason for the resistivity of a Fermi liquid to be a simple function of temperature except in the limiting cases of \( T \lesssim T_{\text{Debye}} \) and \( T \ll T_{\text{Debye}} \) where it has very different scaling (\( T^2 \) and \( T \) respectively).

On the other hand, one of the most widespread fingerprints of the strange metal is an anomalous scaling of the resistivity over a large range of temperatures, with a T-linear scaling being the most widely known. This T-linear resistivity has been observed in cuprates, ruthenates, iron pnictides, heavy fermions and perhaps most spectacularly in La\(_{2-x}\)Sr\(_x\)CuO\(_4\) at optimal doping which shows \( \rho \sim AT \) from the superconducting transition at about 35 K.

\footnote{For example, in the case of a ideal Fermi liquid with an isotropic Fermi surface and no lattice, momentum conservation implies velocity conservation. Thus, current cannot decay and the resistivity is zero. Nonetheless, even in this ideal case, the quasiparticle lifetime can still be finite and behave as normal if there is scattering between quasiparticle states. Electron-electron scattering can only relax current in a non-isotropic system and/or one with multiple species of charge carriers (i.e. multiple bands or lattice). Impurity scattering can also play a role but is not usually temperature dependent unless localization physics comes into play.}
to over 1100 K [44, 45]. Converting temperature into an energy scale via $k_B T \leftrightarrow \hbar \omega$, the quasiparticle lifetime of strange metals would then be linear in energy $\tau_{SM}^{-1} \sim \omega$, compared to the Fermi liquid where it goes as the square $\tau_{FL}^{-1} \sim \omega^2$. Therefore, quasiparticles in a strange metal are never long-lived, unlike a Fermi liquid where their relative linewidth diverges at zero temperature. Similar arguments can be made for strange metals with different temperature scaling behaviors.

One may wonder if electron-phonon scattering may be the cause of T-linear resistivity. However, the Debye temperatures of many strange metals is of order 300 K or more [46, 47], so one would have no reason to expect the same scaling of resistivity above and below $T_{Debye}$, as T-linear resistivity is observed well below $T_D$ (down to at least 40 mK in the heavy fermion CeRh$_6$Ge$_4$ [51]). However, despite its apparent irrelevance, the phonon contribution to resistivity still teaches us the useful lesson that a “soft” boson (effective Debye temperature of $T_D = 0$), may give rise to T-linear resistivity for all temperatures. We will return to this point when we discuss quantum critical views of the strange metal.

In general, contributions to the temperature dependence of the resistivity can be complex, and therefore one should not treat T-linear resistivity as definitive proof for the lack of quasiparticles (nor $T^2$ resistivity as evidence for Fermi liquid behavior for that matter!). As a concrete example, electron-doped cuprates show robust $T^2$ resistivity for a large range of dopings, but do so up to temperatures much larger than 0.2$T_D$, which is not expected for a Fermi liquid and is argued to also be a signature of strange metal behavior [52, 53]. On the other hand, even elemental metals such as Cobalt or Rhenium, which seem to be well-described by Fermi liquid theory, exhibit resistivities that scale as $T^{3.9}$ and $T^{5.1}$ respectively for $T \ll 0.1T_D$ [54]. Thus, if one believes the strange metal is the generic ground state for metals without quasiparticles (i.e. a fixed point for strongly-coupled systems), it is not clear

\[9\]The recent attribution of strange metal behavior to T-linear resistivity in twisted bilayer graphene (TBLG) [48] may be an exception, as the Moire superlattice reduces the Debye temperature considerably and significantly increases the electron-phonon coupling. Indeed, other studies show that T-linear resistivity at low temperature in TBLG is (at least partially) due to electron-phonon scattering [49, 50].
whether it is productive to define strange metals strictly as systems with T-linear resistivity as we will clarify in section 3.2.3.

Another, perhaps more robust, property of strange metals is the large absolute magnitude of their resistivity and their overall disregard for the Mott-Ioffe-Regel (MIR) resistivity bound \([23, 55]\). The MIR bound is a simple estimate for the smallest mean free path \(l\) that is allowable for a Boltzmann-type quasiparticle transport theory to make sense, which is that \(l\) is no smaller than the size of a quasiparticle wavepacket \((l \gtrsim 2\pi k_f^{-1})\). This bound is based on the idea that a quasiparticle should be able to travel a distance at least as long as its own characteristic size \((\lambda = 2\pi k_f^{-1})\) without scattering for quasiparticle descriptions to be self-consistent.

Assuming a Drude form for the DC conductivity and noting that \(\tau = l/v_f = ml/(\hbar k_f)\) and \(n \approx k_f^3\), the MIR limit for the resistivity is approximately \(\rho_{\text{MIR}} \sim (\hbar/e^2)l^{-1}\) (typically about 160 \(\mu\Omega \cdot \text{cm}\)). Most Fermi liquids never reach anywhere near the MIR bound even up to their melting point, and the few that do that do approach \(\rho_{\text{MIR}}\) tend to saturate near it \([44]\). However, strange metals seem to show a complete disregard for the MIR bound \([23, 44, 55]\), with resistivities that continually grow far beyond the MIR bound (by over an order of magnitude in some cases) up until the melting or decomposition temperature of the material. For \(\rho \geq \rho_{\text{MIR}}\) the Fermi liquid and Boltzmann transport approaches predict their own inapplicability, as quasiparticles are no longer good quantum numbers.

At first sight, one may wonder why there is so much attention given to a resistivity over \(\sim 160 \mu\Omega \cdot \text{cm}\), as insulators exceed this bound by many orders of magnitude. The key point here is that strange metals have plenty of charge carriers, and yet are still highly resistive. As a concrete example, elemental Bismuth, which is a Fermi liquid with well-defined Fermi surface \([56]\), has a relatively large room-temperature resistance of about 130 \(\mu\Omega \cdot \text{cm}\) due to its extraordinarily tiny carrier density of \(3 \cdot 10^{-7} \text{Å}^{-3}\) \([56]\). Meanwhile, the strange metal \(\text{Sr}_2\text{RuO}_4\) has a similar room-temperature resistance of about 130 \(\mu\Omega \cdot \text{cm}\) \([40]\), but with a 20,000\(\times\) larger carrier density of \(6 \cdot 10^{-3} \text{Å}^{-3}\) \([57]\).
We end this section on strange metal transport with a novel viewpoint proselytized by reference [58]. Let us say that one was given a material and knew nothing about it other than it behaves according to the laws of quantum mechanics and is bound together by electromagnetism, what order of magnitude for the resistivity would one expect? Making a guess using fundamental constants and dimensional analysis, one can construct a quantum unit of resistivity of \( \rho_q = \frac{\hbar e^2}{2} a_B \approx 137 \mu\Omega \cdot \text{cm} \). By default, one would expect materials to have resistivities of order \( \rho_q \). The Fermi liquid is special in that it introduces a new scale to the problem of \( (\pi k_B T/E_F)^2 \) due its constraints on the phase space for its excitations. Thus, the resistivity of a Fermi liquid would be expected to reduce to \( \rho = \rho_q (\pi k_B T/E_F)^2 \), which can be a factor of \( 10^{-6} \) for a good metal like copper at 30 K. Likewise, for an insulator, the energy gap \( \Delta \) introduces a factor of \( e^{-\Delta/k_B T} \) to the conductivity, thus giving an enhanced resistivity of \( \rho = \rho_q e^{\Delta/k_B T} \). This exponential factor is why insulators, from silicon to teflon, have a range of resistivities spanning over 25 orders of magnitude. On the other hand, strange metals lie somewhere in between Fermi liquids and insulators and, due to some yet to be understood mechanism, only have order unity corrections to \( \rho_q \).

### 3.2.2 Signatures of the strange metal II: spectroscopy

We now turn to the spectroscopic signatures of the strange metal. In particular, we will focus on Angle-resolved Photoemission Spectroscopy (ARPES) and the optical conductivity. Although transport is not able to directly assess the quasiparticle lifetime and Fermi surface, it is possible to measure the resistance of a large number of material families in a broad range of conditions. ARPES plays a complementary role to transport because it is able to directly assess the microscopic parameters relevant for quasiparticles, but is technically much more limited in terms of possible materials and experimental conditions.

The theory of ARPES is quite complex if one seeks rigor [59], but it can be roughly understood by assuming ARPES approximately measures the fermion spectral function \( A(k, \omega) \). This spectral function can be understood in the following way: if one introduces a fermion
into a system instantaneously at a single point in space \((\delta(r)\delta(t))\), then the relative probability for later finding this fermion with momentum \(k\) and energy \(\omega\) is given by \(A(k,\omega)\). In this way, \(A(k,\omega)\) describes the energy and momenta of the fermion states of a system.

For a Fermi liquid, quasiparticle states dominate near the Fermi surface and sharp peaks are visible in \(A(k,\omega)\) when \(k = k_F\) and \(\omega = 0\). Tracking the loci of these peaks gives one the Fermi surface of a material. The width of these peaks in energy indicates the inverse lifetime of the quasiparticle state, while the width in momentum gives the inverse mean free path\(^{10}\). As we have seen earlier, the width of quasiparticle peaks in a Fermi liquid is given by \(\Sigma''(\omega) \propto \omega^2 + b\pi^2(k_BT)^2\) \([19]\). Furthermore, the fraction of the spectral weight of the quasiparticle peak compared to any incoherent background is the quasiparticle weight \(Z\), which is related to the effective mass one may measure with quantum oscillations \([60]\) by \(Z = m/m^*\) if one assumes a momentum-independent self energy. Overall, these signatures of the Fermi liquid in the fermion spectral function seem to agree with ARPES experiments on good metals quite well \([61]\).

In stark contrast, quasiparticle peaks in strange metals are highly damped, with the spectral function being almost entirely “incoherent”. In the case of the strange metal Bi-2212 in its normal state (Figure 3.3c), the spectral function shows broad resonances rather than sharp peaks which essentially rules out the possibility of well-defined quasiparticles \([4, 62]\). Similarly, Sr\(_2\)RuO\(_4\), another strange metal, exhibits a broad plateau rather than a peak above 180 K, but slowly develops a quasiparticle peak as a Fermi liquid-like regime is entered below about 40 K \([21, 42]\). Other materials, such as the iron pnictides, sit somewhere in between, with some orbitals displaying Fermi liquid lifetime scaling, while other bands are incoherent with ill-defined quasiparticles \([63]\). Thus, the ARPES results on strange metals tend to show agreement with transport in the sense that quasiparticle are never long-lived, and in many cases are ill-defined altogether.

\(^{10}\)For good metals, the currently available momentum resolution and/or crystal quality is not usually not enough to give quantitative estimates of the mean free path. The energy resolution on the other hand is quite excellent, allowing quantitative insight into quasiparticle lifetimes.

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Let us now end this section on strange metal spectroscopy with a discussion of optical conductivity. Typically measured with light, optical conductivity \( \sigma(\omega) \) is simply a measure of the current produced by an alternating AC field (i.e. \( j(\omega) = \sigma(\omega)E(\omega) \)) rather than a static DC field as done with resistivity. By using an oscillating field, the transport properties of the excited states can be understood so that inferences about the dynamic scattering rate \( \tau^{-1}(\omega,k_B T) \) can be made. The basic equation for the optical conductivity is the Drude formula, which arises from the classical equation of motion \( m\dot{\mathbf{v}}(t) = -e\mathbf{E}(t) - \tau^{-1}\mathbf{v}(t) \).

\[
\sigma(\omega) = \frac{i ne^2/m^*}{\omega + i\tau^{-1}}
\]  

(3.16)

If we allow \( \tau^{-1} \) to be a function of frequency, this gives a generalized Drude model [64]

\[
\sigma(\omega) = \frac{i ne^2/m^*}{\omega + iM(\omega)}
\]  

(3.17)

where \( M(\omega) \equiv \tau^{-1}(\omega) \) is called the relaxation time function, or memory function. For a Fermi liquid with local interactions, the imaginary part of the scattering rate function, which is related to the quasiparticle self-energy, takes the form [65]

\[
M''(\omega) = \frac{2}{3\pi k_B T_0} \left( \omega^2 + (b\pi k_B T)^2 \right)
\]  

(3.18)

where \( T_0 \) is a type of Fermi liquid coherence scale and \( b \) is a non-universal numerical constant depending on the material-dependent Fermi surface and scattering channels [19, 20, 66]. Surprisingly, this form for the Fermi liquid conductivity has not been experimentally verified as frequently as one might expect for Fermi liquids, primarily due to the fact that \( T_0 \) for good metals is very large so that the absolute scattering rate intensity \( \tau^{-1}(\omega) \) is small in the energy window of interest (\( \lesssim 20 \) meV). The net result is that the Fermi liquid scaling of the scattering rate is manifested as very small changes in the (near perfect) reflectivity of good metals in the very far-infrared/THz regime, hampering verification of equation 3.18.
for metals like silver, gold, and aluminum [67]. Nonetheless, less than perfect Fermi liquids such as stainless steel, elemental chromium, heavy-fermion compounds, and electron-doped iron pnictides have been verified to have the form of equation 3.18 [22, 65, 67]. It should be noted however, that the dynamic scattering rate for Fermi liquids at high enough energy deviates from the Fermi liquid response anyways, usually taking on a non-trivial frequency dependence [68].

For strange metals on the other hand, the dynamical scattering rate does not show the characteristic quadratic dependence on frequency. Instead, a variety of different scaling behaviors are observed. In some cuprates the scattering rate scales linearly in ω for ω < k_B T and continues with a power of 0.5 to 0.7 for ω > k_B T up to about 0.6 eV [13, 69]. However, while deviations from Fermi liquid scaling in the scattering rate are common to many strange metals, the exact scaling in frequency varies significantly from one material family to another, which indicates that such scaling may arise from the proximity to the nearby states in the phase diagram which vary from one system to another [13].

3.2.3 An aside: “strange” or “bad” metals?

Various terms exist in the literature for the anomalous, non-Fermi liquid-like metallic state of many correlated systems and so far we have only used the term “strange” metal. Another well known name given for non-Fermi liquid metals is the “bad” metal [40, 52, 70, 71, 72], with the term bad metal preceding the strange metal historically [70]. Due to the lack of an accepted theory for their properties, there is no precise definition for being a “strange” or “bad” metal. Roughly speaking however, the term strange metal is usually used in the context of metals with anomalous scaling properties (often to facilitate an interpretation in terms of quantum criticality), while the bad metal is associated with metallic states that violate the Mott-Ioffe-Regel (MIR) bound on quasiparticle-based transport. A difficulty with associating the strange metal solely with metals exhibiting anomalous scaling is that, contrary to conventional wisdom, it is unclear what kinds of scaling are truly “anomalous”
In this thesis, we use the definition of the strange and bad metal that is slowly being adopted in the literature as follows. By bad metal we refer to the state of metals at high temperature when their resistivity exceeds the MIR bound and quasiparticles are totally incoherent (i.e. no quasiparticle peaks are observable anywhere in momentum space). The strange metal refers to the lower temperature regime where the resistivity does not exceed the MIR bound and quasiparticles are ill-defined but not totally incoherent (i.e. some broad quasiparticle peaks are visible in ARPES, but they are highly damped compared to $k_B T$).

### 3.2.4 Current theoretical approaches

A wide variety of different theoretical approaches have been pursued in describing strange metals and each aims to address different aspects of the problem. Here we briefly describe two main categories of such theories in increasing levels of abstraction: model microscopic Hamiltonians, and coarse-grained phenomenological approaches.

#### Microscopic approaches

With the high-$T_c$ cuprates being the first well-accepted examples of strange metals, the starting point for microscopic approaches is most often the Hubbard Hamiltonian

$$\mathcal{H} = -t \sum_{i,j,\sigma} (c_{j,\sigma}^\dagger c_{i,\sigma} + c_{i,\sigma}^\dagger c_{j,\sigma}) + U \sum_j n_{j\uparrow} n_{j\downarrow} - \mu \sum_j (n_{j\uparrow} + n_{j\downarrow}),$$

where we explicitly include the filling by the use of a chemical potential $-\mu N$ term. A key feature of the Hubbard model is replacement of the long-range Coulomb repulsion with a short-ranged repulsion $U$ that is purely local and explicitly written to account for Pauli exclusion. If two electrons sit on the same site, the effective Coulomb interaction introduces an energy cost of $U$, but otherwise there is no explicit repulsion between distant sites. The

\footnote{We are ignoring ab-initio approaches here, primarily due to brevity.}
Hubbard model is often considered a prototypical model for strong correlations, just as the Ising model has been for magnetism. That is, the Hubbard Hamiltonian does not exactly describe any specific system, but hopefully has the right ingredients to explore the physics of interest.

The Hubbard model cannot be solved exactly in dimensions larger than one due to the Coulomb repulsion term. Nonetheless, computational studies of the Hubbard model have recently shown evidence for strange metal behavior in finite-sized systems, such as a resistivity which exceeds the MIR bound and T-linear scaling [77], thus giving evidence that the model is on the right track. To build an approximate analytic framework for the strange metal based on the Hubbard model, one would like to treat the kinetic energy term as a perturbation compared the potential term, as it is usual that $U$ is significantly larger than $t$ in strange metals like the cuprates. The key challenge is that the usual framework of many-body perturbation theory and Feynman diagrams is inapplicable if one chooses the starting point as $t = 0$ and $U \neq 0$.

To see why ordinary perturbative approaches are inadequate, consider first the free-particle limit of $U \to 0$ in equation 3.19. We see that we obtain a non-interacting Fermi liquid which is metallic (gapless) with propagating fermions. The energy and behavior of each fermion is completely independent of all other fermions, so one can reduce the $N$-body system to $N$ independent one-particle systems. On the other hand, in the limit of $t \to 0$ but $U \neq 0$, the Hubbard Hamiltonian ground state is one where all electrons are localized to single sites (i.e. the atomic limit) that can be at most doubly occupied because of Pauli exclusion. Crucially, the energy cost of introducing a fermion onto a given site now depends on whether there is a fermion already there (i.e. a cost of $E = 0$ if empty and $U$ is occupied). As a result, one cannot treat the atomic limit of the Hubbard model as a system of non-interacting fermions and the machinery of ordinary perturbation theory using Feynman diagrams based on Wick’s theorem needs to be reworked. One can of course define new operators that diagonalize the atomic Hubbard model and attempt perturbation
theory at finite $t$ with them, but these are not fermion operators and obey more complicated commutation relations that makes diagrammatic treatments no more approachable [16].

Approaches to understanding the strange metal that are ultimately rooted in the Hubbard and related models (Emery, t-J, Kanamori, etc.) are then based on various approximations such as mean-field treatments [78], variational wavefunctions and projective methods [79, 80, 81], perturbative Fermi liquid approaches [82, 83], effective gauge theories [84], mappings onto impurity models [85], and a variety of computational methods on finite systems [77]. At their core, these approaches seem to be divided on whether the strange metal is a bona fide strongly-interacting ground state (as in [79, 80, 81, 84]), or a complicated thermally excited state that always eventually becomes a Fermi liquid (or superconductor) at low temperature [71, 82, 86]. This division seems to also mirror the experimental status of the strange metal, as in some cases it appears to continue to zero temperature [51], while in other cases it becomes well-characterized as a Fermi liquid or superconductor instead [21, 87].

**Phenomenological approaches**

The second branch of theoretical treatments of the strange metal is phenomenological, and seeks out the minimal ingredients needed to account for the anomalous properties of the strange metal. One of the first such treatments was the Marginal Fermi liquid (MFL) hypothesis for the normal state of the cuprates [88]. The MFL hypothesis showed that many strange metal properties in the cuprates, including $T$-linear resistivity and scaling of the optical conductivity, can be accounted for by postulating a polarizability of the form

$$\Pi''(q, \omega) = \begin{cases} 
-N(0)\omega/T & |\omega| < T \\
-N(0)\text{sgn}(\omega) & |\omega| > T,
\end{cases}$$

(3.20)
at least to leading-order in perturbation theory. Here, $T$ is the temperature and $N(0)$ is the single-particle density of states. This form for $\Pi''(\mathbf{q}, \omega)$ can also be more succinctly written as $\Pi''(\mathbf{q}, \omega) = -N(0) \tanh(\omega/T)$. The essential property of the MFL form for $\Pi''$ is that the polarizability is momentum- and energy-independent for a broad range of parameter space, but is proportional to $\omega/T$ when $\omega \lesssim T$. In other words, the system has local collective fluctuations whose energy scale is set by the thermal energy. A key result of this postulate is that the leading order correction to the fermion self-energy gives a logarithmically vanishing quasiparticle weight $Z_k$ (i.e. quasiparticles exist only "marginally") and a linear in frequency contribution to $\Sigma''$ which results in a $T$-linear resistivity.

It should be emphasized that the original MFL hypothesis is not a theory per se, but rather series of observations synthesized into a single statement. The original hypothesis did not have any microscopic mechanism in mind. Much of the phenomenological work on the strange metal thus seeks out an effective model that give the MFL form for the polarizability. In this respect, quite a bit of attention has been given to descriptions of strange metals in terms of quantum criticality [69, 89, 90, 91, 92]. To the uninitiated, quantum criticality is essentially the study of phase transitions that occur at zero temperature via a non-thermal knob (e.g., a magnetic field) and their resulting signatures at finite temperature. The basic approach is to map $d$-dimensional quantum critical models to a $d + 1$-dimensional classical equivalent by noticing that the Boltzmann factor $e^{-\beta H}$ and unitary time evolution $e^{-i\tau H}$ are related by a Wick rotation $i\tau \rightarrow \beta$, so that time in the quantum model becomes an extra spatial dimension in the classical one. Fundamentally, the logic for associating strange metals with criticality is that, by sitting in a critical regime between phases, the Fermi surface itself becomes unstable due to low-energy scale-invariant fluctuations of the order parameter, resulting in ill-defined quasiparticles and possibly an MFL form for the polarizability.

To see a very simple example of why quantum criticality may give rise to $T$-linear resistivity, consider the case of a second-order quantum phase transition of a order parameter that does not carry current. Just as all critical phenomena, the energy of the associated order
parameter goes to zero at the quantum critical point. Then, at finite temperature, scattering from these critical fluctuations is set by $k_B T$, which is the only energy scale available to the critical fluctuations. This energy scale then gives rise to an anomalous power-law scaling of the resistivity with temperature, with various exponents being possible [73, 74]. A very heuristic way to understand this phenomenon is to think about quasiparticle scattering from critical bosons as electron-phonon scattering of the Bloch-Gruneisen type when the Debye temperature $T_D$ is zero. If $T_D = 0$, then one observes T-linear resistivity over all temperature scales (or at least up to the microscopic energy scale of the critical order parameter\(^{12}\)). It should be pointed out that this mechanism for T-linear resistivity does not work for a classical critical point, as the critical fluctuations in the classical case are only gapless at the transition temperature. Quantum criticality exhibiting such gapless excitations at the critical point is known as soft-mode criticality.

There are several challenges for quantum critical approaches to the strange metal. The first is that quantum critical points have only been identified in a select few strange metals, most of which are heavy fermion materials [93, 94, 95]. For other systems, such as the cuprates, key signatures of a quantum critical point are missing, such as the relevant order parameter and the location of the critical point. In fact, while thermodynamic measurements suggest the existence of a quantum critical point in the cuprates [96], spectroscopic probes point not to a critical point, but surprisingly a first order phase transition as a function of doping [97]. In this respect, theories of quantum criticality that go beyond the Landau order-parameter paradigm, such as the deconfined quantum critical point described in [98], may be promising frameworks for resolving these apparent contradictions. Nonetheless, the success of quantum criticality in heavy fermion systems has not translated nearly as well to other strange material families at the current time. At a more basic level, it is quite hard to imagine how quantum criticality in the usual understanding can be the dominant

\(^{12}\)For example, in a quantum critical theory of a magnetic system, the exchange constant $J$ will set the upper limit for critical fluctuations.
contribution to resistivity at temperatures exceeding 1000 K in so many different material families.

The second challenge is that quantum critical models of the strange metal are rarely analytically tractable, and those that are tractable tend to be unphysical. Indeed, up until a few months before the time of writing this thesis, there was not a single known microscopic model with a quantum critical point for spin-1/2 fermions that exhibited a T-linear scattering rate [76].

Recently, an alternative approach for studying quantum criticality approaches to the strange metals has appeared in the form of the AdS/CFT (anti-de-Sitter/conformal field theory) correspondence. This correspondence is a holographic duality between a string theory of a fluctuating spacetime in a special, weakly-curved geometry in \( d + 1 \)-dimensions and a special class of strongly-coupled quantum field theories with conformal invariance in \( d \)-dimensions. Such approaches are promising [99, 100, 101, 102] and, if simply by virtue of their non-traditional nature, may have a crucial role to play in understanding the strange metal in the future, although currently it is unclear how to directly test them experimentally.

Lastly, it is worth mentioning hydrodynamic approaches to the strange metal. Commonly used to understand ordinary fluids, hydrodynamic frameworks seeks to study transport in a system by focusing only on conserved quantities (e.g., energy or momentum) on coarse-grained length scales using only a few transport coefficients such as the diffusion constant and viscosity. For a hydrodynamic approach to work, there must be a separation of length scales between microscopic equilibration scales (e.g., the mean free path) and the macroscopic lengths over which conserved quantities vary. The advantage of hydrodynamic approaches is that they do not rely on any quasiparticle interpretation of transport and can be rather general [103]. The disadvantage is that they are fundamentally incomplete in that they require other theories for the actual values of the transport coefficients, such as quantum criticality, many-body perturbation theory, or AdS/CFT. Furthermore, momentum is not a conserved quantity if one only looks at the electron fluid, as the lattice is crucially responsible
for finite conductivity, which is why hydrodynamics is not used in ordinary metals to begin with. Nevertheless, promising progress has been made by focusing only on conserved charge and energy currents, and hydrodynamical bounds have been put forth for various transport quantities of the strange metal [104].

### 3.2.5 Outstanding questions on the strange metal

It is a recurrent theme in discussions of the strange metal that the key aspects to explain are its anomalous transport and lack of quasiparticles. While these properties are certainly important, an important question is being overlooked, namely, **what is so special about the electron-electron interaction in strange metals that gives rise to its behavior in the first place?** After all, not all strongly correlated systems are strange metals. In particular, it is fundamentally important to understand qualitatively, if not quantitatively, how the strongly correlated nature of charge in the strange metal compares to that of the Fermi liquid.

With the need to understand the nature of correlations in the strange metal in mind, we then end this chapter by outlining some of the most important questions about the strange metal that are model-independent and experimentally addressable.

1. What is so strongly correlated about charge in the strange metal that distinguishes it from the Fermi liquid?

2. How do the strong charge correlations of the strange metal evolve as one leaves the phase (e.g., though doping and temperature)?

3. In what sense, if any, can a Fermi liquid and strange metal coexist? Does one cross over from one regime to the other smoothly, or is there a phase transition?

In this thesis, we will address questions #1 and #2 in our M-EELS study of the cuprate Bi-2212 in Chapter 6. Then, in Chapter 7, we will address question #3 by studying Sr$_2$RuO$_4$. 

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Impatient readers can refer themselves to sections 6.3, 6.4, and 7.6 for the explicit answers to these questions.
Chapter 4

Theory of inelastic electron scattering and M-EELS

In this chapter we put forth the theory of inelastic electron scattering to build the theoretical foundations of reflection momentum-resolved electron energy-loss spectroscopy (M-EELS). We will start by showing that M-EELS is the right tool for measuring the dynamic charge response function $\chi''(q, \omega)$, which quantifies the charge correlations and fluctuations of a solid in momentum and energy. From there, we provide some intuition for the information contained within $\chi''(q, \omega)$ through the solution of some exactly solvable models and reviewing a few previous M-EELS experiments. Then, we demystify multiple scattering, a common complication in electron-based spectroscopies. The discussion of multiple scattering will naturally lead to a derivation of the reflection M-EELS cross section. Then, the various assumptions used to derive the M-EELS cross section will be described and examined to understand their impact on experiment. Subsequently, we derive the connection between the surface and bulk charge susceptibilities and dielectric functions along with the surface sum rules. We end this chapter by discussing outstanding unsolved issues in the current theory of M-EELS and pose them as opportunities for future theoretical study.

4.1 The need for M-EELS

As shown in section 2.3, the dynamic charge susceptibility $\chi''(q, \omega)$ encodes both the effective interactions and charge correlations of a system. Thus, by measuring $\chi''(q, \omega)$ for a strange metal, one can precisely pinpoint how its strongly-correlated nature differs from the Fermi liquid and address the core questions outlined in section 3.2.5. Since $\chi''(q, \omega)$ is the dynamic
charge susceptibility, either photons or charged particles must be used to measure it. In this section, we will show that no form of photon-based spectroscopy measures the desired charge susceptibility. Instead, Momentum-resolved Electron Energy-Loss Spectroscopy (M-EELS), or inelastic electron scattering, is the technique of choice for measuring $\chi''(q, \omega)$.

Before continuing, it should be noted that, unlike more established electron spectroscopies such as photoemission, there is an absence of a self-contained and approachable introduction to the theory of reflection M-EELS in the literature\(^1\). To fill this gap and for the benefit of future M-EELS work, this chapter is written to be as forthcoming as reasonable in the types of assumptions and approximations that are being made. Readers who wish to skip these details can take it for granted that the M-EELS cross section derived in equation 4.70 demonstrates that M-EELS measures the charge response function $\chi''(q, \omega)$, and can skip ahead to Chapter 5.

4.1.1 Photons do not measure the charge susceptibility

It is an unfortunate fact of life that the charge susceptibility $\chi''(q, \omega)$ has not been straightforward to measure in the regime of momentum and energy that are of relevance to condensed matter, namely throughout the Brillouin zone (0.02 - 2 Å\(^{-1}\)) and from $k_B T$ to the plasma frequency (1 - 3000 meV) \(^{108}\). The lack of techniques for measuring $\chi''(q, \omega)$ may come as a surprise to the reader, especially since its spin equivalent can be measured on-demand with magnetic neutron scattering \(^{109}\) and in some special cases by resonant inelastic x-ray scattering (RIXS) \(^{110}\). Because charge couples to both photons and other charged particles, one would assume that some form of photon spectroscopy would measure $\chi''(q, \omega)$. Sadly, photons are unable to do this and charged particles must be used instead. To see why, let us take a look at the light-matter interaction Hamiltonian below.

\(^1\)As an example, the best known and most commonly cited text on reflection EELS by Ibach and Mills \(^{105}\) omits a derivation of the M-EELS cross section, referring readers to \(^{106}\). However, reference \(^{106}\) omits crucial steps in its own derivation of the M-EELS cross section and further refers readers to \(^{107}\). Reference \(^{107}\) itself is written to describe surface interaction with light, not electrons, which leaves the reader on their own to piece together the theory of M-EELS.
\[ \mathcal{H} = \sum_i \frac{(\mathbf{p}_i + q_i \mathbf{A})^2}{2m_i} + \hat{V} \]  

\[ = \sum_i \frac{p_i^2}{2m_i} + \hat{V} + \sum_i \frac{1}{2m_i} \left( q_i (\mathbf{p}_i \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}_i) + q_i^2 \mathbf{A} \cdot \mathbf{A} \right) \]  

(4.1)

Here \( \mathbf{A} \) is the vector potential operator for the photon. The first two terms in the above equations form the original Hamiltonian \( \mathcal{H}_0 \) of the target system, while the second two are the light-matter interaction terms. We can rewrite these interaction terms as

\[ \mathcal{H}_{\text{Light-Matter}} = \mathbf{j} \cdot \mathbf{A} + \left( \sum_i q_i^2 \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{A}(\mathbf{r}_i) \right) \]  

\[ = \mathbf{j} \cdot \mathbf{A} + \left( \sum_i q_i m_i \delta(\mathbf{r} - \mathbf{r}_i) \right) \mathbf{A} \cdot \mathbf{A}. \]  

(4.3)

(4.4)

There are two light-matter interaction terms in equation 4.4, and noticeably neither directly couples to the charge density \( \rho(\mathbf{r}) = \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i) \). The first term, which corresponds to most optical spectroscopies (see Table 2.1 and Appendix A.1), describes absorption of a photon and gives rise to a term proportional to the (transverse) current-current response function. This response function is only related to the charge response \( \chi''(\mathbf{q}, \omega) \) in the limit of \( q \to 0 \) where the longitudinal and transverse response become equivalent. On the other hand, it has been pointed that higher-order \( \mathbf{j} \cdot \mathbf{A} \) processes within resonant inelastic x-ray scattering (RIXS) may have contributions coming from \( \chi''(\mathbf{q}, \omega) \) \cite{111, 112}. While there are definitely contributions from charge excitations to the RIXS cross-section \cite{113}, there are many other orbital, spin, and core-hole excitonic contributions that complicate the extraction of \( \chi''(\mathbf{q}, \omega) \) in general. Furthermore, to date, RIXS has been unable to observe the bulk plasmon and its dispersion even in simple metals such as lithium or aluminum, thus making any claim of measuring \( \chi''(\mathbf{q}, \omega) \) with RIXS difficult to justify.
Figure 4.1: **Charge density versus the electron number density.** (a) Comparison of valence contribution to the charge density (M-EELS, black) compared to the electron number density (IXS, grey) in atomic Cesium calculated using electron orbitals from [115]. At small momenta, the valence electron and screened nucleus make up nearly 50% of the charge density, but only a few percent of the electron number density. (b) Valence contributions to the density correlation function $S(q)$ (or equivalently $\chi''$) for the charge and electron densities. Notice the valence sensitivity is nearly $10^3$ times larger at small momentum transfer for the charge density compared to the electron density.

The second term in equation 4.4, which corresponds to (in)elastic x-ray scattering [114], measures a density-density response function, but the relevant density $\tilde{\rho}(r) = \sum_i \frac{q_i}{m_i} q_i \delta(r-r_i)$ is not the charge density. Instead, each charge carrier is weighted by the charge-mass ratio $q_i/m_i$, which, practically speaking, means there is no contribution from atomic nuclei due to their heavy mass. Therefore, the density probed by photons $\tilde{\rho}(r)$ is equal to the electron number density, not the true charge density.

The distinction between the charge and electron density is dramatic once one realizes that the electron density is dominated by core electrons that play no role in the many-body physics we wish to study. For example, in one unit cell of the strange metal Bi-2212
there are about 3 valence electrons that contribute to the strange metal behavior \cite{116}, but over 1500 core electrons that play no significant role. Since the cross-section goes as the density operator squared (i.e. \( \langle \rho \dagger \rho \rangle \)), we expect a relative valence-to-core contribution to the measured inelastic x-ray scattering signal of about \( 4 \times 10^{-6} \) in Bi-2212. This insensitivity to valence electrons is double-edged sword, as it allows elastic x-ray scattering to robustly determine the crystal structure of a material regardless of the valence behavior, but also means that realistically the only inelastic features that are measurable below a few eV are lattice vibrations (i.e. phonons) \cite{117}.

On the other hand, for the charge density \( \rho(\mathbf{r}) \), the core-electron contributions are canceled out by the positively charged nuclei. As a result, the valence electrons and the screened nuclear charge they feel are the dominant contributions to charge susceptibility on the energy and momentum scales of interest to many-body physics. A numerical comparison of the true charge density to the electron density is shown in Figure 4.1.

### 4.1.2 Measuring \( \chi''(\mathbf{q}, \omega) \) with M-EELS in the bulk limit

With photons ruled out, the only remaining hope to measure the dynamic charge susceptibility is to use charged particles. Needless to say, the only viable choice here is the electron. Then, the idea is to measure \( \chi''(\mathbf{q}, \omega) \) by performing inelastic electron scattering, also known as Momentum-resolved Electron Energy-Loss Spectroscopy (M-EELS), which involves sending an electron with momentum state \( |\mathbf{k}_i\rangle \) to interact with the sample and measure the rate of scattering into \( |\mathbf{k}_f\rangle \). Because we are interested in energy and momentum scales far outside the light cone (\( \omega/q \ll c \)), the predominant interaction between the probe electron and the solid is the instantaneous Coulomb interaction\footnote{Modifications for relativistic electrons traveling close to the speed of light cause the magnetic field of the electron to couple the current-current response function via a diamagnetic \( \mathbf{j} \cdot \mathbf{A} \) term to lowest order in \( (v/c)^2 \). The corresponding magnetic EELS cross section, as well as that of spin-resolved exchange scattering, is described in Appendix B.}.
\[ H_{\text{EELS}} = \frac{1}{2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\hat{\rho}(\mathbf{r}_1)\hat{\rho}_{\text{probe}}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}. \] (4.5)

Here, \( \hat{\rho}(\mathbf{r}_1) \) is the charge density operator of the system, and \( \hat{\rho}_{\text{probe}}(\mathbf{r}_2) \) is the charge density of the probe electron. Unlike photons, it is the true charge density that is probed here, not the electron number density, so that \( \chi''(\mathbf{q}, \omega) \) can truly be measured. In fact, one can immediately see the resemblance between the EELS interaction Hamiltonian and the starting point for the derivation of \( \chi''(\mathbf{q}, \omega) \) from section 2.3. There, the derivation of the charge susceptibility involves looking at the effective potential from a hypothetical external charge fluctuation \( \delta \rho_{\text{ext}} \).

In the case of M-EELS, we are engineering \( \delta \rho_{\text{ext}} \) into existence using a free-electron scattering between states \( |\mathbf{k}_i\rangle \) and \( |\mathbf{k}_f\rangle \) to produce an external charge density of the form

\[
\delta \rho_{\text{ext}}(\mathbf{r}, t) = \rho_{\text{probe}}(\mathbf{r}, t) = \frac{e}{V} e^{i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}} e^{-i\omega t} = \frac{e}{V} e^{i\mathbf{q} \cdot \mathbf{r}} e^{-i\omega t},
\] (4.6)

where \( \mathbf{q} \equiv \mathbf{k}_i - \mathbf{k}_f \). Thus, \( H_{\text{EELS}} \) can be simplified by realizing the action of \( \rho_{\text{probe}} \sim e^{i\mathbf{q} \cdot \mathbf{r}} \) is to perform a Fourier transform on \( \hat{\rho}(\mathbf{r}) \) in equation 4.5, which results in a matrix element of the form

\[
\langle \mathbf{k}_f; n | H_{\text{EELS}} | \mathbf{k}_i; i \rangle = \frac{1}{2} \frac{4\pi}{V q^2} \langle n | \hat{\rho}(\mathbf{q}) | i \rangle \delta(\omega - \omega_{ni}).
\] (4.7)

One can now derive the full M-EELS differential cross section by noting that the cross section is simply the scattering rate divided by the incident flux (particles per square area per unit time). Then, by using the golden rule,

\[
\frac{1}{V} \frac{d\sigma}{d\mathbf{k}_f} = \frac{R(\mathbf{k}_i \rightarrow \mathbf{k}_f)}{\text{Flux}} = \sum_n \frac{2\pi}{V} |\langle \mathbf{k}_f; n | H_{\text{EELS}} | \mathbf{k}_i; i \rangle|^2 \frac{v_0}{V}.
\] (4.8)

Here, \( v_0 \) is the probe electron speed and \( V \) is the probe electron volume. We can simplify \( d\mathbf{k}_f \) by noting \( d\mathbf{k}_f = k_f^2 d\Omega dk_f = \frac{m}{2\pi} k_f d\Omega d\omega \). Then, we can simplify the expression for the
differential cross section by evaluating the matrix elements using equation 4.6 to give

\[
\frac{\partial \sigma}{\partial \Omega \partial \omega} = \frac{2\pi m^2 k_f}{\hbar^4 k_0} V^2 \sum_n |\langle k_f; n|\mathcal{H}_{\text{EELS}}|k_i; i\rangle|^2
\]

\[
= \frac{\pi m^2 k_f}{2e^2 \hbar^4 k_0} \left(\frac{4\pi e^2}{q^2}\right)^2 \sum_n |\langle n|\hat{\rho}(q)|i\rangle|^2 \delta(\omega - \omega_{ni}) \tag{4.9}
\]

\[
= \frac{\pi m^2 k_f}{2e^2 \hbar^4 k_0} V(q)^2 S(q, \omega), \tag{4.10}
\]

where \( V(q) \equiv \frac{4\pi e^2}{q^2} \) is the bare Coulomb interaction and \( S(q, \omega) = \sum_n |\langle n|\hat{\rho}(q)|i\rangle|^2 \delta(\omega - \omega_{ni}) \) is the dynamic structure factor or charge correlation function\(^3\). By assuming thermal equilibrium, we can then relate the M-EELS cross section to the dynamic charge susceptibility in equation 4.12.

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{EELS}} = \frac{\pi m^2 k_f}{2e^2 \hbar^4 k_0} V(q)^2 S(q, \omega) \tag{4.12a}
\]

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{EELS}} = -\frac{m^2 k_f}{2e^2 \hbar^4 k_0} V(q)^2 \frac{1}{1 - e^{-\beta \omega}} \chi''(q, \omega) \tag{4.12b}
\]

\[
S(q, \omega) = \sum_{n,i} e^{-\beta \omega_i} |\langle n|\hat{\rho}(q)|i\rangle|^2 \delta(\omega - \omega_{ni}) = -\frac{1}{\pi} \frac{1}{1 - e^{-\beta \omega}} \chi''(q, \omega). \tag{4.12c}
\]

It is important to notice here that the matrix element prefactors of equation 4.12 only depend on the transferred momentum\(^4\), unlike other techniques such as ARPES or RIXS where there is an energy-dependent matrix element that needs to be carefully disentangled from the response function. **Thus, within the Born approximation, M-EELS directly measures the dynamic charge susceptibility \( \chi''(q, \omega) \) and reveals the nature of...**

\(^3\)\(S(q, \omega)\) is usually written in terms of the number density rather than the charge density [114, 118, 119]. To convert between the two, a factor of \(1/e\) needs to be pulled out from the Coulomb interaction \(V(q)\).

\(^4\)For energy losses small compared to the initial electron energy \(E = \hbar^2 k_i^2 / 2m\), the density of states factor \(k_f/k_i \approx 1\) and is largely irrelevant. For example, a 50 eV electron undergoing a loss of 3 eV has \(k_f/k_i \sim 0.97\).
interactions between charge in a many-body system.

The path forward to measure interactions in a solid is clear: one needs to create a source of electrons with well-defined $|k_i⟩$ and an analyzer capable of measuring $|k_f⟩$ with high accuracy and precision to give $\chi''(q, \omega)$. Naturally, there are challenges with realizing such an instrument. Before delving into those challenges, let us first develop an intuition for what $S(q, \omega)$ (or $\chi''(q, \omega)$) actually measures.

4.2 Building intuition for the charge correlation function

In this section, we will build an understanding of the charge correlation/response function by illustrating its behavior for the harmonic oscillator and hydrogen atom where $S(q, \omega)$ can be exactly solved for. These examples will demonstrate two general, but very important, characteristics of the charge response. The first is that sharp resonances in energy appear whenever the ground state and an excited state primarily differ in their charge distributions (as opposed to e.g., their spin configurations). The second characteristic is that the spatial profile of an excited-state’s charge distribution is encoded in the momentum dependence of $S(q, \omega)$.

4.2.1 The simple harmonic oscillator

Consider now the behavior of a single electron in a harmonic potential. We will work in one dimension for simplicity. The Hamiltonian of the one-dimensional simple harmonic oscillator is then given by

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega_0^2x^2.$$  (4.13)
The energy levels are equally spaced as \( E_n = \hbar \omega_0 (n + 1/2) \) and the eigenstate \( |n\rangle \) can be obtained by defining the creation and annihilation operators \( a^\dagger \) and \( a \) as

\[
\hat{x} = \sqrt{\frac{\hbar}{2m\omega_0}} (a^\dagger + a) \\
\hat{p} = i \sqrt{\frac{m\hbar\omega_0}{2}} (a^\dagger - a),
\]

with all the usual algebraic properties of the harmonic oscillator [120]. Working at zero temperature, the charge response and correlation functions are identical up to an overall constant prefactor and are given by

\[
S(q,\omega) = \sum_n |\langle n|\hat{\rho}(q)|0\rangle|^2 \delta(\omega - n\omega_0). 
\]

By definition, \( \hat{\rho}(x) = \sum_i q_i \delta(x - \hat{x}_i) \) so that \( \hat{\rho}(q) = \sum_i q_i e^{iq\hat{x}_i} \). In this case there is only a single electron, so we will ignore the factors of \(-e\) and can write the charge correlation function as

\[
S(q,\omega) = \sum_n |\langle n|e^{iq\hat{x}}|0\rangle|^2 \delta(\omega - n\omega_0) \\
= \sum_n |\langle n|e^{iq\sqrt{\frac{\hbar}{2m\omega_0}}(a^\dagger + a)}|0\rangle|^2 \delta(\omega - n\omega_0).
\]

Defining \( k \equiv \sqrt{\frac{2m\omega_0}{\hbar}} \), we can see that the transition operator \( e^{iq\hat{x}} = e^{i(q/k)(a^\dagger + a)} \) is actually a coherent state displacement operator \( D(\alpha) \equiv e^{\alpha a^\dagger - \alpha^* a} \) with \( \alpha = i(q/k) \). Using the general properties of displacement operators, we have that the matrix element \( \langle n|e^{iq\hat{x}}|0\rangle \) simplifies to
\( \langle n | e^{i \alpha \hat{x}} | 0 \rangle = \langle n | \mathcal{D} (\alpha) | 0 \rangle \) \hfill (4.19)
\[
= e^{-|\alpha|^2/2} \sum_m \frac{\alpha^m}{\sqrt{m!}} \langle n | m \rangle
\] \hfill (4.20)
\[
= e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}}. \tag{4.21}
\]

Thus we have a complete expression for the charge correlation function as

\[
S(q, \omega) = e^{-|\alpha|^2} \sum_n \frac{|\alpha|^{2n}}{n!} \delta (\omega - n\omega_0) \tag{4.22}
\]
\[
= e^{-(q/k)^2} \sum_n \frac{(q/k)^{2n}}{n!} \delta (\omega - n\omega_0). \tag{4.23}
\]

What equation 4.23 shows is that the charge correlation function consists of sharp resonances whenever \( \omega \) matches a transition between the ground and excited state. Because the charge operator \( \hat{\rho}(x) \) is only a function of spatial position (or, equivalently, momentum), these resonances only occur when the ground and excited states differ solely in their spatial charge distributions. In the absence of further couplings, no change in other quantum numbers, such as spin, can occur.

However, even among transitions that differ in their charge distribution, not all resonances in \( S(q, \omega) \) are equally weighted. Equation 4.23 shows that the dominant term that appears in \( S(q, \omega) \) is a transition from \( |0\rangle \) to \( |1\rangle \) for small \( q \) compared to the natural length scale \( k = \sqrt{\frac{2m\omega_0}{\hbar}} \). This is precisely the dipole selection rule of optics, and can be seen as the first non-trivial term in the expansion of the charge density operator

\[
\hat{\rho}(q) \propto e^{i q \hat{x}} = 1 + \underbrace{1q\hat{x}}_{\text{Dipole}} + \underbrace{\frac{q^2}{2!}(q\hat{x})^2}_{\text{Quadrupole}} + \ldots \tag{4.24}
\]
Figure 4.2: **Charge correlation function of the simple harmonic oscillator.** (a) Energy levels of the simple harmonic oscillator. Dipole, quadrupole, and octupole transitions correspond to $\Delta n = 1, 2, 3$ respectively. (b) Line cuts of the charge correlation function $S(q, \omega)$ as a function of energy for various values of momentum $q$. Here, the spectra are vertically offset and the linewidths of peaks are artificially broadened for visibility. Note that at small $q$, only the dipole transition is possible, while higher-order transitions become allowed as $q$ becomes comparable to $\sqrt{\frac{2m\omega_0}{\hbar}}$. (c) Energy-momentum map of the charge correlation function. Notice that as the spatial structure of the excited states becomes increasingly more oscillatory in real space, transitions to these states only appear at larger values of momentum.

As $q$ becomes larger in comparison to $k$, the $\Delta n = 2$ (quadrupole) and $\Delta n = 3$ (octupole) transitions become allowed, as shown in Figure 4.2b. Moreover, transitions to arbitrary excited states appear as $q$ increases further (see Figure 4.2c). **What we conclude, therefore, is that studying the charge correlation function $S(q, \omega)$ as a function of momentum is crucial, as having a sizable momentum transfer allows all multipole processes to occur.** However, the intensity of transitions into excited states generally decreases as they become the higher in energy due to the overlap with the ground state becoming progressively weaker. This trend is a demonstration of the fact that a measurement of $S(q, \omega)$ with M-EELS probes the charge fluctuations *around* a particular ground state.

### 4.2.2 The Hydrogen atom

Let us now turn to the case of the Hydrogen atom. Defining $\mathbf{r}_e$ as the position of the electron and $\mathbf{r}_p$ for the proton, the Hamiltonian reads
\[\mathcal{H} = \frac{1}{2M} p_p^2 + \frac{1}{2m} p_e^2 - \frac{e^2}{|r_e - r_e|}. \quad (4.25)\]

By defining a center-of-mass coordinate \( R = (m r_e + M r_p)/(m + M) \) and relative coordinate \( r_e - r_p \), the wavefunction \( \Psi(r_e, r_p) \) can be written as a product \( \Psi(r_e, r_p) = \phi(R) \psi(r) \). Taking the limit \( M \gg m \), we can treat the nuclear degrees of freedom as free particles and have \( \Psi(r_e, r_p) = \psi(r_p) \psi(r) \).

To write the charge correlation function we note that \( \hat{\rho}(r) = e \delta(r - r_p) - e\delta(r - r_e) \). Then we can write the Fourier transform of the charge density operator as

\[
\frac{1}{e} \hat{\rho}(q) = e^{i q \cdot r_p} - e^{i q \cdot r_e} = e^{i q \cdot r_p} - e^{i q \cdot r_e} e^{-i q \cdot r_p} e^{i q \cdot r_p} \quad (4.26)
\]

\[
= e^{i q \cdot r_p} - e^{i q \cdot r} e^{i q \cdot r_p} \quad (4.27)
\]

Ignoring units of \( e \), the charge correlation function at zero temperature is then given by

\[
S(q, \omega) = \sum_f |\langle f | e^{i q \cdot r_p} | i \rangle|^2 \delta(\omega - \omega_f) - \sum_f |\langle f | e^{i q \cdot r_e} e^{i q \cdot r_p} | i \rangle|^2 \delta(\omega - \omega_f) \quad (4.28)
\]

\[
= \delta(\omega - \frac{\hbar^2 q^2}{2M}) - \sum_f |\langle f | e^{i q \cdot r} | i \rangle|^2 \delta(\omega - \omega_f - \frac{\hbar^2 q^2}{2M}) \quad (4.29)
\]

Note here that we see resonances in \( S(q, \omega) \) when \( \omega = \frac{\hbar^2 q^2}{2M} \) which simply corresponds to transferring a total momentum \( q \) to the proton. This process has been dubbed electron Compton scattering [121], and is becomes relevant only at extremely large momentum transfer. Since this regime is not of interest, we set \( \frac{\hbar^2 q^2}{2M} \approx 0 \). Thus, we see the presence of the nuclear term from \( e^{i q \cdot r_p} \) acts to cancel the electron term to give \( S(q = 0, \omega = 0) = 0 \), meaning the Hydrogen atom is overall charge-neutral as one expects.

Because there are no valence and core electrons to distinguish between, let us ignore the
Figure 4.3: **Charge correlation function of the Hydrogen** (a) Energy levels of the Hydrogen atom. The dipole selection rule restricts transitions to those that satisfy $\Delta l = \pm 1$. At non-zero momentum transfer however, quadrupole and other multipolar transitions become possible. (b) Charge correlation function $S(q, \omega)$ of the Hydrogen atom as a function of momentum and energy. Notice that, at non-zero momentum transfer, transitions between the 1s ground state to any excited state become possible. Thus, $S(q, \omega)$ allows one to map out all excited states of the Hydrogen atom, not just the dipole transitions. (c) Charge correlation function of the Hydrogen atom as a function of $q_x$ and $q_y$ at a fixed energy corresponding to the transition from the 1s to $3d_{x^2-y^2}$ orbital $\omega = \Delta E_{1s \rightarrow 3d_{x^2-y^2}}$. Notice that the spatial structure of the excited $3d_{x^2-y^2}$ state is directly encoded in the momentum dependence of $S(q, \omega)$.

The effects of screening and look solely at the matrix element $\langle f | e^{i\mathbf{q} \cdot \mathbf{r}} | i \rangle$. The initial state here is the 1s orbital, while the final state can be any state of the form $|nlm\rangle$ where $n, l, m$ are the principal, angular momentum, and magnetic quantum numbers, respectively. We can expand the plane wave in terms of spherical harmonics as

$$e^{i\mathbf{q} \cdot \mathbf{r}} = 4\pi \sum_{l, m} (-1)^m l^j_l(qr)Y^m_l(\hat{r})Y^{-m}_l(\hat{q}), \quad (4.30)$$

Where $j_l$ and $Y^m_l(\hat{r})$ are the spherical Bessel function and spherical harmonic, respectively. The appearance of the spherical harmonic $Y^m_l(\hat{r})$ allows a simplification of the matrix element to
\[ \langle nlm|e^{i \mathbf{q} \cdot \mathbf{r}}|1s \rangle = 4\pi \sum_{l',m'} (-1)^{m'} i^{l'} Y_{l'}^{-m'}(\hat{\mathbf{q}}) \langle nlm|j_{l'}(qr)Y_{l'}^{m'}(\hat{\mathbf{r}})|1s \rangle \]  
(4.31)

\[ = \sqrt{4\pi}(-1)^{m} i^{l} Y_{l}^{-m}(\hat{\mathbf{q}}) \langle nl|j_{l}(qr)|1s \rangle \]  
(4.32)

\[ \implies |\langle nlm|e^{i \mathbf{q} \cdot \mathbf{r}}|1s \rangle|^2 = 4\pi |Y_{l}^{m}(\hat{\mathbf{q}})|^2 |\langle nl|j_{l}(qr)|1s \rangle|^2 \]  
(4.33)

Thus we have an expression for the electronic part of the charge correlation function

\[ S(\mathbf{q}, \omega) = 4\pi \sum_{n,l,m} |Y_{l}^{m}(\hat{\mathbf{q}})|^2 |\langle nl|j_{l}(qr)|1s \rangle|^2 \delta(\omega - \omega_{1s\rightarrow nl}). \]  
(4.34)

Or, in the case of radial averaging over \(m\) states (and in the absence of magnetic fields etc.)

\[ S(q, \omega) = 4\pi \sum_{n,l} (2l + 1) |\langle nl|j_{l}(qr)|1s \rangle|^2 \delta(\omega - \omega_{1s\rightarrow nl}). \]  
(4.35)

Where the step above relies on \(\int \int \sum_{m} |Y_{l}^{m}|^2 = 2l + 1\). A plot of the radially averaged \(S(q, \omega)\) is shown in Figure 4.3b. Noting that in the limit of small \(q\), \(j_{l}(qr) \approx (qr)^{l}\), we can expand \(S(q, \omega)\) to give

\[ S(q, \omega) \approx 4\pi \sum_{n,l} (2l + 1) |\langle nl|(qr)^{l}|1s \rangle|^2 \delta(\omega - \omega_{1s\rightarrow nl}). \]  
(4.36)

Just as in the case of the harmonic oscillator, we see that at small \(q\), only the dipole transition to the \(2p\) state is allowed, while higher order multipole transitions are possible at larger momentum.

A more important lesson is learned from the expression for \(S(\mathbf{q}, \omega)\) without radial averaging in equation 4.34. Let us assume that all energy levels are split and set \(\omega = E_{3,2,2} - E_{1s}\), so that we are studying the transition from the \(1s\) orbital to the \(3d_{x^2-y^2}\) orbital. Then we have

\[ S(\mathbf{q}, \omega) \approx 4\pi \sum_{n,l} (2l + 1) |\langle nl|(qr)^{l}|1s \rangle|^2 \delta(\omega - \omega_{1s\rightarrow nl}). \]
\[ S(\mathbf{q}, \omega = \Delta E_{1s \rightarrow 3d_{x^2-y^2}}) \propto f(qr) |Y_2^2(\mathbf{q})|^2, \]  

(4.37)

where \( f(qr) = |\langle 3d| j_2(qr)|1s \rangle|^2 \). As shown in Figure 4.3c, what equation 4.37 demonstrates is a general principle, by measuring the momentum dependence of the charge correlation function, \( S(\mathbf{q}, \omega = \text{fixed}) \), one can uncover the full spatial structure of the excited state charge density. In the case of \( \omega = \Delta E_{1s \rightarrow 3d_{x^2-y^2}} \), Figure 4.3c shows that the M-EELS response exhibits the expected appearance of the \( 3d_{x^2-y^2} \) orbital, but in momentum space rather than real space.

It should be noted that, while a charge fluctuation due to the density operator \( \hat{\rho}(\mathbf{q}) \) can change the \( n, l, m \) quantum numbers, it cannot directly change the direction of spin. However, if there is spin-orbit coupling that mixes \( L \) and \( S \), then an indirect change of spin is indeed possible. This point will be discussed in further detail when we come to M-EELS of Sr\(_2\)RuO\(_4\), whose Ruthenium atoms have a sizable degree of spin-orbit coupling that mixes spin and charge fluctuations.

### 4.2.3 Some examples of M-EELS in practice

Let us now give some brief examples of the kind of information obtainable by measuring the charge response function with M-EELS in real experiments. Figure 4.4a shows the dispersion of a soft exciton mode in TiSe\(_2\) using M-EELS from [10]. As a function of temperature, this exciton mode at goes to zero energy \( \mathbf{q} = \mathbf{q}_{\text{cdw}} \), indicating that the spatial structure of this mode (i.e. a charge-density wave) becomes a static property of the ground state. This result was taken as a signature of an “excitonium” at non-zero-\( q \), which is a spatially-varying Bose condensate of electron-hole pairs. This experiment thus demonstrates the power of M-EELS in probing amplitude modes of broken symmetry states across the Brillouin zone.

Another common use of M-EELS is to study phonons and electron-phonon coupling in materials [122, 123]. Figure 4.4b shows the phonon dispersion on the surface of copper
Figure 4.4: **Examples of the charge correlation function in practice** (a) Observation of a soft exciton with M-EELS in TiSe$_2$, indicating that the mode is an amplitudon of an excitonic condensate [10]. (b) Phonon dispersions of Cu(111) and graphene [122, 123]. Measurements of the phonons in the charge correlation function give momentum-resolved insight into the electron-phonon coupling present in the system through the intensity and linewidth of the phonon peaks. (c) Evidence for a topologically-protected acoustic plasmon at the surface of Bi$_2$Se$_3$ along two high symmetry directions [124]. The disappearance of this mode upon introducing magnetic dopants gives evidence that this mode is related to the topological properties of Bi$_2$Se$_3$ protected by time-reversal symmetry.

In addition to measuring the phonon dispersion, the intensity and linewidth of the phonons in the charge correlation function indicate the (momentum-resolved) strength of electron-phonon coupling in the system.

A final example is shown in Figure 4.4c, where the authors in [124] find a low-energy collective mode at the surface of the topological insulator Bi$_2$Se$_3$. This mode does not track onto any of the bulk modes of the system, and disperses straight through into the second Brillouin zone, implying this collective mode is decoupled from the lattice. Furthermore, the introduction of magnetic dopants completely suppresses the mode intensity, leading the authors to conclude that this excitation is a topologically-protected acoustic plasmon. Thus, one concludes that the charge correlation function is also a powerful method to probe the collective topological properties of materials.
4.3 Demystifying multiple scattering

As mentioned before, to measure the charge response of a system, one needs to build a momentum-resolved electron energy-loss spectrometer to measure the scattering of electrons in state $|k_i\rangle$ into $|k_f\rangle$. Needless to say, this is easier said than done. In particular, there are two challenges that need to be overcome: a theory of multiple scattering and developing the proper instrumentation.

The first challenge is conceptual, in that electrons interact strongly with solids, so we need to understand when “multiple” scattering beyond first-order perturbation theory occurs and how to mitigate it. In this section we will define multiple scattering more carefully by differentiating between incoherent and coherent multiple scattering. For the energy and momentum regime of interest to condensed matter, we will see that incoherent multiple scattering is mostly irrelevant. On the other hand, coherent multiple scattering is relevant, but only acts to change elastic intensities at Bragg reflections ($q = G, \omega = 0$) and can be accounted for using the same dynamical diffraction methods used in x-ray and neutron analyses. Thus, the fact that M-EELS measures the dynamic charge susceptibility in the region of interest is largely maintained even after taking multiple scattering into consideration. We will then use the formalism of dynamical scattering in the next section to derive the reflection M-EELS cross section.

The second challenge for developing M-EELS is technical. For electrons to penetrate through a sample, their incident energy needs to be on the order of 60-300 keV to transmit through a 100 nm thick material. While reaching such incident energies is straightforward, to resolve excitations at the scale of a few meV one requires a large resolving power of $R \sim 10^7$ to $10^8$. Such resolving power is possible [125, 126, 127], but is currently very expensive [128], with meV-resolved electron microscopes costing millions of US dollars. The route taken in this thesis is to use a monochromator that works at 1 eV electron energy so that a much lower resolving power is needed for meV resolution ($R \sim 500$ to 1000) and subsequently
accelerate the beam to 50 eV. This approach gives great meV energy-resolution, technical simplicity, and is much more affordable (∼120,000 USD). We will discuss more details about the instrumentation in Chapter 5. The drawback with this low-energy M-EELS approach is that 50 eV electrons cannot penetrate beyond a few nanometers in a solid, so only reflection measurements can be performed. We will present the theory of reflection M-EELS shortly.

4.3.1 Incoherent multiple scattering

The measured transition probabilities of any scattering experiment can deviate from the Born approximation in two conceptually distinct ways, which are confusingly both termed “multiple scattering”. The first is incoherent multiple scattering, and it occurs when the sample volume (i.e. density of scatterers) is large, in which case there is a high likelihood that the incident beam will scatter multiple times in a purely random and incoherent manner [129]. Rather than a failure of the Born approximation, it is more sensible to understand this type of multiple scattering as a sample that is too large\(^5\) (i.e. thickness much larger than some mean free path). As soon as one shrinks the sample thickness, this type of multiple scattering disappears\(^6\).

To quantify incoherent multiple scattering, let us take the intensity of the incoming beam as \(I_0\) and assume there is a mode at frequency \(\omega_0\) that we expect to scatter from an average of \(p\) times. Then, incoherent multiple scattering will follow a Poisson distribution [129] such that

\[
I(n\omega) = I_0 \frac{p^n}{n!} e^{-p}.
\]

One can now define a mean free path \(\lambda = t/p\), where \(t\) is the sample thickness. For large

---

\(^5\)Contrary to common belief, incoherent multiple scattering can also be useful. The most profound example is seen in the original Franck-Hertz experiments which were instrumental in establishing the quantum nature of the atom. These were arguably the first EELS experiments to be done, and incoherent multiple inelastic scattering provided the crucial evidence that atoms absorb energy in quantized integer multiples.

\(^6\)For example, cold neutrons will exhibit incoherent multiple scattering upon passing through one centimeter of vanadium, which is a strong neutron scatterer [130].
enough \( t \), peaks at multiples of the mode energy \( n\omega_0 \) will always be visible in the EELS spectrum\(^7\).

Incoherent scattering is largely irrelevant for our purposes because inelastic features below 3 eV typically have very little total spectral weight (i.e. small \( p \)), as the vast majority of spectral weight lies in higher-energy excitations between 10 eV and 120 eV. Said differently, multiply-scattered electrons will typically have lost energies much larger than 3 eV, so they will not be measured in the low-energy spectrum we are interested in\(^8\). As a example, in the case of \( \text{Sr}_2\text{RuO}_4 \), the spectral weight above 3 eV comprises about 99.5% of the total spectral weight (see Figure 4.5), implying that it is highly unlikely that any multiple-scattered electrons will remain in the energy window below 3 eV.

To be more concrete, the most intense features in the low-energy M-EELS spectra are usually optical phonons which are orders of magnitude weaker than the direct, reflected beam (\( p \sim 0.05\% \) to 2\%). Thus, the relative weight of higher-order scattering of low-energy excitations is negligibly small (\( 10^{-7} \) to \( 10^{-4} \) times smaller than the direct beam)\(^9\). Indeed, no evidence for multiple phonon peaks was observed in the M-EELS data presented in Chapter 6 and 7 on Bi-2212 and \( \text{Sr}_2\text{RuO}_4 \), validating the assumption that incoherent multiple scattering is not of primary concern.

### 4.3.2 Coherent multiple scattering and dynamical diffraction

The second type of multiple scattering is coherent, and occurs when the interaction is sufficiently strong to require higher order perturbative contributions beyond the first order matrix element \( \mathcal{M}^{(1)} \). The distinction between incoherent and coherent multiple scattering

\(^7\)One should note that harmonics of any excitation can also be seen without multiple scattering due to anharmonicity [117]. As such, the mere existence of higher order peaks of an excitation does not necessarily imply multiple scattering.

\(^8\)On the other hand, if one was interested in studying high-energy phenomena (e.g., core edges and their fine structure above 100 eV), incoherent multiple scattering is a major concern [129].

\(^9\)An exception occurs in the case of c-axis polarized optical phonons of ionic materials (e.g. \( \text{Ca}_2\text{RuO}_4 \) or \( \text{SrTiO}_3 \)) with high intensities. For \( q \sim 0 \), these phonons can be up to 10\% of the quasi-elastic peak so that weak harmonic phonon peaks can be visible.
Figure 4.5: **Multiple incoherent scattering.** Angle-integrated EELS spectrum of \( \text{Sr}_2\text{RuO}_4 \) from 0 to 120 eV. Notice that the spectral weight below 3 eV is minuscule compared to the spectral weight from 10 to 120 eV. Thus, multiple incoherent scattering predominantly occurs in the high-energy regime, not the low-energy one. This spectra was taken by combining high-resolution data taken below 5 eV with the Nion UltraSTEM at Rutgers (with 10 meV resolution) and the loss spectrum from 5 eV to 120 eV taken with the Themis Z Scanning Transmission Electron Microscope located at the Illinois Materials Research Laboratory. The data were combined by matching the overlapping regions in between the two spectra.
is shown in equation 4.40. One can also understand coherent multiple scattering as the regime where scattering events are sufficiently close in time and space that they cannot be treated as independent events.

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{Incoherent}} = |M^{(1)}|^2 + \frac{a^2}{2!} |M^{(1)}|^4 + \frac{a^3}{3!} |M^{(1)}|^6 + \ldots \tag{4.39}
\]

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{Coherent}} = |M^{(1)} + M^{(2)} + M^{(3)} + \ldots|^2 \tag{4.40}
\]

To understand when coherent multiple scattering occurs and how to deal with it, let us look at the probe-sample interaction from the point of view of the probe electron. Roughly speaking, the probe electron sees a time-dependent Coulomb potential due to the (thermally) fluctuating electron and nuclei positions of the sample \(V(q, \omega)\). Thus, we can write the probe electron Hamiltonian as

\[
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 = \frac{\hbar^2 k^2}{2m} + V(q, \omega). \tag{4.41}
\]

If there is a component of \(V(q, \omega)\) that is comparable to the kinetic energy \(\mathcal{H}_0\) of the probe electron, we expect that we cannot treat the potential as a first order perturbation and instead must either use higher-order perturbation theory or solve the Schrödinger equation for the probe wavefunction \(|\psi_i\rangle\) outright. However, not all components of \(V(q, \omega)\) are of equal strength. Our strategy, then, is to remove the “strong” components of \(V(q_s, \omega_s)\) and incorporate them into the probe electron’s \(\mathcal{H}_0\) so that we can perturbatively treat the rest of \(V(q, \omega)\) as a new interaction term \(\mathcal{H}_1'\).

\[
\mathcal{H} = \mathcal{H}_0 + \sum_{q_s, \omega_s} \mathcal{H}_0' + \mathcal{H}_1' = \mathcal{H}_0 + \sum_{q_s, \omega_s} V(q_s, \omega_s) + \bar{V}(q, \omega) \tag{4.42}
\]
Here, $\bar{V}(q, \omega)$ is the remaining “weak” part of the sample’s Coulomb potential. The power of this approach is that we are still able to measure $\chi''(q, \omega)$ for some range of momenta and energy. The catch is that the probe electron will no longer be in a plane wave state $|k\rangle$ before and after scattering, but rather in some distorted plane wave eigenstate of $\mathcal{H}'_0$ with the form $|\psi\rangle = \sum_k a(k)|k\rangle$.

To determine the form of $|\psi\rangle$, let us assume that the sample is crystalline, so that the sample’s potential is strongly peaked at the elastic Bragg peaks $V(G, \omega = 0)$, where $G$ are the reciprocal lattice vectors. On simple energetic grounds, we can argue that the fluctuating part of the potential $V(q, \omega \neq 0)$ is minuscule compared to static part. The characteristic energy scale of the static part of $V$, which can be approximated by the cohesive energy or work function, is on the order of 4 to 6 eV per atom, while the energy scale for the fluctuating part of $V$ goes as the thermal energy $k_B T$ ranging from 0.001 to 0.035 eV. Thus, to a good approximation, the only possibility for coherent multiple scattering comes from the (static) lattice potential terms (i.e. $V_{\text{static}} = \sum_G V(G, 0) = \sum_G V_G e^{iG \cdot r}$).

We now need to solve the Schrödinger equation for $\sum_{q_s, \omega_s} V(q_s, \omega_s) = \sum_G V_G e^{iG \cdot r}$.

$$E\psi = \left( \frac{\hbar^2}{2m} \nabla^2 + \sum_G V_G e^{iG \cdot r} \right) \psi$$

(4.43)

A careful eye will notice that this equation is no different than an electron in a periodic potential as in ordinary solid-state band theory [133, 134], and thus the solution is a Bloch wave of the form

$$\psi(r) = u(r) e^{i\mathbf{k}_i \cdot r} = \sum_G a_G e^{i(k_i + G) \cdot r}.$$  

(4.44)

where $u(r)$ is a function with the same periodicity as the crystal and $\mathbf{k}_i$ is the momentum of electron before approaching the solid. It is crucial here to realize that $a_G$ has no simple

$^{10}$For driven non-equilibrium systems, the fluctuating part of the potential can become extremely strong and therefore a dominating contribution. Such effects arises in systems driven by lasers and probed with electrons as in “photon-induced near-field microscopy” (PINEM) [131, 132].
relationship with $V_G$, which means we are in the limit of dynamical diffraction\textsuperscript{11}. For comparison, in ordinary kinematic diffraction, we have that the coefficients of the wavefunction and potential are directly proportional (i.e. $a_G \propto V_G$)\textsuperscript{12}. We can now demand boundary conditions such that the wavefunction outside the crystal has energy $E = \hbar k_i^2/2m$, which means that $G$ satisfies $k \cdot k = (k + G) \cdot (k + G)$. This condition is nothing more than the well-known Bragg condition for diffraction.

If we repeat the calculations of section 4.1.2 but use a Bloch wave $|\psi\rangle$ as our starting electron wavefunction instead of a plane wave $|k_i\rangle$, we get the following $M$-EELS cross section which accounts for coherent multiple scattering (or dynamical diffraction)

\[
(\frac{\partial \sigma}{\partial \Omega \partial \omega})_{\text{Mult. Scatt.}} \propto \sum_{G_1, G_2} a_{G_2}^* a_{G_1} V(q + G_1)V(q + G_2) \langle \rho(q + G_2) \rho(q + G_1) \rangle \tag{4.45}
\]

\[
= \sum_{G_1, G_2} a_{G_2}^* a_{G_1} V(q + G_1)V(q + G_2) S(q + G_1, q + G_2; \omega). \tag{4.46}
\]

To put things simply, dynamical diffraction means that we are effectively probing the target system with multiple beams of electrons with different incident wavevectors $k_i + G$, rather than a single beam with $k_i$. Thus, when one measures the final momentum of the electron $k_f$, the momentum transfer is not given by $q = k_i - k_f$, but could also be $q - G$ for any reciprocal lattice vector $G$. Therefore, one is (coherently) summing over various components of the charge response function at different momentum transfer and generally cannot extract $\chi''(q, \omega)$ in a simple manner.

Nonetheless, the situation is not as grim as it seems because (1) the undiffracted beam is

\textsuperscript{11}In general, dynamical diffraction is the regime where the resulting wavefunction or field must be evaluated using the full microscopic theory. For neutrons and electrons, this means the Schrödinger equation, while for light this means solving Maxwell’s equations for the electromagnetic fields from a material with a spatially-varying index of refraction $n(r, \omega)$.

\textsuperscript{12}This relationship implies that a measurement of the wavefunction $\psi$ allows one to obtain the amplitude of the lattice potentials $|V_G|^2$ and therefore determine the crystal structure. To do crystallography, one needs to be in a kinematic regime.
in practice much stronger than the diffracted beams\textsuperscript{13} (i.e. $|a_0| \gg |a_G|$) and (2) the Coulomb matrix element $V(Q + G)$ heavily suppresses large momentum scattering so that the $G = 0$ term dominates in the first Brillouin zone which is the region of primary interest.

The net result then, after considering coherent multiple scattering in bulk M-EELS, is that the cross section is reduced by an overall constant factor $|a_0|^2 \leq 1$, but still allows a direct measure of the dynamic charge susceptibility, at least within the first Brillouin zone. This effective reduction of the incident beam flux is due to the fact that some fraction of the beam is “lost” into other Brillouin zones and no longer contributes to the scattering cross-section under study. In terms of equations this means that

$$\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{Mult.Scatt.}} = |a_0|^2 \left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M--EELS}} \propto |V(q)|^2 S(q, \omega).$$

(4.47)

We can now summarize this section on the role of multiple scattering in bulk M-EELS. For the energy and momenta range of interest, the primary role of multiple scattering in M-EELS is to deplete the effective incident electron flux by scattering some fraction of the beam outside the energy/momentum range under study. For incoherent multiple scattering, the beam is \textit{inelastically} scattered outside of the \textit{energy} window of interest ($> 10$ eV). On the other hand, for coherent multiple scattering, the beam is scattered \textit{elastically} to large momenta and is outside the \textit{momentum} window of interest (higher order Brillouin zones).

### 4.4 M-EELS in the reflection geometry

In this section we will use the concepts of dynamical diffraction presented previously to derive an expression for the M-EELS cross section in reflection for low-energy (sub-100 eV)

\textsuperscript{13}This is not necessarily the case, but is true as long as one is not sitting \textit{precisely} at the Bragg condition in a thick crystal [134].
Figure 4.6: **Geometry of Reflection M-EELS.** (a) In reflection M-EELS, an electron with initial momentum and energy \((k_i, E_i)\) specularly reflects from a surface, while also undergoing an inelastic scattering event exchanging in-plane momentum \(q\) and energy \(\omega\) with the material. (b) The specular reflection of the incoming electron can be understood as the reflection of a particle in an effective 1D model with an unknown material potential \(V(z)\). Rather than a single plane wave, the electron in reflection M-EELS is a superposition of a forward moving wave \(e^{i\kappa z}\) and a reflected wave \(Re^{-i\kappa z}\).

Electrons. Unlike in a three-dimensional infinite crystal, the presence of a surface inherently breaks translation symmetry and requires one work in both momentum and real space. We will see that the cross section is related to a surface charge susceptibility \(\chi''_{\text{surf}}(q, \omega)\) and will discuss its relationship with the ordinary bulk \(\chi''(q, \omega)\).

### 4.4.1 The reflection M-EELS cross section

Scattering by reflection from a flat surface requires more care than ordinary scattering from an infinite crystal because of the explicit breaking of translation symmetry in one direction (i.e. there is material to scatter from for \(z < 0\) but only empty space for \(z \geq 0\)). On the other hand, translation symmetry is preserved in the direction parallel to the sample surface (up to a lattice vector for a crystal). Thus, we expect momentum parallel to the sample surface \(k_\parallel\) to be conserved, while momentum perpendicular to the sample surface \(k_\perp\) will not be conserved. This lack of conservation along \(z\) should come at no surprise, as this is precisely the same physics behind the specular reflection of light from a surface, which quite evidently does not preserve \(k_\perp\).
As in section 4.3.2, we will utilize a dynamical diffraction description to deal with the strong static parts of the surface potential nonperturbatively, but treat the inelastic events perturbatively within the Born approximation. A key difference from before however, is that we will not use plane waves \( \psi(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \), but rather a distorted plane wave of the form \( \psi(\mathbf{r})_{\text{dist.}} = e^{i\mathbf{k} \parallel \cdot \mathbf{r}}A(z) \), where \( \mathbf{r} = (x, y) \). By starting with this mixed representation of momentum space in \((x, y)\) and real space in \(z\), we hope to account for the lack of translation symmetry along the \(z\)-direction perpendicular to the surface.

In what follows, take \(z\) to be the direction perpendicular to the sample surface and \(\mathbf{r}\) to be directions parallel to it (see Figure 4.6a). We will also assume that the surface is oriented such that \(z\) is parallel to the crystal’s \(c\)-axis. For the sake of simplicity, let us also make the following definitions:

\[
\mathbf{k} \equiv \mathbf{k} \parallel, \quad \mathbf{G} \equiv \mathbf{G} \parallel, \quad \kappa \equiv k \perp, \quad \mathbf{r} \equiv \mathbf{r} \parallel. \tag{4.48}
\]

Then, we can write the effective Hamiltonian for the probe electron in a form very similar to that of 4.43 as

\[
\mathcal{H}_0' = \left( \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m} \nabla_z^2 \right) + \sum_{\mathbf{G}} V_{\mathbf{G}}(z) e^{i\mathbf{G} \cdot \mathbf{r}}. \tag{4.49}
\]

Apart from the explicit dependence on the out of plane direction \(z\), there is a key distinction between equation 4.49 and equation 4.43 for the 3D bulk case. In the bulk case, the static contribution of \(V(\mathbf{G} = 0, \omega = 0)\) vanishes because the system is overall neutral\(^{14}\). Thus, there is no potential that directly gives rise to a \(\mathbf{q} = 0\) term in the infinite crystal case. In contrast, the equivalent term in the surface potential \(V(\mathbf{G} \parallel = 0, z; \omega = 0)\), which corresponds to the potential averaged over the \((x, y)\) directions, is not identically zero (see Figure 4.6b) and will generically be the dominant contribution to 4.49 compared to the \(V(\mathbf{G} \parallel \neq 0, z; \omega = 0)\)\(^{14}\)

\(^{14}\)Recall \(V(\mathbf{G}) \propto \int d\mathbf{r} \, \rho(\mathbf{r})e^{i\mathbf{G} \cdot \mathbf{r}}\) so that \(V(\mathbf{G} = 0) \propto \int d\mathbf{r} \, \rho(\mathbf{r}) = 0\) for an overall charge-neutral system.
terms due to the Coulomb interaction which goes decreases with momentum as $\sim G^{-2}$.

Thus, we should primarily focus on solving for the wavefunctions of equation 4.49 for $G = 0$. In this case, we can write the wave function as a separable function of in-plane and out-of-plane variables $\psi(R) = e^{ikr}\psi(z)$ which results in

$$E_\perp\psi(z) = \left(\frac{\hbar^2}{2m} \nabla_z^2 + V(z)\right)\psi(z), \quad (4.50)$$

where $E_\perp = E - \frac{\hbar^2 k^2}{2m}$. In general, $V(z)$ will have the form of a step because the surface terminates the charge distribution (see Figure 4.6b). We can guess from basic quantum mechanics that the form of $\psi(z)$ will consist of a forward moving wave $e^{ikz}$, a reflected wave $Re^{-ikz}$, and a transmitted wave with different wavevector $Te^{i\tilde{\kappa}z}$. Note here that our convention is such that an electron moving toward the sample has $\kappa < 0$. Thus we can write

$$\psi(z) = \begin{cases} e^{ikz} + Re^{-ikz} & \text{Outside sample } (z > 0) \\ Te^{i\tilde{\kappa}z} & \text{Inside sample } (z < 0), \end{cases} \quad (4.51)$$

where $\tilde{\kappa} \sim \kappa \sqrt{1 - V(z)/E_\perp}$.

Before proceeding, let us make an order of magnitude estimate for the reflection coefficient $R$. Assume that the potential $V(z)$ is a step function of depth $V_0$. Then, we can use the elementary solution [135] for the reflection coefficient from a constant potential barrier of $R[\kappa, V(z)] = (\kappa - \tilde{\kappa})/(\kappa + \tilde{\kappa})$ which can be approximated as $R \approx \frac{1}{4}V_0/E_\perp \propto 1/\kappa^2$ when $V_0 < E_\perp$. For a 50 eV electron incident at a 45° angle from the surface, we have $E_\perp$ of about 25 eV. An estimate for the work function for a typical material is $V_0 \approx -4.5$ eV, thus giving an overall reflectance $|R|^2 \approx 0.2\%$. This number is consistent with reflection M-EELS experiments on Bi-2212, where the specular reflection from roughly 30 pA of beam current has intensity about 30 kHz, or 0.16% of the incoming beam. The remaining 99.8% beam is therefore transmitted into the sample. We will now make the assumption that
transmitted electrons cannot scatter back out of the sample. This assumption means that the effective portion of $\psi(z < 0)$ that contributes to the reflection M-EELS scattering process is zero, or at least exponentially decaying. Therefore, we can modify equation 4.52 to be

$$
\psi(z) = \begin{cases} 
  e^{ikz} + Re^{-ikz} & \text{Outside sample } (z > 0) \\
  0 \text{ or } Te^{-k_0z} & \text{Inside sample } (z < 0).
\end{cases}
$$

(4.52)

Here, $k_0$ is some constant that depends on the beam energy of the impinging electrons and can be taken to be some inelastic mean free path. For the moment, we take $k_0 \rightarrow \infty$ so that $\psi(z < 0) = 0$, but we will revisit the role of $k_0$ in section 4.5.3.

The justification for ignoring the transmitted beam is based on two reasons. The first is that valence plasmons, the most probable scattering channel for electrons as we saw in Figure 4.5, are on the order of 10-100 eV and rapidly reduce the probe electron energy to below the work function. Once the probe electron’s energy dips below the work function, they will never leave the sample again. The second reason is that the cross-section for a scattering event that reverses the direction of the transmitted beam by changing $-\kappa$ to $+\kappa$ is weak because it suppressed via the Coulomb interaction by a factor of about $\sim (2\kappa)^{-2}$.

The net result, then, is that we have a distorted plane-wave wavefunction for the incident and scattering electron in reflection M-EELS of the form

$$
\psi_i(\mathbf{R}) = N_i e^{i\mathbf{k}_i \cdot \mathbf{r}} (e^{ik_{iz}} + Re^{-ik_{iz}}) \theta(z)
$$

$$
\psi_f(\mathbf{R}) = N_f e^{i\mathbf{k}_f \cdot \mathbf{r}} (e^{ik_{fz}} + Re^{-ik_{fz}}) \theta(z),
$$

(4.53)

(4.54)

where the normalization factor is given by $N^2 = \frac{2}{\sqrt{1+|R|^2}} \approx \frac{2}{V}$, with a factor of two to account for the integral being done only for $z > 0$. We can now proceed in the same way as in previous sections (e.g., Section 4.1.2), by using Fermi’s golden rule to calculate the matrix
Figure 4.7: Scattering channels of reflection M-EELS. Using Fermi’s golden rule on the reflection M-EELS wavefunction (see equation 4.54), we obtain four terms (a) the Direct Coulomb term (D-Channel) where the unreflected beam is directly scattered without a reflection, (b) the Reflect-Coulomb term (RC-Channel) where the reflection occurs before the inelastic scattering event, (c) The Coulomb-Reflect term (CR-Channel) where reflection occurs after the inelastic event, and (d) the Direct Coulomb (RR-Channel) where the reflection of the probe electron is effectively canceled-out by being reflected twice (before and after the inelastic event). The D- and RR-channels are the least probable and are ignored, as they require a very large change in total momentum, which is unlikely due to the Coulomb matrix element.

What is different now is that we will have four distinct terms that result from evaluating matrix elements on the distorted wavefunctions $\langle \psi_f | O | \psi_i \rangle$, as shown in Figure 4.7.

Recall that to detect the final electron, we need $\kappa_f \approx -\kappa_i$ (i.e. the electron reflects back away from the sample). Backscattering, or large momentum transfer, due to the Coulomb interaction is extremely weak as a matter of principle, so how can such an event take place? To understand this point, we rank the four processes in Figure 4.7 by how much momentum needs to be provided by the Coulomb interaction for an electron to reach the detector. The direct Coulomb scattering processes D and RR (Figure 4.7a,d) require $q_\perp \approx 2\kappa_i$ and $-2\kappa_i$ respectively. In other words, these scattering channels rely on an (in)elastic scattering event that transfers a large momentum, but such events are unlikely because the cross section decreases as $q_\perp^{-2}$. On the other hand, the single-reflection processes RC and CR (Figure 4.7b,c) have $q_\perp \approx 0$ and are much more favorable by comparison. We argue, therefore,
that the primary mechanism for backscattered electrons relevant to our purposes occurs via these two single-reflection processes (RC and CR), with the large change in perpendicular momentum fundamentally occurring through the action of the strong $V(0, z)$ component of the potential, rather than from a single scattering event from the weaker $V(q \neq 0, z)$ terms.

Thus, we will ignore the contributions of the direct Coulomb processes for the calculation of the reflection M-EELS cross section\textsuperscript{15}, leaving the RC and CR single-reflection channels in Figure 4.7b,c.

Noting that the matrix elements for the RC and CR terms are identical upon the replacement $R_i \leftrightarrow R' \psi$ and $(\kappa_i + \kappa_f) \leftrightarrow -(\kappa_i + \kappa_f)$, we can focus on evaluating just one of the matrix elements. For brevity, we will ignore constant prefactors and focus solely on the transition matrix element.

\[
\mathcal{M} = \langle f | \hat{H}_1 | i \rangle = \iint dR_1 dR_2 \frac{\psi^*_f(R_2) \psi_i(R_2)}{|R_1 - R_2|} \langle f | \hat{\rho}(R_1) | i \rangle \tag{4.55}
\]

\[
= \iint dR_1 dR_2 \frac{e^{i \mathbf{q} \cdot \mathbf{r}_2} \psi^*_f(z_2) \psi_i(z_2)}{|R_1 - R_2|} \langle f | \hat{\rho}(R_1) | i \rangle \tag{4.56}
\]

\[
= \frac{2\pi e^2}{q^2} \iint dz_1 dz_2 \langle f | \hat{\rho}(q, z_1) | i \rangle \left( \psi^*_f(z_2) \psi_i(z_2) e^{-q|z_1 - z_2|} \right) \tag{4.57}
\]

We will now assume that the charge density operator is only non-zero for $z < 0$ (i.e. $z = 0$ defines the surface of the material). Putting this assumption together with the form of $\psi(z) \propto \theta(z)$ means that we are assuming there is no spatial overlap between

\textsuperscript{15}This point of ignoring the D- and RR-channels is more subtle than it may seem from reading references [136, 137]. The characteristic momentum for a reflection of an electron due to the direct Coulomb interaction at 50 eV is on the order of 5.5 Å\textsuperscript{-1} ($\lambda = 1.1$ Å). Thus, the direct channel’s relative contribution due to the Coulomb matrix element is about 2% of that of the single-reflection channel at the Brillouin zone boundary of Bi-2212 (0.82 Å\textsuperscript{-1}). However, this relative contribution is still an order of magnitude larger than $|R|^2$, which we have estimated earlier to be about 0.2 %. On this basis, one can disregard the RR-channel direct Coulomb process of Figure 4.7d, but an argument based on matrix elements alone cannot do away with the D process in Figure 4.7a. Instead, one must appeal to the length scales involved, as 1.1 Å is much smaller than the “size” of the delocalized valence electrons. Therefore, such a large momentum transfer event must have happened through scattering from deeper core electrons which do not contribute to the inelastic features of interest and are therefore irrelevant.
the probe electron and sample charge densities. This assumption will be relaxed in section 4.5.3 to understand its implications. We can then write the reflection M-EELS matrix element as

\[
\mathcal{M} = \frac{2\pi e^2}{q^2} R \int_{-\infty}^{0} dz_1 \int_{0}^{\infty} dz_2 \langle f | \hat{\rho}(q, z_1) | i \rangle \left( e^{i(\kappa_i + \kappa_f) z_2} e^{-q|z_1 - z_2|} \right) (4.58)
\]

\[
= \frac{2\pi e^2}{q^2} \frac{1}{i(\kappa_i + \kappa_f) + q} R \int_{-\infty}^{0} dz_1 \langle f | \hat{\rho}(q, z_1) | i \rangle e^{-q|z_1|} (4.59)
\]

We will next assume that the reflection coefficient is purely real and independent of perpendicular momentum \(\kappa\) so that \(R_i = R_f = R\). Let us also define \(\mathcal{K} = \kappa_i + \kappa_f\). The two matrix elements for the RC and CR processes are

\[
\mathcal{M}_{RC} = \frac{2\pi e^2}{q^2} \frac{1}{i\mathcal{K} + q} R \int_{-\infty}^{0} dz_1 \langle f | \hat{\rho}(q, z_1) | i \rangle e^{-q|z_1|} (4.60)
\]

\[
\mathcal{M}_{CR} = \frac{2\pi e^2}{q^2} \frac{1}{-i\mathcal{K} + q} R \int_{-\infty}^{0} dz_1 \langle f | \hat{\rho}(q, z_1) | i \rangle e^{-q|z_1|}. (4.61)
\]

To obtain the cross section, the RC and CR processes must be added together to get the total matrix element \(\mathcal{M}\)

\[
\mathcal{M} = \mathcal{M}_{RC} + \mathcal{M}_{CR} = \frac{4\pi e^2}{q^2 + \mathcal{K}^2} R \int_{-\infty}^{0} dz_1 \langle f | \hat{\rho}(q, z_1) | i \rangle e^{-q|z_1|}. (4.62)
\]

Retaining all coefficients as in reference [137] we obtain the expression for reflection M-EELS cross section
\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} = \sigma_0 V^2_{\text{eff}}(q,K) \sum_f \int \int \, dz_1 dz_2 \langle i | \hat{\rho}(q,z_1)|f \rangle \langle f | \hat{\rho}(q,z_2)|i \rangle e^{-|q|z_1} e^{-|q|z_2},
\]

where \( \sigma_0 \) and \( V_{\text{eff}}(q,K) \) are defined as

\[
\sigma_0 = \frac{m^2}{2\pi^2 \hbar^4} \sqrt{\frac{E_f}{E_i}} \frac{|R|^2}{(1 + |R|^2)^2} \quad (4.64)
\]
\[
V_{\text{eff}}(q,K) = \frac{4\pi e^2}{K^2 + q^2} \quad (4.65)
\]
\[
q = k_i - k_f \quad (4.66)
\]
\[
K = \kappa_i + \kappa_f. \quad (4.67)
\]

Note here that it is the sum of the perpendicular momenta \( K = \kappa_i + \kappa_f \), which is zero at the specular reflection condition, that appears in \( V_{\text{eff}} \), not their difference \( q_\perp = \kappa_i - \kappa_f \).

Recall now the definition of the the charge correlation function \( S(R_1,R_2; \omega) \) in terms of the charge density operator \( \hat{\rho} \) as \( S(R_1,R_2; \omega) = \langle \hat{\rho}(R_2,\omega) \hat{\rho}(R_1) \rangle \). If we assume translation invariance in the in-plane \( r \) directions, but not \( z \), we can write this as \( S(r_1 - r_2, z_1, z_2; \omega) = \langle \hat{\rho}(r_1 - r_2, z_2, \omega) \hat{\rho}(0, z_1) \rangle \). Then, taking the Fourier transform with respect to \( r \), but not \( z \), gives \( S(q, z_1, z_2; \omega) = \langle \hat{\rho}(q, z_2, \omega) \hat{\rho}(0, z_1) \rangle \) and by the fluctuation-dissipation theorem

\[-\frac{1}{\pi} n(\omega) \chi''(q, z_1, z_2; \omega).\]

We can then write the reflection M-EELS cross section as below.
\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} = \sigma_0 V_{\text{eff}}^2(q, K) \int_{-\infty}^{0} \int_{-\infty}^{0} dz_1 dz_2 S(q, z_1, z_2; \omega) e^{-|q|z_1} e^{-|q|z_2} \quad (4.68)
\]
\[
= -\frac{1}{\pi} \sigma_0 V_{\text{eff}}^2(q, K) n(\omega) \int_{-\infty}^{0} \int_{-\infty}^{0} dz_1 dz_2 \chi''(q, z_1, z_2; \omega) e^{-|q|z_1} e^{-|q|z_2} \quad (4.69)
\]
\[\equiv -\frac{1}{\pi} \sigma_0 V_{\text{eff}}^2(q, K) n(\omega) \chi''_{\text{surf}}(q, \omega), \quad (4.70)\]

where \(\chi''_{\text{surf}}(q, \omega) \equiv \int_{-\infty}^{0} \int_{-\infty}^{0} dz_1 dz_2 \chi''(q, z_1, z_2; \omega) e^{-|q|z_1} e^{-|q|z_2}\) is something akin to a surface charge response function.

The M-EELS cross section in Equation 4.70 tells us that, within our assumptions, reflection M-EELS measures a surface charge response function \(\chi''_{\text{surf}}(q, \omega)\). The surface nature of the response function is apparent when one notices the factors of \(e^{-|q|z}\) within the integral rapidly decay as one goes deeper into the sample. For sufficiently large \(q\), we then expect to be measuring \(\chi''(q, 0, 0; \omega)\), which is the response function of charge fluctuations that only propagate at the surface \(z = 0\). We will further connect this surface charge response to the bulk response in section 4.6.

One also sees that the effective “thickness” in \(z\) over which charge fluctuations contribute to the M-EELS cross section is \(q\)-dependent, going as approximately \(1/q\). This depth sensitivity is very different than the inelastic mean free path of low-energy electrons inside a solid used in ARPES\(^{16}\). The difference here is that we assume the probe electrons never enter the sample, but instead scatter while they are in the vacuum due to the non-local Coulomb interaction. We can understand this penetration depth in the following way. For non-radiative electromagnetic waves, a fluctuating field decays into the vacuum as \(e^{-|q|z}\) due to Laplace’s equation. Thus, for small \(q\) (i.e. the so-called “dipole” regime [105]), the probe electron can feel sample’s potential from much farther away than at larger \(q\) (the “impact scattering” regime [105]) where the sample’s field decays more quickly in \(z\).

\(^{16}\)Note that the “universal” curve for the electron inelastic mean free path in a solid is not correct below 50 eV anyways [138].
4.5 Extensions of the M-EELS cross section

Let us now recount the key assumptions that we have taken along the way in deriving the reflection M-EELS cross section in equation 4.70.

1. The electron reflectivity $R$ is only due to the $\mathbf{G} = 0$ surface potential term $V(\mathbf{G} = 0, z)$, and it is only this part of the surface potential that needs to be treated non-perturbatively (i.e. through dynamical diffraction).

2. $R$ is purely real and independent of both energy and momentum

3. There is no spatial overlap between the probe electron wavefunction and sample charge density (i.e. $\psi_{\text{probe}}(\mathbf{R}) \propto \theta(z)$ and $\hat{\rho}_{\text{sample}}(\mathbf{R}) \propto \theta(-z)$)

We will now look at each of these assumptions to understand their impact on the M-EELS cross section and their signatures in experiment.

4.5.1 Dynamical Bragg scattering in reflection M-EELS

In the previous section, we assumed that the only strong part of the sample’s potential that needs to be non-perturbatively incorporated into the probe electron’s Hamiltonian $\mathcal{H}_0$ is the in-plane-averaged potential $V(\mathbf{G} = 0, z)$. However, because we are interested in studying crystals, the Bragg potential terms $V(\mathbf{G} = \mathbf{G}_i, z)$ can also be significant and give rise to the same effects we saw with bulk M-EELS in section 4.3.2. We can therefore guess the modified form of the probe electron wavefunction with incident energy $E_0$ and initial momentum $(\mathbf{k}_i, \kappa_i)$ in the presence of these Bragg potentials is

$$\psi(\mathbf{R}) = \left( e^{i\mathbf{k}_i \cdot \mathbf{r}} e^{ik_i z} + \sum_{\mathbf{G}} R_G e^{i(\mathbf{k}_i + \mathbf{G})} e^{-i\kappa_{G,i} z} \right) \theta(z).$$

This form for the wavefunction is equivalent to the so-called LEED wavefunction [59, 139].
Note however, that not all reciprocal lattice vectors $\mathbf{G}$ can contribute to the sum in equation 4.71 because we must have conservation of energy. For all of these waves to have the same energy in the far field as $z \to \infty$ where $V(\mathbf{G}, z) \to 0$, we require that the energy of each final wave satisfies

\[
\frac{2m}{\hbar^2} E_0 = (k_i + \mathbf{G})^2 + \kappa_{\mathbf{G},i}^2 = k_i^2 + \kappa_i^2 \quad (4.72)
\]

\[
\Rightarrow \kappa_{\mathbf{G},i}^2 = k_i^2 - 2k_i \cdot \mathbf{G} - G^2 \quad (4.73)
\]

\[
\Rightarrow |\kappa_{\mathbf{G},i}| = \sqrt{k_i^2 - 2k_i \cdot \mathbf{G} - G^2} > 0 \quad (4.74)
\]

If $\mathbf{G}$ is too large, the out-of-plane wavevector is imaginary and therefore does not propagate away from the sample, implying the sum in equation 4.71 should be restricted to $G^2 > \kappa_i^2 - 2k_i G$. Moreover, Bragg’s law no longer applies because there is no constrain that $\kappa_{\mathbf{G},i} = \kappa_i$, so that $G^2 \neq 2K \cdot \mathbf{G}$ in general. The failure of Bragg’s law is sensible, as out-of-plane momentum is no longer conserved, giving rise to rods in reciprocal space rather than points. This result is in line with experiments using low-energy electron diffraction (LEED) where Bragg reflections can be seen regardless of incident electron orientation.

If the energy is low enough ($< 10$ eV typically) and the geometry is fine-tuned, the out-of-plane momentum can be nearly zero $|\kappa_{\mathbf{G},i}| \approx 0$. This is known as the “surface resonance” condition [140], and physically corresponds to the electron being nearly parallel to the sample surface after Bragg scattering, and results in waveguide-like partial confinement of the electron [140]. The net result is that the electron stays near the sample surface for much longer than usual scattering conditions, and many multiple inelastic scattering events can occur (e.g. up to 8th order phonon harmonics are observed in reference [141]). In this work we exclusively work at 50 eV and away from glancing angles, so surface resonance effects can be neglected.

One can then repeat the procedures of section 4.3.2 to obtain the modified M-EELS...
Figure 4.8: **Dynamical Bragg diffraction in reflection M-EELS.** A scan of the elastic ($\omega = 0$) M-EELS signal as a function of in-plane momentum along (H,0) in Sr$_2$RuO$_4$. Notice there are two peaks, the first at the specular condition $q = 0$ and the second at the first Bragg reflection $q = 2\pi/a$. We ignore the effects of $R_G$ because the specular reflection is stronger than the Bragg reflection and is closer in momentum to the first Brillouin zone where we are interested.

As this thesis is concerned with the behavior of charge fluctuations within the first Brillouin zone, we will ignore effects of $V(G, z)$ from here on.

---

[17] This is not always true, in some circumstances the intensity of the specular peak and first Bragg reflection are comparable.
4.5.2 Electron reflectivity at surfaces

Perhaps the biggest unknown in the theory of M-EELS is the behavior of the electron reflectivity $R$. Though we have assumed for simplicity the reflectivity is a constant real number independent of both energy and momentum, basic arguments show this cannot be the case.

In section 4.4.1 we showed that even an elementary estimate for the reflectivity gave $R \approx V/4E_\perp$, which is clearly not independent of either energy or momentum. In fact, a true determination of the electron reflectivity $R$ is equivalent to determining the unoccupied band structure of a material. In addition, to do such a calculation properly, one must also include the $R_G$ terms described in the previous section. In any case, we would expect a low reflectivity for $(\mathbf{k}_i, \kappa_i)$ near unoccupied bands where the electron can couple to unoccupied states inside the crystal. On the other hand, the reflectivity should be larger for $(\mathbf{k}_i, \kappa_i)$ that lie within unoccupied bandgaps, as there are relatively less states to couple into. Additionally, one would guess from ordinary wave mechanics that if the probe electron energy and momentum lies within an unoccupied bandgap, reflection would also induce a phase shift as well.

The relation between electron reflectivity and unoccupied bands suggests that an angle- and energy-resolved measurement of the electron reflectivity is an alternative to inverse photoemission (i.e. inverse-ARPES, electron-in and photon-out). Indeed such a technique, named ARRES (Angle-Resolved Reflected-Electron Spectroscopy), has been implemented in a rather spectacular fashion by the van der Molen group at Leiden University in references [138, 142, 143] In the region $E_0 \gtrsim 20$ eV, the short lifetime of unoccupied bands means that the energy and momentum dependence of the reflectivity $R$ is very broad. Thus, we can assume $R$ is constant on the energy scales we are interested in (0 to 3 eV) but must also keep in mind that M-EELS at large losses ($\gtrsim 5$ eV) has artifacts from a changing reflectivity, as noted in [139]. On the other hand, the momentum dependence of $R$ can be non-negligible,
changing by nearly an order of magnitude from the center to the edge of the Brillouin zone in the ARRES spectra of [138, 142, 143].

The momentum dependence of $R$ may seem alarming, but is not as detrimental as it seems. Since we will measure the charge susceptibility at fixed in-plane momentum transfer $q$ as a function of energy loss $\omega$, the incoming and outgoing electron momenta $(k_i, \kappa_i)$ and $(k_f, \kappa_f)$ are approximately constant as energy is changed. In other words, while the momentum-dependence of experimentally determined $\chi''(q, \omega)$ may have complications, the energy dependence is left intact. We will see that these momentum-dependent artifacts can be removed because of the f-sum rule on $\chi''(q, \omega)$.

We will conclude this section by re-deriving the M-EELS cross section for complex values of the reflectivity and distinct incoming and outgoing reflectivities $R_i$ and $R_f$. As the matrix elements $\mathcal{M}_{RC}$ and $\mathcal{M}_{CR}$ are nearly identical, the only effect of non-constant reflectivity will be to change the effective Coulomb matrix element$^{18} V_{\text{eff}}(q, \kappa)$.

Recalling

$$\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} \propto |\mathcal{M}_{RC} + \mathcal{M}_{CR}|^2,$$  \hspace{1cm} (4.75)

we can rewrite the transition amplitude as

$$|\mathcal{M}_{RC} + \mathcal{M}_{CR}|^2 = \left| \frac{R_i}{i\kappa + q} + \frac{R_f^*}{-i\kappa + q} \right|^2 \left| \frac{2\pi e^2}{q} \right|^2 |\mathcal{M}|^2,$$  \hspace{1cm} (4.76)

where $\mathcal{M}$ are the remaining terms which are independent of $\kappa$ and $R_{i,f}$. Then we can further simplify this expression to

$^{18}$Technically the normalization of the wavefunction differs for the incoming and outgoing waves which changes $\sigma_0$. However, since $|R| \ll 1$ such a change is negligible.
\[ |M_{RC} + M_{CR}|^2 = \left| \frac{R_i(-iK + q) + R_f^*(iK + q)}{K^2 + q^2} \right|^2 \left| \frac{2\pi e^2}{q} \right|^2 |M|^2 \]  
\[ = \left| \frac{q(R_i + R_f^*) - iK(R_i - R_f^*)}{K^2 + q^2} \right|^2 \left| \frac{2\pi e^2}{q} \right|^2 |M|^2. \]  

(4.77)

We then get that the new effective Coulomb matrix element is complex with the form

\[ V_{\text{eff}}(q, K, r, \theta) = \frac{2\pi e^2}{q} \left( \frac{q(R_i + R_f^*) - iK(R_i - R_f^*)}{q^2 + K^2} \right) \]  
\[ = \frac{4\pi e^2}{K^2 + q^2} \times \frac{1}{2} \left[ \left( R_i + R_f^* \right) + i\frac{K}{q}(R_i - R_f^*) \right] \]  
\[ = V_{\text{eff}}^{\text{old}}(q, K) \times \frac{1}{2} \left[ \left( R_i + R_f^* \right) + i\frac{K}{q}(R_i - R_f^*) \right], \]  

(4.79)

(4.80)

(4.81)

where \( V_{\text{eff}}^{\text{old}}(q, K) = \frac{4\pi e^2}{K^2 + q^2} \) is the original M-EELS Coulomb matrix element from equation 4.70.

Thus we obtain a modified form for the M-EELS cross section for complex and inequivalent reflectivities \( R_i \) and \( R_f \)

\[ \left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} = -\frac{1}{\pi} \sigma_0 |V_{\text{eff}}(q, K, R_i, R_f)|^2 n(\omega) \chi''_{\text{surf}}(q, \omega) \]  
\[ = -\frac{1}{\pi} \sigma_0 |V_{\text{eff}}(k, k_f, \kappa_i, \kappa_f)|^2 n(\omega) \chi''_{\text{surf}}(q, \omega) \]  

(4.82)

(4.83)

Noting that \( R_i = R_f = R \) and \( R \) is a real number, we find that the effective Coulomb matrix element is purely a function of incoming and outgoing momenta \( V_{\text{eff}}(k, k_f, \kappa, \kappa_f) \), but crucially not a function of energy due to the weak dependence of the reflectivity for energy losses below about 5 eV. Note also that in the special case where \( R_i = R_f = R \) and \( R \) is a real number, the above expression reduces to that of equation 4.70.
For simplicity, and because there is no experimentally verified method to measure the phase of the reflectivity, we will still use equation 4.70 to obtain the charge susceptibility \( \chi''_{\text{surf}}(q, \omega) \) from the measured M-EELS spectra. However, it should be kept in mind that the simple form of the Coulomb matrix element in equation 4.70 may be incorrect.

4.5.3 Spatial overlap between the probe and sample charge densities

In the derivation of the M-EELS cross section we had assumed that there is no spatial overlap between the probe and sample charge densities because both end abruptly at \( z = 0 \). In reality, both of these quantities are continuous objects, so one would expect a smooth overlap region. In this section, we will derive a modified M-EELS expression that accounts for a non-zero spatial overlap between the probe and sample. We will find that this expression both changes the effective Coulomb matrix element by a term that goes as \( \lambda q \), where \( \lambda \) is the depth of the overlap region, as well as adds another contribution to the total cross section which has a constant, \( q \)-independent penetration depth and decouples excitations parallel and perpendicular to the surface.

To model a spatial overlap between the probe and sample charge densities, let us assume the probe electron penetrates the sample in an exponentially decaying fashion, rather than being strictly zero within the sample as assumed previously. Then, the probe electron wavefunction takes the form

\[
\psi(R) = \begin{cases} 
  e^{ik\cdot r}(e^{i\kappa z} + R e^{-i\kappa z}) & \text{Outside sample (} z > 0 \text{)} \\
  e^{ik\cdot r} e^{\frac{1}{2}k_0 z} & \text{Inside sample (} z < 0 \text{)}.
\end{cases}
\]  

(4.84)

Here, \( k_0 \equiv \frac{2}{\lambda} \) is twice the inverse penetration depth into the sample. For simplicity we assume \( k_0 \) is a fixed constant independent of the direction of the probe electron beam. With this new form for the wavefunction, let us evaluate the M-EELS matrix element.
\[ \mathcal{M} = \frac{2\pi e^2}{q} \int \int dz_1 dz_2 \langle f|\hat{\rho}(\mathbf{q}, z_1)|i\rangle \theta(-z_1) e^{iKz_2} \psi_f^*(z_2) \psi_i(z_2) e^{-q|z_1-z_2|}. \] (4.85)

Next, we evaluate the integral over the probe electron coordinate \( z_2 \). As \( z_1 \) is restricted to be negative (the sample charge density still ends at \( z_1 = 0 \)), the integral over \( z_2 \) must be done in three parts: \((-\infty, z_1), (z_1, 0), \) and \((0, \infty)\). The last of these intervals is identical to the usual range of integration for the M-EELS wavefunction from equation 4.52. The integral over \( z_2 \) can then be written as

\[
\int_{-\infty}^{z_1} dz_2 e^{-k_0z} e^{-q(z_1-z_2)} + \int_{z_1}^{0} dz_2 e^{-k_0z} e^{-q(z_2-z_1)} + \int_{0}^{\infty} dz_2 e^{iKz_2} e^{-q(z_2-z_1)} \quad (4.86)
\]

\[
= \frac{1}{q - iK} e^{qz_1} + \frac{1}{q + k_0} e^{k_0z_1 - qz_1} + \frac{e^{k_0z_1} - e^{qz_1}}{q - k_0} \quad (4.87)
\]

\[
= \left( \frac{1}{q - iK} - \frac{1}{q - k_0} \right) e^{qz_1} + \frac{2q}{q^2 - k_0^2} e^{k_0z} \quad (4.88)
\]

Thus, the total M-EELS matrix element becomes

\[
\mathcal{M} = \frac{2\pi e^2}{q} \left( \frac{1}{q - iK} - \frac{1}{q - k_0} \right) \int_{-\infty}^{0} dz_1 \langle f|\hat{\rho}(\mathbf{q}, z_1)|i\rangle e^{-q|z_1|} \quad (4.89)
\]

\[ + \frac{4\pi e^2}{q^2 - k_0^2} \int_{0}^{\infty} dz_1 \langle f|\hat{\rho}(\mathbf{q}, z_1)|i\rangle e^{-k_0|z_1|}. \quad (4.90)
\]

Let us now discuss the key properties of this modified expression for the M-EELS matrix element. The first term in equation 4.90 is identical to that of the usual M-EELS matrix element of equation 4.70, but with the effective Coulomb interaction modified by a term that is of order \( \lambda q \), implying this correction vanishes as the penetration depth goes to zero as expected. On the other hand, the second term in equation 4.90 is new and interestingly decouples the spatial frequencies of the charge fluctuation parallel and perpendicular to the surface, giving them momenta of \( k_0 \) and \( q \), respectively. For comparison, the first term
in equation 4.90, which corresponds to the usual M-EELS cross section, fixes the spatial frequency of the charge fluctuation fixed to $q$ regardless of direction. We will return to this decoupling shortly in section 4.6.1 to derive the surface dipole selection rule.

Finally, it is notable that for highly two-dimensional materials (i.e. $\rho(q, z) \approx \rho(q) \delta(z)$), both terms in equation 4.90 reduce to the surface charge response function at $z_1 = z_2 = 0$, or $\chi''_{\text{surf}}(q, 0, 0; \omega)$. Because the focus of this thesis is on highly 2D materials, we conclude therefore that the primary effect of having a non-zero probe penetration depth is a modification of the effective M-EELS Coulomb matrix element, rather than a modification of the response function itself.

### 4.6 Connecting the bulk and surface response functions

Now that we have derived the reflection M-EELS cross section and its various extensions, we will next examine the similarities and differences between the bulk and surface charge response functions. To do this, we will first derive the surface dipole selection rule which permits $z$-polarized transitions regardless of the direction of $q$, unlike the ordinary bulk case where transitions are locked to be along $\hat{q}$. From there, we derive a general relationship between the surface charge susceptibility and the dielectric function which will demonstrate that the widely-held belief that reflection M-EELS at $q \sim 0$ measures $\text{Im} \left[ \frac{2}{\varepsilon(\omega) + 1} \right]$ (i.e. rather than $\text{Im} \left[ \frac{1}{\varepsilon(\omega)} \right]$) is not strictly true. In fact, in the layered two-dimensional limit which we are most interested in, we will see that the surface and bulk charge response coincide, with both response functions being related to the inverse dielectric function $\text{Im} \left[ \frac{1}{\varepsilon(\omega)} \right]$. Finally, we will derive the f-sum rule for the surface charge response which we will find is different from the bulk case, but, again, becomes identical to the bulk sum rule in the limit of a highly two-dimensional system.
4.6.1 Surface dipole selection rule

For the ordinary bulk charge response function, we can expand the charge density operator \( \hat{\rho}(Q) \) as a series in \( Q \cdot r \) for small momentum transfer as

\[
\hat{\rho}(Q) = \sum_{n} Z_{n} e^{iQ \cdot r_{n}} = \sum_{n} Z_{n}(1 + iQ \cdot r_{n} + \mathcal{O}(Q^{2}))
\]

(4.91)

\[
= 0
\]

(4.92)

where the sum over charged particles \( \sum_{n} Z_{n} \) is identically zero for an overall neutral system. We can use this expansion of \( \hat{\rho}(Q) \) to write the charge correlation function \( S(Q, \omega) \) as

\[
S(Q, \omega) = \sum_{f} |\langle f | \hat{\rho}(Q) | i \rangle|^2 \delta(\omega - \omega_{if})
\]

(4.93)

\[
\approx \sum_{f,n} |\langle f | Q \cdot r_{n} | i \rangle|^2 \delta(\omega - \omega_{if}) + \mathcal{O}(Q^{2})
\]

(4.94)

The above equation resembles the familiar matrix element for an optical transition due to an electric field \( E \) in the dipole approximation, which has the form \( \langle f | E \cdot r | i \rangle \). Thus, by identifying the momentum transfer \( Q \) with the electric field vector \( E \), we conclude that the predominant contributions to \( S(Q, \omega) \) at small momenta are dipole transitions oriented along the direction of the momentum transfer \( \hat{Q} \). For example, if the ground state \( |i\rangle \) is connected to an excited state by \( |f\rangle \) by a z-oriented dipole transition \( \langle f | \hat{z} | i \rangle \), this transition would only be visible in \( S(Q, \omega) \) when \( Q \) has a non-zero z-component \( Q_{z} \).

In reflection M-EELS however, while the in-plane momentum transfer can be set to zero, the out-of-plane momentum transfer is always non-zero due to the reflection process. Thus,
we expect the M-EELS measurement of the surface charge correlation function $S_{\text{surf}}(\mathbf{q},\omega)$ distinguishes between dipole transitions parallel ($\mathbf{r}$) and perpendicular ($z$) to the sample surface.

To see how this difference comes about, let us focus on the reflection M-EELS matrix element from equation 4.62

\[
\mathcal{M} = \frac{4\pi e^2}{q^2 + \mathcal{K}^2} R \int_{-\infty}^{0} dz \langle f | \hat{\rho}(\mathbf{q}, z) | i \rangle e^{-q|z|}. \tag{4.95}
\]

We can write out the density operator $\hat{\rho}(\mathbf{q}, z)$ as

\[
\hat{\rho}(\mathbf{q}, z) = \sum_n Z_n e^{i\mathbf{q} \cdot \mathbf{r}_n} \delta(z - z_n). \tag{4.96}
\]

Then we can write the matrix element $\mathcal{M}$ as

\[
\mathcal{M} = \frac{4\pi e^2}{q^2 + \mathcal{K}^2} R \sum_n Z_n \int_{-\infty}^{0} dz \langle f | e^{i\mathbf{q} \cdot \mathbf{r}_n} \delta(z - z_n) | i \rangle e^{-q|z|}, \tag{4.97}
\]

\[
= \frac{4\pi e^2}{q^2 + \mathcal{K}^2} R \sum_n Z_n \langle f | e^{i\mathbf{q} \cdot \mathbf{r}_n} e^{-q|z_n|} | i \rangle. \tag{4.98}
\]

If we now look at the expansion in powers of $q$, the first non-zero term is given by

\[
\mathcal{M} = \frac{4\pi e^2}{q^2 + \mathcal{K}^2} R \sum_n Z_n \langle f | i\mathbf{q} \cdot \mathbf{r}_n - q|z_n| | i \rangle. \tag{4.99}
\]

Thus, unlike the bulk dipole selection rule, a momentum transfer $\mathbf{q}$ parallel to the sample surface can always couple to excitations perpendicular to the surface because the electron undergoes a specular reflection in the scattering process. However, what the above equation also seems to suggest is that reflection M-EELS couples to in-plane and out-of-plane dipole
transitions equally at small $q$. Experimentally however, it is known that out-of-plane dipole transitions are actually much stronger in reflection M-EELS than in-plane transitions in the limit as $q \to 0$ [105]. We are forced to reason, therefore, that something is missing in the M-EELS cross section derived previously.

In fact, the M-EELS cross section of equation 4.70 from reference [137] incorrectly predicts the behavior at small $q$ in general. To see this flaw more clearly, let us set the in-plane momentum transfer $q$ strictly to zero but keep a non-zero out-of-plane momentum transfer $K$. That is, we are looking at the M-EELS response when the momentum transfer is only along the $z$-axis.

The reflection M-EELS matrix element in this case is

$$M(q = 0) = \frac{4\pi e^2}{K^2} R \sum_n Z_n \langle f| i \rangle = 0. \quad (4.100)$$

Therefore, the derivation of the M-EELS cross section, as described in references [106, 137, 144], naively implies that the M-EELS scattering cross section vanishes as $q \to 0$, which is not observed experimentally [105]. In fact, experimentally the cross section is strongest as $q \to 0$. One underlying reason for this incorrect prediction is the assumption of zero spatial overlap between the probe electron and sample charge densities. Let us now relax this assumption and allow for probe-sample spatial overlap as we did in section 4.5.3. Then, recall from equation 4.90 that the modified matrix element which accounts for non-zero probe-sample overlap has an additional term of the form

$$\frac{4\pi e^2}{q^2 - k_0^2} \int_0^\infty dz \langle f| \hat{\rho}(q, z)| i \rangle e^{-k_0|z|}, \quad (4.101)$$

where $2/k_0$ is the penetration depth into the sample. Unlike before, this term does not
vanish upon letting \( q = 0 \), and instead becomes
\[
\lim_{q \to 0} \frac{4\pi e^2}{q^2 - k_0^2} \int_{-\infty}^{0} dz \langle f|\hat{\rho}(q, z)|i\rangle e^{-k_0|z|} = -\frac{4\pi e^2}{k_0} \sum_n Z_n \langle f|z_n|i\rangle. \tag{4.102}
\]
Thus, for reflection M-EELS, dipole transitions that are purely polarized in-plane vanish at \( q = 0 \). On the other hand, dipole transition polarized perpendicular to the sample surface persist down to \( q = 0 \). This special preference of reflection M-EELS for perpendicular-polarized dipole transitions at small momentum transfer is known as the surface dipole selection rule \[145\].

A simpler way to see how the surface selection rule arises from a non-zero overlap is to consider the spatial charge density due to the scattering probe electron at \( q = 0 \) using the original M-EELS wavefunctions from equation 4.54

\[
\rho_{probe}(q = 0, z) = e\psi_f^*(z)\psi_i(z) = eN^2 R^2 \theta(z)(e^{iKz} + e^{-iKz}) \tag{4.103}
\]
\[
= \frac{4e}{V} R^2 \theta(z) \cos(\kappa z). \tag{4.104}
\]
Then, the electric field due to the probe electron is obtained from Laplace’s equation and given by

\[
E(z) = \left(\frac{16\pi e}{V} R^2\right) \theta(z) \frac{\sin(\kappa z)}{\kappa} \hat{z} \tag{4.105}
\]
\[
\Rightarrow E(z < 0) = 0. \tag{4.106}
\]
While the electric field at \( q = 0 \) is purely polarized along \( z \) as one would expect, the factor of \( \theta(z) \) means that it is strictly zero within the sample and thus the M-EELS cross section vanishes.

If we relax the form of the M-EELS wavefunction to allow non-zero penetration into the
sample (see equation 4.84), then the charge density of the probe electron inside the sample is 
\[ \rho_{\text{probe}}(q = 0, z < 0) \propto e^{-k_0|z|} \]
and the electric field at \( q = 0 \) is given by

\[ E(z < 0) \propto \frac{e^{-k_0|z|}}{k_0} \hat{z}, \quad (4.107) \]

which is non-zero within the sample and therefore drives \( z \)-polarized transitions. Thus, relaxing the assumption of non-overlapping charge densities is an important element for understanding the manifestation of the surface dipole selection rule at \( q = 0 \).

4.6.2 Does M-EELS measure \( \text{Im} \left[ \frac{2}{\epsilon(\omega)+1} \right] \)?

It is commonly stated in the HREELS literature that reflection EELS measures \( \text{Im} \left[ \frac{2}{\epsilon(\omega)+1} \right] \) in the limit of \( q \to 0 \) [105, 106, 136, 144, 146]. This expression should be compared to the bulk charge susceptibility which is proportional to \( \text{Im} \left[ \frac{1}{\epsilon(\omega)} \right] \). In fact, the statement that reflection EELS measures \( \text{Im} \left[ \frac{2}{\epsilon(\omega)+1} \right] \) is not always true, and in this section we will derive a more general relationship between the M-EELS cross section, the surface charge response \( \chi''(q, z, z', \omega) \), and the dielectric function of a material \( \epsilon^{-1}(q, z, z', \omega) \). To derive this relationship, let us first examine the general equation relating the inverse dielectric function and the charge susceptibility

\[ \epsilon^{-1}(r, r', \omega) = \delta(r - r') + \int dr'' V(r - r'') \chi(r'', r', \omega), \quad (4.108) \]

where \( V(r - r'') = \frac{\epsilon^2}{r - r''} \) is the bare Coulomb interaction. This expression is the most general relationship between a nonlocal dielectric function and a nonlocal charge response. If we assume translation symmetry in-plane, than \( \chi(r'', r', \omega) = \chi(r'' - r', z'', z', \omega) \) and the above
The equation can be written as

\[
\epsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') + \int d\mathbf{r}'' V(\mathbf{r} - \mathbf{r}'', z, z'') \chi(\mathbf{r}'' - \mathbf{r}', z'', z', \omega). \tag{4.109}
\]

Note that the integral above has the form of a convolution and can be simplified by taking the Fourier transform of the in-plane coordinates

\[
\epsilon^{-1}(\mathbf{q}, z, z', \omega) = \delta(z - z') + \int dz'' V(q, z - z'') \chi(\mathbf{q}, z'', z', \omega). \tag{4.110}
\]

Writing out the form of \( V(q, z - z'') \), one then obtains

\[
\epsilon^{-1}(\mathbf{q}, z, z', \omega) = \delta(z - z') + \frac{2\pi e^2}{q} \int dz'' e^{-q|z - z''|} \chi(\mathbf{q}, z'', z', \omega). \tag{4.111}
\]

Since we are concerned with the dissipative, imaginary part of the inverse dielectric function, we can write

\[
\text{Im} \left[ \epsilon^{-1}(\mathbf{q}, z, z', \omega) \right] = \frac{2\pi e^2}{q} \int dz'' e^{-q|z - z''|} \chi(\mathbf{q}, z'', z', \omega). \tag{4.112}
\]

Thus, the surface response function \( \chi''(\mathbf{q}, z'', z', \omega) \) is related to the mixed representation inverse dielectric function \( \text{Im} \left[ \epsilon^{-1}(\mathbf{q}, z, z', \omega) \right] \).

One should now notice the resemblance between equation 4.112 and that of the reflection M-EELS cross section in equation 4.70 which had the form:

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right) \text{M-EELS} = -\frac{1}{\pi} \sigma_0 V_{\text{eff}}^2(q, \mathcal{K}) n(\omega) \int_{-\infty}^{0} \int_{-\infty}^{0} dz_1 dz_2 \chi''(\mathbf{q}, z_1, z_2; \omega) e^{-q|z_1|} e^{-q|z_2|}. \tag{4.113}
\]

Thus, we have that the reflection M-EELS cross-section can be related to the inverse dielectric function as
\[
\left(\frac{\partial \sigma}{\partial \Omega \partial \omega}\right)_{\text{M-EELS}} = -\frac{1}{\pi} \sigma_0 \left(\frac{2\pi e^2}{q}\right)^{-1} V_{\text{eff}}^2(q, K) n(\omega) \int_{-\infty}^{0} d z_1 \text{Im} [\epsilon^{-1}(q, z = 0, z_1, \omega)] e^{-q|z_1|}.
\]

(4.114)

Here, we have assumed that \(\chi''\) is non-zero only for \(z_1, z_2 < 0\) because the system’s charge vanishes for positive values of \(z_1, z_2\). In fact, this is the same assumption that was used to derive the M-EELS cross section originally. What equation 4.114 shows, therefore, is that the reflection M-EELS cross section is proportional to an integral over the (mixed-representation) loss function \(\text{Im} [\epsilon^{-1}(q, z = 0, z_1, \omega)]\).

With the relationship between the surface charge response and dielectric function in hand, there are two useful limits to take. The first is the two-dimensional limit, which is relevant to the materials under study in this thesis, where we have

\[
\text{Im} [\epsilon^{-1}(q, z, z_1, \omega)] = \text{Im} [\epsilon^{-1}(q, z, \omega)] \delta(z - z_1).
\]

(4.115)

In this two-dimensional limit, the M-EELS cross section is given by

\[
\left(\frac{\partial \sigma}{\partial \Omega \partial \omega}\right)_{\text{M-EELS}} = -\frac{1}{\pi} \sigma_0 \left(\frac{2\pi e^2}{q}\right)^{-1} V_{\text{eff}}^2(q, K) n(\omega) \text{Im} [\epsilon^{-1}(q, z = 0, z_1 = 0, \omega)]
\]

(4.116)

and

\[
\left(\frac{\partial \sigma}{\partial \Omega \partial \omega}\right)_{\text{M-EELS}} = -\frac{1}{\pi} \sigma_0 \left(\frac{2\pi e^2}{q}\right)^{-1} V_{\text{eff}}^2(q, K) n(\omega) \text{Im} [\epsilon^{-1}(q, \omega)]
\]

(4.117)

which is to say that reflection M-EELS of a 2D system measures the 2D loss function, as one intuitively expects.

The second useful limit is that of large momentum transfer \(q\). In this limit, the factor \(e^{-q|z_1|}\) in the integral of equation 4.114 is strongly peaked at \(z_1 = 0\) and, if the loss function does not vary as a function of \(z_1\) on the scale of \(1/q\), one then obtains a similar expression...
as that of the 2D limit

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} \propto \int_{-\infty}^{0} dz_1 \text{Im} \left[ \epsilon^{-1}(q, z = 0, z_1, \omega) \right] e^{-q|z_1|} \quad (4.118)
\]

\[
\Rightarrow \lim_{q \to \infty} \left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} \propto \text{Im} \left[ \epsilon^{-1}(q, z = 0, z_1 = 0, \omega) \right] \int_{-\infty}^{0} dz_1 e^{-q|z_1|} \quad (4.119)
\]

\[
\approx \frac{1}{q} \text{Im} \left[ \epsilon^{-1}(q, \omega) \right] . \quad (4.120)
\]

Let us now return to the question of whether reflection M-EELS measures \( \text{Im} \left[ \frac{2}{1+\epsilon(\omega)} \right] \).

This relation can be derived if one considers a semi-infinite, but perfectly homogeneous, system in the limit as \( q \to 0 \). Then, one can postulate that the dielectric function of this system is completely local and has the form

\[
\epsilon(z, z', \omega) = \delta(z - z') [\theta(z) + \theta(-z) \epsilon(\omega)] . \quad (4.121)
\]

This form simply means that the dielectric function is given by \( \epsilon(\omega) \) inside the material \( (z < 0) \) and unity in vacuum \( (z > 0) \). Then, the inverse dielectric function must satisfy

\[
\int dz' \epsilon(z, z'', \omega) \epsilon^{-1}(z'', z', \omega) = \delta(z'' - z') , \quad (4.122)
\]

meaning that

\[
\epsilon^{-1}(z, z', \omega) = \frac{\delta(z - z')}{\theta(z) + \theta(-z) \epsilon(\omega)} . \quad (4.123)
\]

Thus, the M-EELS cross section is given by
\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} \propto \int_{-\infty}^{0} dz_1 \text{Im} \left[ \epsilon^{-1}(\mathbf{q}, z = 0, z_1, \omega) \right] e^{-q|z_1|} \quad (4.124)
\]

\[
\propto \int_{-\infty}^{0} dz_1 \text{Im} \left[ \frac{\delta(z - z_1)}{\theta(z) + \theta(-z)\epsilon(\omega)} \right] \bigg|_{z = 0} e^{-q|z_1|} \quad (4.125)
\]

\[
\propto \text{Im} \left[ \frac{2}{1 + \epsilon(\omega)} \right], \quad (4.126)
\]

where in the last step we used\(^{19}\) \(\theta(z = 0) = \frac{1}{2}\).

In general, the treatment of a sample as a semi-infinite homogeneous system seems to only make physical sense for ionic insulators, such as SrTiO\(_3\). For the systems studied in this thesis, and most cleavable materials in general, the two-dimensional limit derived above is more relevant, which means that we generally expect the following equation (modulo factors of \(q\))

\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} \propto \text{Im} \left[ \epsilon^{-1}(\mathbf{q}, \omega) \right]. \quad (4.127)
\]

Lastly, let us point out the connection between the M-EELS cross section and the Coulomb energy of the system. In the mixed representation, the total Coulomb potential is given by

\[
V_{\text{tot}}(\mathbf{q}, z, \omega) = \int dz' V_{\text{ext}}(\mathbf{q}, z, z', \omega) \epsilon^{-1}(\mathbf{q}, z, z', \omega) \quad (4.128)
\]

\[
= \frac{2\pi e^2}{q} \int dz' e^{-q|z-z'|} \epsilon^{-1}(\mathbf{q}, z, z', \omega). \quad (4.129)
\]

One notices a resemblance to the M-EELS cross section by taking \(z = 0\) in the above equation

\(^{19}\)In general, if the inverse dielectric function is local (i.e. goes as \(\delta(z - z')\)), then the M-EELS cross section is proportional to the loss function at the surface \(\text{Im} \left[ \epsilon^{-1}(\mathbf{q}, z = 0, z' = 0, \omega) \right]\).
which gives
\[
V_{\text{tot}}(q, z = 0, \omega) = \frac{2\pi e^2}{q} \int dz' e^{-q|z'|} \epsilon^{-1}(q, z = 0, z', \omega).
\] (4.130)

The M-EELS cross section can then be written as
\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} = -\frac{1}{\pi} \sigma_0 \left( \frac{2\pi e^2}{q} \right)^{-1} V_{\text{eff}}^2(q, K) n(\omega) \int_{-\infty}^{0} dz_1 \text{Im} \left[ \epsilon^{-1}(q, z = 0, z_1, \omega) \right] e^{-q|z_1|}
\] (4.131)
\[
= -\frac{1}{\pi} \sigma_0 \left( \frac{2\pi e^2}{q} \right)^{-2} V_{\text{eff}}^2(q, K) n(\omega) \text{Im} \left[ V_{\text{tot}}(q, z = 0, \omega) \right].
\] (4.132)

Thus, the M-EELS cross section is proportional to the differential Coulomb energy at the surface \(V_{\text{tot}}''(q, z = 0, \omega)\). This expression can be compared to the bulk response, which is proportional to \(V_{\text{tot}}''(q, q_z, \omega)\) instead.

Let us now end this section by briefly pointing out the lingering issue of how one incorporates the finite overlap term in the M-EELS cross section into the discussion above. This overlap term, as we saw in the previous section, can be important as \(q \to 0\). However, due to the factor of \(e^{-k_0|z|}\), rather than \(e^{-q|z|}\), it does not appear that it can be written neatly in terms of the dielectric function. Further theoretical and experimental work is needed to relate the overlap term to the bulk response, especially in the low-momentum regime \(q \approx 0\) where the overlap term is most important. On the other hand, for sizable momentum transfer, it is likely that this term is negligible as it is smaller than the usual M-EELS cross section by a factor of \((q/k_0)^4\), where \(k_0\) is larger than typical values of \(q\) due to the short penetration depth.
4.6.3 Sum rule for the surface density response function

In section 4.5, we saw that more sophisticated treatments of the reflection M-EELS cross section resulted in a number of modifications which largely enter through modifications to the effective Coulomb matrix element. A key feature of these modifications is that the resulting matrix element continues to only depend on the incoming and outgoing momentum, not the energy loss. The net result is that the M-EELS cross section goes as

$$\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{M\text{-EELS}} = n(\omega)f(q,K)\chi''_{\text{surf}}(q,\omega)$$

(4.133)

where $f(q,K)$ is a model-dependent function of momentum whose form we do not know precisely, but is not a function of energy loss. Thus, while the momentum-dependence of the reflection M-EELS cross section may not reflect the true behavior of $\chi''_{\text{surf}}(q,\omega)$, the energy-dependence of the cross section is directly related to $\chi''_{\text{surf}}(q,\omega)$ at a fixed momentum transfer. To “fix” the momentum-dependence, one can use a sum rule on the density response that relates an integral over the energy domain to a known function of momentum.

Sum rules are special commutator identities that relate the time derivatives of a response function to commutators with the Hamiltonian. More concretely, consider a response function of the form $\chi_{AB}(t) = [A(t), B(0)]$. Examine the behavior of $\frac{d}{dt}\chi_{AB}(t)|_{t=0}$, which is the rate of change of the response function at $t = 0$. Using the Heisenberg equation of motion, this quantity can be written as

$$\frac{d}{dt}\chi_{AB}(t)|_{t=0} = \left[ \frac{d}{dt}A(t), B(0) \right]|_{t=0} = i[[H, A(0)], B(0)].$$

(4.134)

The left hand side of this equation can be written in the frequency domain as
\[
\frac{d}{dt} \chi_{AB}(t)|_{t=0} = \int d\omega \frac{d}{dt} \chi_{AB}(\omega) e^{i\omega t}|_{t=0} = i \int d\omega \omega \chi_{AB}(\omega),
\]

so that we have

\[
\int d\omega \omega \chi_{AB}(\omega) = [[H, A(0)], B(0)] = \int d\omega \omega \chi_{AB}(\omega) = [[H, A], B].
\]  

Thus, the first moment of the response function is fixed to be \([[H, A], B]\). In general, the commutators \([[H, A], B]\) does not have a simple closed form and cannot be exactly evaluated. However, in the case of the charge response function, we have a very simple closed form for the first moment sum rule when the Hamiltonian is Galilean-invariant (i.e. depends on momentum/velocity solely through the kinetic energy term) so that \(H\) has the form

\[
H = \sum_i \frac{\hbar^2 p_i^2}{2m} + \frac{1}{2} \sum_{ij} V(r_i, r_j).
\]  

In this case, the density operator commutes with the potential and one can exactly evaluate the commutator of the density operator and kinetic energy terms. The result of this straightforward calculation gives \([[H, \rho(-q)], \rho(q)] = -\frac{\hbar^2 q^2}{m} \hat{N}\), where \(\hat{N}\) is the electron number density. Thus, we have a sum rule for the charge response function of the form

\[
\int d\omega \chi_{AB}(\omega) = [[H, \rho(-\mathbf{q})], \rho(\mathbf{q})] = -\frac{\hbar^2 q^2}{m} \hat{N},
\]

where \(\hat{N}\) is the electron number density.

---

20One can also form a zeroth moment sum rule for the response function as \(\int d\omega \chi_{AB}(\omega) = [A, B]_\omega\), which is a trivial result from how the Fourier transform is defined.

21Relativistic terms in the Hamiltonian, such as spin-orbit coupling, generally do not respect Galilean invariance and would require modifications to the sum rule. In general, these terms are negligible in the energy/momentum regimes of interest to condensed matter. On the other hand, such contributions may be important for understanding the spectral weight of core-level excitations.

22Technically the nuclei contribute to this commutator as well, but they are smaller by factors of \(m/M\).
\[
\int d\omega \omega \chi(q, \omega) = -\frac{\hbar^2 q^2}{m} N. \tag{4.139}
\]

Noting that the real part of the response function is even, only the odd part of \(\chi\) contributes to this integral. Furthermore, one only needs to perform the sum for positive frequencies because the odd part is antisymmetric. Thus, the first moment sum rule for the charge response is

\[
-\int_0^\infty d\omega \omega \chi''(q, \omega) = \frac{\hbar^2 q^2}{2m} N. \tag{4.140}
\]

This sum rule is known as the f-sum rule or, more precisely, the Bethe sum rule. The right hand side can be evaluated exactly, provided one knows the electron density. One can then obtain exact form of \(\chi''(q, \omega)\) in absolute units from the experimentally measured M-EELS cross section by multiplying it by a constant prefactor \(\alpha\) such that

\[
\chi''(q, \omega) = \left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} \times \left( \frac{\alpha}{\int_0^\infty d\omega \omega \left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}}} \right). \tag{4.141}
\]

An analogous sum rule for the surface response function can be obtained by taking the spatial Fourier transform of the ordinary f-sum rule with respect to \(z, z'\) to give

\[
-\int d\omega \omega \chi''(q, z, z', \omega) = \frac{\hbar^2}{2m} \left( q^2 + \frac{d}{dz} \frac{d}{dz'} \right) \hat{N}(z) \delta(z - z'). \tag{4.142}
\]

Then, the surface response function \(\chi''_{\text{surf.}}(q, \omega)\), which integrates over \(z, z'\), obeys the sum rule
\[- \int d\omega \chi''_{\text{surf}}(q, \omega) = - \int d\omega \int_{-\infty}^{0} dz_1 \int_{-\infty}^{0} dz_2 \chi''(q, z_1, z_2; \omega) e^{-q|z_1|} e^{-q|z_2|} \]

\[= \frac{\hbar^2 q^2}{2m} \int_{-\infty}^{0} N(z) e^{-2q|z|}, \]

so that

\[- \int d\omega \chi''_{\text{surf}}(q, \omega) = \frac{\hbar^2 q^2}{2m} \int_{-\infty}^{0} \rho(z) e^{-2q|z|} \]

where we write \(\rho(z) = N(z)\) to connect with literature references [147]. In the limit of a 2D system, we have \(\rho(z) = N\delta(z)\) and the surface sum rule reduces to

\[- \int d\omega \chi''_{\text{surf}}(q, \omega) = \frac{\hbar^2 q^2}{2m} N, \]

which is consistent with our previous observation that the surface response function is identical to the bulk response for a highly two-dimensional system.

### 4.7 Opportunities in the theory of M-EELS

We will now end this chapter by looking forward at the future of M-EELS theory. Throughout this chapter, we have seen that the Coulomb matrix element is essentially the only unconfirmed element in the theory of reflection M-EELS. In this thesis we largely circumvent the problem of the M-EELS matrix element by enforcing the f-sum rule to correct the momentum scaling of the M-EELS spectra. Nonetheless, this situation is not satisfactory, and the ultimate judge should be a side-by-side comparison of experimental M-EELS data and the theoretical calculations of the matrix element. Despite the fifty-year long history
of reflection EELS, a detailed quantitative comparison between the theory and experiment with regards to the matrix element has not been performed. The situation is different now however, as modern computation methods should enable a complete calculation of the matrix element using ab-initio methods to compare with experimental data. Indeed, reflection M-EELS can learn valuable lessons from ARPES [4] and RIXS [111], which have even more complicated matrix element effects, but where comparisons between theory and experiment are the norm.
Chapter 5

Experimental implementation of M-EELS

In this chapter we will give an overview of the experimental implementation of Momentum-resolved Electron Energy-Loss Spectroscopy (M-EELS) at the University of Illinois. The strange metal response in the cuprates and ruthenates have very low absolute count rates (about 3 Hz in many cases), thus requiring very long acquisition times for a point detector to understand the strange metal continuum as a function of doping, temperature, momentum, and energy. Accordingly, with the help of my labmates, my main contribution to the experimental state of M-EELS at Urbana is the systematic improvement of instrument stability from being practically limited to about 24 hours measurements at LHe temperature, to acquisition times of 9 days or more.

We will begin the chapter with an overview of the vacuum and control systems, and then describe the steps taken to improve the system’s stability. Subsequently, we will describe the electron optics of M-EELS and the new procedure I have introduced to properly determine the energy and momentum resolution by measuring the electron beam’s phase space profile. The M-EELS data acquisition and analysis procedures will then be described. Following that, we will shift gears and discuss sample preparation and experimental procedures for several transmission EELS experiments with the Nion Scanning Transmission Electron Microscope that will be discussed in later chapters. Finally, we dedicate a section towards a discussion of the future of M-EELS and the most promising areas for development.
Figure 5.1: **Photograph of the Urbana M-EELS instrument.** This image shows the M-EELS and sample preparation vacuum chambers along with their associated vacuum equipment. The chamber on the right houses the M-EELS spectrometer, while the chamber on the left is for sample preparation.

5.1 **Overview of the M-EELS experimental apparatus**

The M-EELS system at the University of Illinois can be divided into two main sections: the vacuum system which houses the M-EELS spectrometer, and the control electronics connected to the master control computer which interfaces with the user. The ultrahigh vacuum (UHV) chamber houses two sub-chambers: a sample preparation chamber for cleaving/annealing which has a Low-Energy Electron Diffraction (LEED) unit, and the main M-EELS chamber where the M-EELS spectrometer and sample goniometer are located. The control electronics are used to scan the M-EELS lens voltages, amplify and count the single electron pulses, and control the sample motions and cryostat. The master control computer is a Linux machine running the SPEC software with modules for communicating with all motors, electronics, and pulse counters.
In what follows, we will provide details for each of these sections of the M-EELS system. We will purposely skim over more technical aspects of the system, such as the circuit design of the lens control boards. Readers interested in such details are encouraged to read the thesis of labmate Sean Vig [148] or textbooks by Harald Ibach [105, 146].

5.1.1 The M-EELS spectrometer

Because M-EELS is surface-sensitive, experiments must be done under ultrahigh vacuum conditions with atomically clean surfaces. Accordingly a custom-built UHV chamber is used to house the M-EELS and associated equipment, as shown in Figure 5.1. The system has three levels of vacuum, starting from a rough high-vacuum load-lock where samples are introduced, a preparation chamber held at UHV conditions of $1 \times 10^{-10}$ torr where samples are cleaved, and the actual M-EELS measurement chamber where samples are measured at 5 to $8 \times 10^{-11}$ torr. Distortions of the electron trajectories due to quasi-static magnetic fields are suppressed by a double mu-metal shield which reduces the ambient field of about 500 Gauss to below 3 milligauss. Fluctuating AC fields are blocked by both the mu-metal shields and vacuum chamber walls, although their magnitude and impact on M-EELS counting noise have not yet been characterized. The rest of the components used to maintain vacuum are relatively standard, so we will not dwell on them here.

The sample itself sits at the bottom of a LHe flow-cryostat and has five translation degrees of freedom ($xy$, $xyz$) with two rotations axes ($\theta, \phi$) perpendicular and parallel to the scattering plane respectively. The purpose of the first set of $xy$ degrees of freedom is to translate the sample crystal into the center of rotation of the sample stage (i.e. the eucentric point), while the second $xyz$ set functions to move the center of rotation of the sample stage into the center of rotation of the M-EELS spectrometer. All translation stages and $\theta$-axis rotary seal were custom-designed by our group and manufactured by Thermionics. The $\phi$ motion is performed by a nonmagnetic UHV low temperature piezorotator from attocube.

More recently at $\sim 1 \times 10^{-10}$ torr due to the introduction of some new vacuum components
The M-EELS spectrometer itself is an HR-EELS spectrometer manufactured by L.K. Technologies (ELS-5000) according to the design of Prof. Dr. Harald Ibach patented in 1994 [149] and described in technical detail in references [105, 146]. Simply put, it consists of an electron gun, monochromator, focusing lenses, analyzer, and detector. We will discuss the optical qualities of these elements in more detail later. The beam optics consists solely of all-electrostatic lenses including monopoles (flat plates of metal), dipole (two-way split metal plates), and quadrupoles (four-way split metal plates). The lenses themselves are laser-cut/machined copper beryllium (CuBe), rather than pure OHFC copper which is too soft. The CuBe lenses are then completely coated with graphite (DAG 154 Acheson, or its modern equivalent ElectroDAG 154). This smooth coating of amorphous graphite provides an even workfunction across the lens, because polycrystalline copper has a different workfunctions depending on its crystallographic orientation. Electrical connections to lenses are done with single strands of CuBe to minimize possible ground loops.

Moving on to the mechanical properties of the EELS spectrometer, all meV-resolved HR-EELS systems to date are designed to change momentum transfer by manually rotating the analyzer with a hand-crank, which is highly primitive to say the least. In practice, this manual mechanism means that although the angular precision intrinsic to the electron beam optics in HR-EELS is high, the angular accuracy of the momentum transfer is poor due to sloppy movements. Moreover, manual rotation practically means there is no metric for assessing the crystallinity and mosaicity using the HR-EELS electron beam, as one cannot measure the specular reflection and Bragg peak linewidths.

To put the “M” in M-EELS, the Urbana HR-EELS spectrometer was mechanically retrofitted with a flex coupling and a precision stepper motor to allow for computerized control of the scattering angle. Furthermore, a eucentric sample stage was used to minimize the sphere of confusion. Though simple in principle, there is a dramatic improvement in data quality and reliability upon doing so. We will discuss these points in more detail in section 5.3.
5.1.2 Electronics and control computer

The control electronics for the M-EELS apparatus can be divided into those controlling the sample goniometer degrees of freedom and those of the M-EELS spectrometer. The various components and connections are shown in Figure 5.2. At the head of all controls is a master computer running the command-line interface program SPEC by Certified Scientific Software, which is standard at many synchrotron and neutron facilities. The most important achievement of this setup is that the control system can simultaneously control all lens voltages, motors, etc. independently and robustly. Thus, completely arbitrary cuts in energy and momentum can be taken. For comparison, ordinary HR-EELS systems have no motorized controls for sample or spectrometer angles and incapable of taking M-EELS energy scans at constant momentum or scanning momentum at constant energy.

The sample motion control at the hardware-level is done with off-the-shelf controllers from Thermionics, attocube, and Lakeshore cryotronics. Similarly, the counting electronics and two-theta motion for the M-EELS are commercially available products from Photonis, Ametek, Keithley, and Schneider Electric Motion.

On the other hand, the M-EELS lens electronics are hand-assembled by LK Technologies and are not widely available. These lenses are supplied with voltages through a series of low-pass filters from an array of digital-to-analog converters (DACs). These DACs are powered by a dedicated EELS power supply unit which we have separated from the noisy wall power through an uninterrupted power supply (UPS) battery to decrease AC noise in the EELS spectra.

Unfortunately, the design of the EELS DAC system and lens control has not evolved much since the original Ibach design of the 1980’s. Communication to the EELS DAC system is one-way, with no way to monitor the status of the lenses and verify their voltages besides monitoring one lens at a time manually with a voltmeter. In addition, the original software used to set the EELS lens DACs and acquire data has numerous issues such as
Figure 5.2: **M-EELS hardware block diagram.** The sample stage consists of mechanical motors and a temperature controller. The M-EELS spectrometer consists of electrostatic lenses, a filament, current readout, and electron pulse counting. At the top of the control system is the master SPEC computer, which interfaces with the user and provides automated access to all controls.

being undocumented and highly unstable, retaining no voltage records, completely lacking in automation capability, and forbids users from acquiring data for longer than 1000 seconds. To remedy this situation, labmate Sean Vig replaced this control software with his own GUI program, but this replacement suffered from a few other various issues and was unstable. Subsequently Sean and I worked to fully replace both the EELS DAC software and hardware with an Arduino-based microcontroller that communicates with the SPEC in a fully-automated fashion. To date, the new microcontroller-based lens controls system has not failed despite three years of nearly continuous operation.

### 5.2 Systemic improvement of M-EELS stability and robustness

Because of the low absolute counts rates of the strange metal features in the cuprates and ruthenates (often 1-3 Hz) and large amount of parameter space to be explored, it is crucial
to have a M-EELS system with high stability and high throughput. To study the momentum-dependence of the strange metal charge fluctuations, the system must be stable for at least five days at a single temperature. As stated previously, the longest energy scan allowed by the commercial HR-EELS system was 1000 seconds, which is insufficient. This software/hardware limitation was removed by the work of labmate Sean Vig, and so the ultimate bottleneck became the practical unreliability and instability of the combined control system, hardware, and vacuum. Thus, measurements at liquid Helium temperatures were, for a variety of reasons, practically limited to about 24 hours, which was still insufficient. My primary contribution to the M-EELS apparatus at Urbana was the systematic improvement of experimental conditions such that experiments at LHe temperature lasting nearly 10 days are now possible.

There is no glory in these systematic improvements and they are mostly “obvious”. Nonetheless, these improvements are presented here for the benefit of future M-EELS development.

1. Vacuum System

- Improvement of sample vacuum from $9 \times 10^{-10}$ torr to $\sim 5 \times 10^{-11}$ to $1 \times 10^{-10}$ torr by installing a much higher pumping speed cryopump which replaced an ion pump, overhaul of the vacuum baking procedure, identification and removal of outgassing components, and the use of all-dry pumps. Sample lifetime in the M-EELS vacuum chamber therefore increased by a factor of ten to fifty.

- Increasing the sample throughput from being limited to one cleave attempt per day in the M-EELS to six cleaves per day. This increase in throughput was made by first improving the load-lock vacuum system base pressure to $10^{-8}$ torr from its old pressure of $10^{-4}$ torr. Further work by labmate Samantha Rubeck in designing a new sample magazine now allows up to ten attempted cleaves per day in principle.
• Liquid Helium consumption monitoring and flow-rate control to allow controlled exchanges of the dewar without exposing the sample to poor vacuum and outgassing due to rapid temperature rises. Stable measurements at LHe temperature lasting over a week long have become routine and predictable.

• Motorized xy stage to allow automatic compensation of sample drifts between scans. Because the M-EELS scattering angles are scanned frequently, sample drift out of the beam is frequent and previously only addressable with slow manual adjustments. This stage is currently in commissioning.

2. Control System

• Full incorporation of the EELS lens voltage control system into the SPEC master computer with a microcontroller replacement for the original communications system. Lens voltages and relays can now be automatically changed, allowing for automated tuning and refinement of the beam during measurements.

• Development of an automated recording system so that lens voltages, relays, and currents/counts are recorded for every EELS dataset. Thus, reproducible voltage settings are now possible, as is the analysis of the tuning procedure and monitoring of the M-EELS electron-optical performance.

• Automated monitoring of the sample crystallinity during a measurement by programmed scans of the specular and Bragg reflection peaks in between EELS spectrum acquisitions. This method allows one to directly monitor sample drifts and surface degradation as data is being acquired.

• Introduction of a new method for determining the true energy and momentum resolution by mapping the phase space of the direct beam through a meshed energy loss and angle scan. Ordinary HR-EELS measures the energy resolution
at a single angle and is blind to aberrations of the beam profile. The result is that
the HR-EELS energy resolution at $q \approx 0$ is quite good, but at larger momentum
transfer it is 3-4 times worse than the nominal FWHM. The new phase-space
tuning method prevents this loss of resolution and facilitates the correction of
beam aberrations. This method will be discussed in more detail in section 5.5.

5.3 Achieving momentum precision and accuracy

Momentum-resolved EELS requires that the momentum transfer is known both with high
precision and accuracy. While the electron beam optics defines the momentum precision, it
is the mechanical rotation system which limits the momentum accuracy. In principle, HR-
EELS systems can have the same momentum precision as M-EELS, but their momentum
accuracy is guaranteed to be much poorer. In this section we will explain how to improve
the momentum accuracy, leaving the discussion of tuning to improve momentum precision
for section 5.5.

In an ordinary HR-EELS system, the detector angle is changed by a hand crank, and the
sample sits on a rotatable cryostat. There are two major problems here that need to be fixed
to turn HR-EELS into M-EELS. The first is that the sloppy detector rotation makes the
overall momentum transfer non-reproducible and inaccurate. This problem is easily fixed by
retrofitting the system with a flex coupling and stepper motor. The second problem is that
ordinary sample manipulators used in, for example, ARPES are inadequate for diffraction
techniques. The central issue is that the sample does not lie in the center of rotation (i.e.
eucentric point) of the goniometer unless an effort is made to put it there. In other words,
the sample does not stay in the same physical position as it rotates. For an unaligned
goniometer, the sample will move several millimeters as one scans from $q = (0, 0)$ to a Bragg
reflection at $q = (1, 0)$. The sphere which contains the range of movement of the sample
positions is known as the sphere of confusion.
One can make an estimate as to how serious a sphere of confusion of several millimeters is to the momentum accuracy. An estimate for the inaccuracy in angle due to a sphere of confusion with diameter $D$ is $\Delta q = k_i \arctan(D/2r)$, where $r$ is the distance from the sample to the analyzer and $k_i$ is the momentum of the incoming beam. For a 50 eV electron and realistic values for $r, D$ of $r \approx 30$ mm and $D \approx 3$ mm, one has a momentum inaccuracy of about 0.18 Å$^{-1}$ for HR-EELS. For reference, this is more than one fifth of the way to Brillouin zone boundary in Bi-2212.

To reduce this massive momentum inaccuracy, the sample goniometer needs separate translation stages to place the sample into the true center of rotation. To this end, the Urbana M-EELS system has two separate $xy$ translation stages. The upper translation stage moves the sample into the center of rotation of the goniometer, while the lower stage moves the center of rotation of the entire goniometer into the center of rotation of the M-EELS spectrometer. The end result is that center of rotation of the detector, goniometer, and sample position are all positioned at the same point in space. This procedure reduces sphere of confusion and allows for big improvements in the momentum accuracy (see Figure 5.3). Because the electron beam is about 0.5 mm itself, it is typically quite difficult to reduce the sphere of confusion far below 0.5 mm. Nonetheless, the reduction in sphere of confusion to 0.5 mm with M-EELS translates to a momentum inaccuracy of about 0.02 Å$^{-1}$, which is near the momentum precision of the spectrometer itself. We will compare the net M-EELS momentum resolution to that of HR-EELS in section 5.5.

5.4 Electron optics

Let us now give a brief overview of the electron optics that make up the Ibach-style EELS spectrometer used in M-EELS. A photograph of the spectrometer is shown in Figure 5.4a. An overview of the beam optics of M-EELS is shown in Figure 5.4b and is described in more detail below:
Figure 5.3: The sphere of confusion. If a sample is not located in the center of rotation of the goniometer and analyzer, it will move in space as it rotates. The sphere containing the path mapped out by the sample as it rotates is known as the sphere of confusion. (a) For a large sphere of confusion, the momentum inaccuracy becomes a serious issue, and one no longer knows what momentum transfer they are measuring. (b) By reducing the size of the sphere of confusion, the momentum transfer becomes more accurate, and one knows with confidence where they are in momentum space.
Figure 5.4: **M-EELS spectrometer and lens layout.** (a) Photograph of the M-EELS spectrometer outside of the vacuum chamber. (b) Block diagram of the electron optics of the spectrometer shown in (a). Electrons are emitted from a thermionic source and focused onto the entrance of a pre-monochromator which is limited by space charge. The pre-monochromator partially monochromates the beam and sends it to a second monochromator that does the final monochromation. The beam is then accelerated towards the sample and scattered. Scattered electrons enter the analyzer if they have the appropriate angle. The scattered beam is then dispersed so that only electrons with a specified energy pass the exit slit and arrive at the Channeltron detector.
1. **Extraction of beam current:** a heated (about 1800 K) LaB₆ filament from Kimball Physics (model # LaB6 ES-423E-6006) boils off about 7 µA of electron current with a 150 meV bandwidth and feeds it into a pre-monochromator (M1) through an Einzel lens system (A1, A2, A3). A slit is used before the pre-monochromator to decrease the emittance of the beam by limiting the range of entrance angles (at the cost of only ∼0.2 µA current making it through).

2. **First monochromation stage:** A dispersive toroidal monochromator cuts down the energy bandwidth of the electrons from 150 meV to about 25 meV. At this stage, the large Coulomb repulsion (i.e. space charge) does not allow for better than 25 meV resolution, so the rest of the beam (about 1 nA) is sent through a second monochromator.

3. **Second monochromation stage:** the second toroidal monochromator has sufficiently low current that space charge is no longer a problem. Thus, this monochromator can reduce the energy bandwidth down to 0.5 - 4 meV with better resolution coming at a tradeoff with lower beam current. Typical currents that exit this stage and hit the sample lie between 20 to 170 pA.

4. **Focusing and acceleration:** condenser lenses (i.e. zoom lenses) shape the beam exiting the second monochromator and then accelerate them to the desired beam energy (50 eV for most of this thesis).

5. **Scattering from the sample:** the beam is scatters off of the sample both elastically and inelastically.

6. **Deceleration and re-focusing:** The scattered beam is decelerated to the energy of interest and focused by the objective lenses onto the entrance of an analyzer which is a mirror copy of the second monochromator. By rotating the objective and analyzer,
different directions of the scattered beam are measured, thus providing momentum-resolving capability.

7. **Dispersion and energy-selection:** The (in)elastically scattered beam is dispersed and an exit slit selects the energy that will leave the analyzer and enter the detection apparatus. By varying the voltages of the analyzer, different energies of the scattered beam are measured, thus providing energy resolution to M-EELS.

8. **Angular aperturing and measurement:** A final set of lenses is used to truncate aberrations by rejecting electrons with large exit angles. The remaining electrons are accelerated to 3 keV and fed into a Channeltron electron multiplier where they cause a cascade of secondary electrons. This multiplier thus produces a current pulse which is read out by detection electronics.

Readers interested in a more detailed and quantitative discussion of the beam optics of the M-EELS spectrometer are referred to [146].

### 5.5 A new M-EELS “phase-space” tuning method

An ideally tuned electron beam with energy $E_0$ and momentum $k_0$ for M-EELS has a momentum and angle distribution of the form

$$R(k, E) = \exp \left[ -\frac{(E - E_0)^2}{2\sigma_E^2} - \frac{(\theta - \theta_k)^2}{2\sigma_k^2} \right], \quad (5.1)$$

where $\sigma_E$ and $\sigma_k$ are the energy and momentum resolution. The key feature of the above resolution function is that it is a Gaussian with no correlation between energy and momentum. In practice, however, all electrostatic lenses are aberrated and no tune is perfect, so one would expect that the resolution function to deviate from an uncorrelated Gaussian into a more complicated shape. The traditional HR-EELS method to improve the resolution
Figure 5.5: **Simulated M-EELS beam aberrations** Comparison of (a) a well-focused beam to (b) a sharp, but aberrated beam. (c) Linecut of the well-focused beam compared to the angle-integrated energy profile. For a well-focused beam these two curves are virtually identical. (d) Same as (c) but for the aberrated beam. Although a linecut in energy at fixed angle is sharper than in (c), the angle-integrated resolution is much worse.
function of the electron beam is to optimize the energy profile of the beam at a fixed angle. Indeed, this is the original method used by our group for a number of years.

The traditional HR-EELS tuning method only works if the beam is an uncorrelated Gaussian. Otherwise, an optimization of the energy profile at fixed angle can give rise to a strongly aberrated beam, as shown in Figure 5.5a-d. Although the aberrated beam in Figure 5.5b is very sharp, its angle-integrated energy profile is extremely poor (Figure 5.5d), unlike the well-focused beam where they are virtually identical (Figure 5.5c).

The signature of a poorly-focused beam is subtle. Because the Coulomb matrix element goes as $q^{-2}$, the sharp but aberrated beam in Figure 5.5b can give significantly higher resolution that the well-focused beam of 5.5a at zero momentum transfer $q = 0$. However, as one goes to non-zero momentum transfer, the large tails of the aberrated beam at $q = 0$ contaminate the rest of the spectra at non-zero $q$ and give rise to very poor energy and momentum resolution. Thus, an aberrated beam is detrimental for studying the momentum-dependence of the charge response function $\chi''(q, \omega)$ at high energy/momentum resolution.

To properly focus the M-EELS electron beam, it is imperative to measure the full phase space structure of the beam (i.e. the beam emittance). A measurement of the beam emittance is impossible in HR-EELS, as the manual hand-crank motion is too sloppy to allow such a measurement. To solve this issue, I introduced a “phase space” tuning procedure where a two-dimensional map of the beam profile is made by scanning both energy and detector angle in a coordinated fashion. This automated scan gives feedback to the M-EELS operator on how their voltage settings impact the beam’s emittance. A comparison of the HR-EELS and phase-space tuning procedures is shown in Figure 5.6.

One may wonder what lens elements are the primary cause for the aberrated form of the electron beam in M-EELS and HR-EELS. We conjecture that this aberration is due to the electron beam entering into one of the monochromators with a large tilt angle, as the monochromators are the main dispersive elements in the M-EELS spectrometer. The logic is as follows. The cylindrical monochromators used in Ibach-style EELS spectrometers...
are designed to have a first order focus at their exit plane. What this means is that the exit position $r_{\text{exit}}$ of the electron coming into the monochromator does not depend on the electron’s entrance angle to first-order in $\theta$ (but does depend quadratically on $\theta$), and instead only depends linearly on their kinetic energy. However, a pre-condition of this first-order focus is that the electron entrance angles are centered around zero. If, instead, electrons enter at a non-zero tilt angle, then the exit position will be a coupled function of kinetic energy and angle, giving rise to an aberrated resolution function.
Figure 5.6: **M-EELS phase space tuning.** A comparison between the traditional HR-EELS tuning procedure where one optimizes at fixed angle, and the new phase-space tuning procedure in M-EELS. (a) The starting, factory beam emittance for a generic M-EELS tune file. Notice the strongly aberrated beam profile. (b) Conventional HR-EELS tuning gives a sharp, but strongly aberrated beam profile. Although the energy profile at fixed angle is excellent, the angle-integrated profile is very poor. (d) In comparison, the M-EELS phase-space tuning procedure results in a round, well-focused beam. (d) Unlike the conventional approach, the fixed-angle and angle-integrated energy profiles are identical.
The natural solution to a tilted incoming electron angle is to use a set of two dipole lenses to “untilt” the beam and then translate it back onto the optical axis. Unfortunately, the Ibach-style spectrometer does not have such lenses between the monochromators, and the only possibility for tilting in the scattering plane comes from the A-lenses near the electron emission source (see Figure 5.4b). Thus, one must align the A-lenses perfectly and rely on that alignment throughout the rest of the spectrometer which is a difficult task. What we have found by experience is that a very careful and systematic tuning is needed to achieve a well-focused beam, often taking months. In addition, if one does not tune up this lens configuration frequently, it quickly returns to being aberrated.

Nonetheless, the development of phase space tuning is crucial for our studies of the Fermi liquid mode Sr$_2$RuO$_4$ in Chapter 7. There, a rapidly dispersing mode appears below 0.13 Å$^{-1}$. To observe this mode, one needs both a small sphere of confusion and well-focused beam achieved through phase space tuning. In fact, previous studies of Sr$_2$RuO$_4$ have been performed with HR-EELS [150]; however, their momentum resolution of about 0.14 Å$^{-1}$ was so poor that the entire dispersion of the Fermi liquid mode in Sr$_2$RuO$_4$ would have been averaged over. For comparison, M-EELS achieves 0.03 Å$^{-1}$ resolution, allowing the mode to be seen. A comparison of the HR-EELS and M-EELS momentum resolution is shown in Figure 5.7.

5.6 On the unsuitability of line-detection for reflection M-EELS

During the course of this thesis work, our group pursued an upgrade of the channeltron point detector to a line detector based on a microchannel plate (MCP). This system, known as the MCA-EELS (LK technologies EA5000-MCA), records about 250 energies simultaneously, as shown in Figure 5.8. The working principle here is that a microchannel plate area detector
Figure 5.7: Comparing the momentum resolution of HR-EELS and M-EELS. Comparison of the specular reflection from the surface of Sr$_2$RuO$_4$ using HR-EELS [150] and with M-EELS. Because [150] only reports positive momentum transfer, we mirror their data to negative momentum transfer and indicate doing so with a dashed blue line. Notice that the full-width at half-maximum of the specular reflection for M-EELS is about 0.03 Å$^{-1}$, which is nearly five times sharper than that of HR-EELS (0.14 Å$^{-1}$), despite working at a significantly higher beam energy (50 eV compared to 20 eV).
(Figure 5.8b) replaces the Channeltron slit (Figure 5.8a) at the exit plane of the analyzer, enabling a range of electron energies to be obtained in parallel. Because the analyzer only disperses in one direction, the MCP detector acts as a line detector. The design of this system is described in a patent by Donald David at CU Boulder [151].

In principle, the replacement of a point detector by a line detector should achieve a factor of $\sim 250x$ speed-up in data acquisition. Unfortunately, we observed that the actual throughput of the MCA-EELS was worse than a point detector. There are three essential problems with the current MCA-EELS design that make it unsuitable for M-EELS. The first is that the lens optics reduced the overall beam intensity hitting the detector by at least a factor of 100x compared to the point detector design. As a result, the MCA-EELS was found to always have much lower count rates at a given energy when compared to the point detector system.

The second problem with the MCA-EELS has to do with the gain of the MCP itself. Because the quasielastic peak in M-EELS is very sharp and intense, the gain of the MCP would be highly non-uniform and non-linear depending on its historical dosage, as shown in Figure 5.9a. In principle this gain can be divided out; however, it was found to change rapidly during the course of an experiment and needed constant monitoring. One may think that reducing the bias on the MCP would help solve the problem. Indeed, while that it is true, the bias can only be decreased so much before single electrons can no longer be counted. Moreover, the reduction in signal that comes with lowering the bias further reduces the throughput of the MCA-EELS, at which point one is simply better off using a point detector.

The last, and most serious, problem with the MCA-EELS design is the poor point spread function of MCP detectors in general. Figure 5.9b shows a comparison of the MCA-EELS and ordinary Channeltron M-EELS on Bi-2212. One immediately notices the massive tails present in the MCA-EELS response which are absent in the Channeltron system. In other words, while the FWHM of both peaks are similar, their tail structure is very different, with
Figure 5.8: Microchannel plate-based MCA-EELS compared to a Channeltron-based point detector EELS (a) In an ordinary point-detector Channeltron EELS, one measures a single energy at a time through the use of a slit at the exit plane of the monochromator. (b) In comparison, the MCP-based EELS system records energies in parallel, offering a 250-fold increase in efficiency in principle.

the MCA-EELS tail obscuring essentially all features below 100 meV in this particular case.

5.7 Transmission EELS in a Scanning Transmission Electron Microscope

In Chapters 6 and 7 we will show comparisons between transmission EELS and reflection M-EELS on Bi-2212 and Sr$_2$RuO$_4$. These measurements were done using a Scanning Transmission Electron Microscope (STEM-EELS). In the case of Bi-2212, STEM-EELS measurements and the associated sample preparation were performed by our collaborators Katia Marche and Christian Dwyer at Arizona State University. For Sr$_2$RuO$_4$ on the other hand, both the STEM-EELS measurement and sample preparation of Sr$_2$RuO$_4$ were done by myself in collaboration with Philip Batson and Hongbin Yang at Rutgers University. A photograph
of the Rutgers Nion UltraSTEM STEM-EELS instrument is shown in Figure 5.10. Details about the STEM-EELS instrument itself are discussed in detail in [152, 153], so we focus here on the sample preparation of Sr$_2$RuO$_4$.

Unlike reflection M-EELS where one cleaves the surface of a sample in vacuum, sample preparation for STEM-EELS is more difficult, as one needs a sample that is about 50 nm thick. To prepare Sr$_2$RuO$_4$ for STEM-EELS, we used the Focused Ion Beam (FIB) instruments at the Illinois Materials Research Laboratory (FEI Scios 2 and FEI Helios 600i). Sample preparation with FIB has a large learning curve, so we report here an optimized recipe that future researchers can use to prepare STEM-EELS samples of crystalline materials for condensed matter studies. The most important ingredient of this recipe is to use 30 keV Gallium ions to mill the sample until it is 160 nm thick and then immediately switch to the ion voltage to 1 keV for final thinning. This procedure works best for samples that are homogeneous single crystals, but does not work well for thin films. The detailed recipe is listed below.
Figure 5.10: **Scanning Transmission Electron Microscope (STEM-EELS) at Rutgers University.** Nion UltraSTEM instrument at Rutgers University. The electron gun is located at the floor, and the EELS spectrometer is located at the top of the instrument. Details about the instrument are discussed in [152, 153].
1. Lift-out and Initial Mill (Scios 2)

(a) Orient the sample and mount it onto a SEM holder with line drawn along the crystal axes. Then, align the line inside the FIB to the milling direction.

(b) Deposit 0.15 µm of e-beam carbon in a 15 µm × 2 µm region.

(c) Deposit 1.0 µm of e-beam platinum on top of the previous protection layer.

(d) Deposit 2.5 µm of ion-beam platinum on top of the previous protection layer.

(e) Cut out the 15 µm × 2 µm slab, making sure to make a cut which is at least 6 µm deep.

(f) Connect the tungsten needle and lift out sample.

(g) Attach the sample to a Molybdenum FIB grid with platinum.

2. Final Polishing (Helios 600i)

(a) Fill up the cold trap with LN2 and turn off the platinum gas heating to avoid redeposition.

(b) Thin down a 4 µm wide region at 30 keV ion beam by alternating between ±1 degree incident beam angle until the sample is about 160 nm thick.

(c) Immediately lower the beam energy to 1 keV for the ion beam and 2 keV for the electron beam. Then, locate the sample and make sure it is visible by both the electron and ion beams.

(d) Thin the sample down at 1 keV ion beam energy with 45 pA of ion current at +8 degrees incident angle for 5 minutes.
Figure 5.11: **FIB sample preparation for STEM-EELS (a)-(f)** electron beam images of a Sr2RuO4 sample prepared with FIB after 5-10 minute milling cycles with 1 keV Gallium ions using 45 pA of current. The bright region in (f) is approximately 25 nm thick. (g-h) High-angle annular dark-field images of Sr2RuO4 and LSCO (x = 0.20) respectively using the Themis Z STEM. (i) Core-loss EELS spectrum of the LSCO FIB sample showing the pre-edge peak at about 527 eV, thus indicating the oxygen stoichiometry is unharmed by the FIB milling process.

(e) Thin the sample down at 1 keV ion beam energy with 45 pA of ion current at −8 degrees incident angle for 25 to 50 minutes, or until it looks transparent to 5 keV or 2 keV electrons.

Images of the above FIB procedure are shown in Figures 5.11a-f for Sr2RuO4 and La2−xSrxCuO4 (LSCO). The sample quality is confirmed by directly looking at the structure with the Themis Z electron microscope using a high-angle annular dark-field detector in Figures 5.11g-h, along with the Oxygen core-edge structure in LSCO to confirm the oxygen stoichiometry is left intact.

### 5.8 Pathways for next-generation M-EELS instruments

M-EELS, as an experimental technique, has enormous opportunities in three main areas: more efficient detectors, improving the electron source and beam optics, and novel designs
for new forms of spectroscopies and sample environments. Below, we describe some of these possibilities and the kinds of science they would enable.

1. **More efficient detection**: Single-channel detection with a point detector is highly inefficient and results in a constant battle against surface degradation. More efficient detectors, such as a hemispherical analyzer or time-of-flight detector, would enable a $10^5$ to $10^8$ increase in data acquisition speed. At these speeds, the entire dispersion of all collective modes across the Brillouin zone can be studied as a function of temperature. Time-of-flight detection is particularly interesting, as it naturally requires a pulsed electron source and thus opens the door for ultrafast EELS of materials out of equilibrium.

Practically, all M-EELS experiments will benefit from this detection speed-up, but it is perhaps most important for materials with very low-energy collective excitations. To see why, one should note that the Ibach-style spectrometer is capable of 0.5 meV resolution \[146\], but this resolution is almost never used in practice due to the prohibitively low beam current. More efficient detection would therefore allow one to make full use of the spectrometer at its highest energy resolution.

One should note however, that simply using a parallel detection scheme is not enough, as we saw with the MCA-EELS in section 5.6. Instead, the detector must have a very high dynamic range ($10^5$ or better) and a very sharp point-spread to avoid contamination of the elastic line into the inelastic features (e.g., as shown in Figure 5.9). This challenge has been pointed to occur in hemispherical analyzers in \[123\].

2. **Modern beam optics and electron sources**: The lens optics of M-EELS spectrometers have not significantly changed for over twenty years despite numerous advances in electron optics. New electron optical designs with better focusing capabilities would allow for smaller beam spot sizes which opens the door to many materials that cannot be made larger the 0.5 mm in size. The use of hemispherical monochromators with
higher resolving power could also enable even better energy resolution that currently achievable.

Another interesting avenue worth pursuing is the use of field emission, rather than thermionic emission, for overall brighter electron beams. In principle, one achieves orders of magnitude increases in beam brightness by using field emission sources over thermionic sources. This increase in brightness can either be used to produce more beam current at the same energy/momentum/spatial resolution compared to thermionic sources, or vastly improve the resolution while keeping the beam current the same. A key challenge here is that field emission sources need to operate on the kilovolt scale, so one must either develop keV monochromators that achieve meV resolution or decelerate the beam to the eV level to use ordinary HR-EELS monochromators. The former requires extremely high resolving power, while a key problem with the latter approach is that space charge effects (i.e. Coulomb repulsion) can easily nullify the increase in brightness at low energies if the beam optics is not designed accordingly. Nonetheless, field emission sources should in principle enable studying much smaller samples (i.e. tens of microns in size) with sub-meV resolution. Materials that do not cleave very well (i.e. most three-dimensional crystals) will highly benefit from smaller beam spot sizes, as one can search for a portion of the surface that is atomically flat like one does with Scanning Tunneling Microscopy.

3. Novel spectroscopies and sample environments: Beyond “vanilla” M-EELS, there are other novel spectroscopies that can be performed. One of these is “resonant” M-EELS, where one acquires high energy-resolution M-EELS spectra as a function of beam energy, similar to other resonant spectroscopies such as RIXS. Resonant M-EELS would allow one to explore the effect of exchange interactions by tuning the incident beam’s wavelength to maximize exchange transitions over the direct Coulomb interaction (see Appendix B for details). When the wavelength of the incident beam
nears the wavelength of the target system’s electrons, there is an enhancement of exchange interactions and sensitivity to spin excitations. Resonant M-EELS would allow one to measure, for example, spin exchange excitations in magnetic materials without the need for a spin analyzer. To achieve resonant M-EELS, one needs a redesign of the electron optics to allow for scanning the incident beam energy without changing the focus of the beam. Some early work on resonant EELS along these lines has been done by looking at higher energy excitations [141], so it would be very interesting to do the same in the meV energy range.

Another interesting avenue, which is currently being pursued by our group in Urbana, is “coincidence” M-EELS where one uses two electron beams to scatter from a sample and looks at the coincidence scattering events. This technique would allow one to measure the second-order non-linear charge response function (i.e. $\langle \rho \rho \rho \rho \rangle - \langle \rho \rho \rangle \langle \rho \rho \rangle$), and may have other interesting exchange contributions as well.

Finally, with regards to sample environments, opportunities exist for introducing external knobs to tune the ground state of a material in-situ. For example, a strain holder or electrical biasing system would allow one to study the behavior of collective modes as a function of non-thermal control parameters. These tuning knobs would be very powerful in the study of oxides, such as ruthenates, where changes in structure can result in very different electronic behavior.
Chapter 6
Strange metal continuum in Bi-2212

In this chapter, we will address the main question pursued by this thesis. Namely, what is so strongly correlated about the strange metal compared to the Fermi liquid? To answer this question, we first use M-EELS to measure the charge response of Bi$_{2,1}$Sr$_{1,9}$Ca$_{1,0}$Cu$_2$O$_8+x$ (Bi-2212), a superconducting cuprate and well-known strange metal, at optimal doping where its strange metal behavior is most prominent. What we find is a featureless continuum of charge fluctuations up to about 1 eV that is momentum-independent over 90% of the Brillouin zone, in stark contrast to the well-defined, dispersing Fermi liquid plasmon. This finding implies that the strange metal is characterized by local, non-propagating collective charge fluctuations. In other words, charge fluctuations of the strange metal are localized in time and space rather than energy and momentum like in the Fermi liquid.

We then move on to study the charge response of Bi-2212 across its doping-temperature phase diagram to address the question of how the charge fluctuations evolve as one leaves the strange metal regime. At room temperature, we find that the charge response is doping independent, with all dopings exhibiting a featureless continuum of charge fluctuations. Upon cooling to low temperature however, dramatic changes in spectral weight are observed below 0.5 eV. We find spectral weight to be enhanced below 0.5 eV in the underdoped regime, suppressed in the overdoped regime, and unchanged at optimal doping. By tracking this spectral weight change as a function of doping and temperature, we then construct a phase diagram based on the charge response function. This phase diagram shows that a featureless continuum is present in a fan-like region centered around optimal doping, which coincides with the location of the strange metal. We conclude, therefore, that the charge
response of the strange metal evolves from its featureless continuum form by rearranging its low-energy spectral weight to be enhanced or suppressed depending on the doping. These findings can be contrasted with the Fermi liquid, where doping only acts to rigidly shift the plasmon energy and temperature plays no significant role in the charge response. We conclude this chapter with a discussion of the possible theoretical explanations of the strange metal continuum and the outstanding questions that remain on the topic.

6.1 A brief introduction to cuprate phenomenology

The high-T\textsubscript{c} cuprates are a family of compounds with the highest superconducting transition temperatures of any material at ambient pressure. Members of the family generally contain two-dimensional layers of metallic copper oxide where the superconducting electrons are located, and insulating buffer layers in between these layers. There is an enormous body of literature about the cuprates, second only to ordinary semiconductors and metals, with almost any measurement imaginable being attempted at some point in time\textsuperscript{1} [154]. Giving a summary of all these properties is certainly outside the scope of this thesis. Instead, we will provide a rough overview of the cuprate phenomenology and center the discussion on one particular question: “what is so special about the strange metal normal state at optimal doping that gives rise to high-temperature superconductivity?”

Superconductivity in the cuprates occurs by doping holes (or electrons) into the antiferromagnetic (Mott) insulating parent compound, with the highest T\textsubscript{c} appearing when chemically doped to roughly x = 0.16 carriers per unit cell. These holes give rise to a single band that crosses the Fermi level with mixed copper 3d and oxygen 2p character (i.e. the Zhang-Rice singlet) [155]. Unlike most conventional superconductors, the pairing symmetry of the cuprates is d\textsubscript{x\textsuperscript{2}-y\textsuperscript{2}}, with the superconducting gap being largest along the copper-oxygen bond direction and zero along the diagonal. Structurally, the cuprates are a theorist’s night-

\textsuperscript{1}Whether these measurements are successful or not is a separate matter.
mare: they are highly two-dimensional (tetragonal or lower crystal symmetry), chemically complex (dozens of atoms of various types per unit cell), and very disordered. Astonishingly, despite all of their structural complexity, cuprate superconductivity is incredibly robust. In fact, one can make optimally-doped polycrystalline YBa$_2$Cu$_3$O$_{7-x}$ in their garage by following a crude YouTube recipe [156]. These features collectively defy the famous empirical rules for BCS superconductivity set by Bernd Matthias [157], with the exception of the last rule which warns experimentalists to “stay away from theorists”. In addition, the close proximity to magnetism, the robustness of d-wave superconductivity against disorder, and lack of the characteristic isotope effect make it clear that many modifications would be needed for any BCS/Eliashberg-type pairing mechanism to apply.

Within the superconducting state itself, the cuprates are surprisingly well-behaved, all things considered. Superconductivity occurs through condensation of Cooper pairs of quasi-particles with charge $2e$, and most of the usual theoretical descriptions for the practical behavior of superconductivity using Landau-Ginzburg theory, the Josephson relations, etc. still apply.

What are much more difficult to understand are the non-superconducting phases of the cuprates. As shown in Figure 6.1a, the doping-temperature phase diagram outside of the superconducting region is very complicated. As a matter of convention, we take the underdoped regime to be $x < 0.16$, optimally doped as $x \approx 0.16$, and overdoped in the range $x > 0.16$. At very low doping levels, one leaves the parent antiferromagnetic insulator and enters a poorly conducting state with a “pseudo-gap”. The pseudo-gap is a partial gap in the single-particle spectrum with d-wave symmetry (see Figure 6.1b) but, crucially, occurs without the appearance of superconductivity. Transport in the pseudogap regime is qualitatively somewhere in between an insulator and conductor, as one might expect because of the partial gap. At lower temperatures on the underdoped side, numerous types of spatially-inhomogeneous ordered states appear, including spin- and charge-density waves (also known as charge order). These density wave orderings are very short-ranged when
Figure 6.1: **Bi-2212 phase diagram and crystal structure.** (a) Generic phase diagram of high-$T_c$ cuprate superconductors from [36]. There is a superconducting dome around $x = 0.16$ above which is the strange metal normal state. On the underdoped side, various forms of ordering occur including the pseudogap, charge order, spin order, and eventually antiferromagnetism. In contrast, the overdoped regime is often considered to be more well-behaved and Fermi liquid-like. (b) Gap structure and Fermi surface of hole-doped cuprates from [36]. The cuprates have an incomplete Fermi surface (i.e. Fermi arcs) and a d-wave gap structure. The nodal direction is along (1,±1) and the antinode is along (1,0). (c) Crystal structure of Bi$_{2.1}$Sr$_{1.9}$Ca$_{1.0}$Cu$_2$O$_{8+x}$ (Bi-2212), a well-known strange metal. The unit cell consists of two copper oxide bilayers spaced with insulating layers of Bi, Sr, and Ca.

compared to conventional SDW’s and CDW’s [9], with correlation lengths ranging from 6 lattice parameters in Bi-2212 [158, 159] up to 130 lattice parameters in La$_{2-x}$Ba$_x$CuO$_4$. Moreover, these density waves are even more short-ranged between layers, sometimes with correlation lengths smaller than a single unit cell. When these density waves are strongest, typically around $x = 1/8$, superconductivity is suppressed, giving rise to what is known as the 1/8th-anomaly. Then, as one nears optimal doping, the normal state becomes a highly anomalous strange metal, with many signatures pointing to the absence of a well-defined Fermi surface and quasiparticles. At high enough dopings on the overdoped side, one eventually enters a regime where some signatures of a well-defined Fermi liquid reappear.

Some cuprate phase diagrams show a putative quantum critical point (QCP) somewhere beneath the superconducting dome between $x = 0.16$ and $x = 0.20$. Experimentally, evidence for a quantum critical point in the cuprates is quite mixed, especially when compared to heavy fermion systems where they are well established [93, 94, 95]. In particular, there is no well-defined order parameter to associate with a quantum critical point, much less 

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one that has a diverging correlation length in the critical regime. Thus, the experimental status of quantum criticality in the cuprates remains unclear, with some rather convincing thermodynamic evidence in support of a QCP [96], but also spectroscopic evidence that the critical point is actually a first-order transition phase boundary instead [97].

Overall, a key challenge of the cuprates is that the strange metal normal state at optimal doping seems to preclude any meaningful description in terms of quasiparticles and Fermi liquid theory, presumably because of strong correlations of an unknown type. The apparently non-Fermi liquid character of the strange metal is highly problematic, as one can no longer write down a pairing wavefunction as in BCS theory to address when and why the strange metal becomes superconducting. Some of the anomalous scaling properties in the strange metal regime include T-linear resistivity [45], lack of saturation at the Mott-Ioffe-Regel (MIR) bound [23, 36], approximately $\omega^{-2/3}$ scaling of optical conductivity [13, 69], $\omega/T$ scaling of the electronic Raman susceptibility [160], violation of Kohler’s rule for magnetoresistance [161], T-linear scaling of the NMR relaxation rate $T_1^{-1}$ on the copper sites [162], and, probably most direct of all, ill-defined quasiparticles peaks in ARPES with inverse lifetimes that scale linearly with temperature [163].

With this long list of anomalous strange metal properties, one may question whether doing any further experiments will have anything particularly useful to add. Indeed, instead of adding one more item to this long laundry list of strange metal oddities, let us take a step back and ask a more basic question: what is so unique about electron-electron interactions in the strange metal that gives rise to its behavior in the first place? More specifically, can we quantify what is so strongly correlated about charge in the strange metal that differentiates it from the Fermi liquid?

The right quantity to measure to address these questions is the dynamic charge susceptibility $\chi''(q, \omega)$, as it directly quantifies the charge correlations and effective interaction between electrons in a solid. What we expect to see, then, is that the structure of $\chi''(q, \omega)$
for the strange metal is fundamentally different than that of the Fermi liquid discussed in Chapter 3. In what follows, we will use M-EELS to study the nature of $\chi''(q, \omega)$ in the strange metal regime of $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{Ca}_{1.0}\text{Cu}_2\text{O}_{8+x}$, one of the best characterized cuprates, and track its behavior across the doping-temperature phase diagram.

### 6.2 Sample preparation and experimental design

Samples of $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{Ca}_{1.0}\text{Cu}_2\text{O}_{8+x}$ at four different doping levels were grown by Ruidan Zhong, John Schneeloch, and Genda Gu at Brookhaven National Laboratory for M-EELS experiments using a Floating-Zone growth method [164]. In particular, these dopings are heavily underdoped with $T_c = 50$K (UD50K), moderately underdoped with $T_c = 70$K (UD70K), optimally doped with $T_c = 91$K (OP91K), and heavily overdoped with $T_c = 50$K (OD50K). Transition temperatures were verified by measuring the AC/DC magnetization as a function of temperature to look for the onset of the Meissner effect. It is not straightforward to verify the actual hole dopings of Bi-2212 [165], but we estimate the dopings to be approximately $x = 0.08, 0.10, 0.16,$ and 0.23 respectively.

Throughout this chapter we will use Miller indices to denote the momentum transfer of the M-EELS response using reciprocal lattice units (r.l.u.) where $1$ r.l.u. $= \frac{2\pi}{a}$ and $a = 3.81\text{Å}$ is the lattice spacing of Bi-2212 in the tetragonal unit cell. In this convention, the superlattice reflections of Bi-2212 appear along the $(1,1)$ direction, and the Brillouin zone boundary is at $q = 0.5$ r.l.u. $= \pi/a$. To avoid contributions from the superlattice, measurements along the antinode are exclusively measured along $(1,-1)$ instead. The spectra shown in this chapter were taken with a direct beam energy resolution of about 4 meV, 170 pA of beam current, and a momentum resolution of 0.02 to 0.03 Å$^{-1}$. To improve signal statistics, energy scans were binned into 30 meV groups$^2$.

$^2$It should be noted that these measurements in this chapter predate the introduction of the phase-space tuning method introduced in chapter 5, but because of the large energy regime of interest (100 meV to 2000 meV) effects of beam aberrations are not important.
Figure 6.2: **Bi-2212 M-EELS sample preparation.** (a) Cleaved single crystal of OP91K Bi-2212 mounted for a M-EELS measurement. The orientation of the sample is done in-situ by measuring the Bragg reflections with M-EELS at zero energy loss. (b) Electron diffraction image of Bi-2212 showing the superlattice reflections along the diagonal (1,1) direction. (c) Fermi surface of Bi-2212 including the superlattice replica bands. The (1,1) direction lies along the superlattice, (1,0) lies along the copper-oxygen bond direction, and (1,-1) lies perpendicular to the superlattice. In the measurements presented here, we focus mainly on the nodal (1,-1) direction, with some data presented along the anti-node (1,0). (d) Distorted copper oxide plane in Bi-2212 showing the superlattice along the diagonal.
The M-EELS spectra generally can be divided into two regimes, the low-energy ($\omega < 100$ meV) region which is mostly dominated by optical phonons, and energy regime from 100 meV to 2000 meV where the collective charge dynamics are located. Example spectra in these two regimes are shown in Figure 6.3. Measurements of the low-energy spectra as a function of momentum did not reveal clear evidence for excitations besides optical phonons within the experimental resolution (see Appendix C). As such, we turn our focus to the electronic excitations relevant to the charge dynamics of the strange metal in the energy region between 100 meV to 2000 meV.

To obtain $\chi''(q,\omega)$ from the experimental M-EELS data, one first divides the matrix elements of equation 4.70 from the raw M-EELS spectrum. Then, $\chi''(q,\omega)$ is put in absolute units of eV$^{-1}$Å$^{-3}$ by applying the partial f-sum rule (see section 4.6.3)

$$\int_0^{2eV} \omega \chi''(q,\omega) d\omega = -\pi N_{\text{eff}} \frac{\hbar^2 q^2}{2m},$$

(6.1)

using an effective carrier density $N_{\text{eff}}$ obtained from the optical loss function at the same temperature and nearest doping level from [116]. For reference, $N_{\text{eff}} = 1.81 \times 10^{-4}$Å$^{-3}$ in the case of OP91K Bi-2212 at 300 K.

In principle, one would like to map the dynamic charge susceptibility as a function of five variables: energy, the two orthogonal in-plane momenta, temperature, and doping. However, surface degradation limits the amount of data that can be collected on a single sample because of the small absolute count rate in the energy window of interest (3-30 Hz). Accordingly, measurements for each doping are taken in two distinct ways: energy scans at 4-7 momenta at two temperatures, and energy scans at two momenta for 5-6 temperatures.
Figure 6.3: **Energy regimes of M-EELS on Bi-2212.** (a) a raw M-EELS spectrum on Bi-2212 at \( q = 0 \) r.l.u. from our previous work [108] in the low energy phonon regime below 150 meV. This energy window is dominated by optical phonons studied previously in Bi-2212 [108, 166]. (b) Raw M-EELS spectrum of Bi-2212 at \( q = 0.16 \) r.l.u. up to 2 eV. (inset) same as (b) but with a zoomed-out vertical scale. Notice the much lower absolute intensity of the charge response in this energy regime, which is 100 times weaker than the quasielastic line.

### 6.3 M-EELS results at optimal doping: fluctuations localized in time and space, not energy and momentum

To characterize the dynamic charge response of the strange metal, we begin by studying the M-EELS response in Bi-2212 at optimal doping and \( T = 300 \) K. As Figure 6.1a shows, this doping and temperature configuration lies at the heart of the strange metal regime.

Before reporting the M-EELS spectra for the strange metal, let us first understand what the charge response of Bi-2212 would look like if it were well-described by a Fermi liquid within the random phase approximation (RPA) (see Chapter 3). By using the tight-binding parameterization of the Fermi surface, one can calculate the RPA polarizability \( \Pi(q, \omega) \) and

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The work presented in this section has been published in [167].
Figure 6.4: Fermi liquid RPA charge response of Bi-2212. Calculated plots by collaborator Jörg Schmalian from reference [167] of the imaginary part of (a) the polarizability $\Pi''(q, \omega)$ and (b) charge response function $\chi''(q, \omega)$ (note the logarithmic vertical scale) for Bi-2212 with $q$ along (1, -1) using a realistic tight-binding band structure within the RPA. Notice that both $\Pi''(q, \omega)$ and $\chi''(q, \omega)$ are strongly momentum dependent. Furthermore, the charge response function is strongly peaked, indicated a well-defined plasmon mode dominates the charge response of a Fermi liquid.

resulting charge response function $\chi(q, \omega)$ according to

$$\Pi(q, \omega) = \sum_k \frac{n_k - n_{k+q}}{\omega - (\epsilon_{k+q} - \epsilon_k) + i\eta}, \tag{6.2}$$

and

$$\chi(q, \omega) = \frac{\Pi(q, \omega)}{\epsilon_\infty - V(q)\Pi(q, \omega)}. \tag{6.3}$$

where $n_k$ is the quasiparticle occupation number of the momentum state $k$, $\epsilon_k$ is the band-structure energy for momentum $k$, and the constant $\epsilon_\infty \approx 4.5$ accounts for the contributions from higher energies due to the presence of other bands [116]. The realistic tight-binding form of the band-structure based on ARPES measurements can be used for $\epsilon_k$ from Table 1 of reference [168]. While the out-of-plane dispersion is much too small for ARPES to measure, the $k_z$ dependence can be obtained by using the layered electron gas Coulomb interaction given in [169].
There are two major messages from the expected Fermi liquid $\Pi''(q, \omega)$ and $\chi''(q, \omega)$ for Bi-2212 shown in Figure 6.4. The first is that the existence of a Fermi surface means that both the polarizability and susceptibility will be strongly momentum-dependent. The reason is simply that the number of allowed particle-hole excitations across a Fermi surface is highly dependent on their momentum, and shrinks to zero as $q \to 0$ purely due to kinematics. More abstractly, the existence of a Fermi surface introduces an emergent length scale through the Fermi momentum ($k_F \approx 0.18$ r.l.u. [168]) and energy scale through the product of the momentum transfer and Fermi velocity ($v_F q \approx 2.8$ eV/r.l.u. [170]). The second message is that the primary feature of the charge response $\chi''(q, \omega)$ is a plasmon collective mode which is sharply defined in energy and disperses as a function of momentum. In other words, charge excitations are good degrees of freedom in a Fermi liquid, as they propagate in space with both well-defined energy and momentum.

With the theoretical Fermi liquid response for optimally-doped Bi-2212 at 300 K in mind, let us now turn to the experimentally obtained M-EELS spectra shown in Figure 6.5a-c. What is striking about the measured M-EELS response in Figure 6.5c is the presence of a featureless continuum of charge fluctuations extending up to 1 eV, rather than a sharply-defined dispersing plasmon expected for a Fermi liquid. This continuum is by no means a weak feature in Bi-2212, as its spectral weight fully saturates the f-sum rule\(^4\). While the magnitude of $\chi''(q, \omega)$ scales as $q^2$, as required to satisfy the f-sum rule, its shape as a function of energy is momentum-independent for about 90% of the Brillouin zone ($q \gtrsim 0.15$ r.l.u.)\(^5\). Thus, we have that the dynamic charge response of the strange metal is a separable function of momentum and energy $\chi''(q, \omega) = f(q)g(\omega)$ for a large range of parameter space (see Figure 6.6). In particular, we have $f(q) = q^2$, and $g(\omega) \approx \text{const.}$ for $\omega \lesssim 1$ eV and $g(\omega) \propto \omega^{-2}$ for $\omega \gtrsim 1$ eV.

That the continuum is virtually energy and momentum-independent over 90% of the

\(^4\)In comparison, optical phonons and other excitations below 0.1 eV comprise less than 1% of the f-sum rule spectral weight.

\(^5\)We will leave a discussion the low-momentum region for section 6.5
Figure 6.5: Strange metal continuum in optimally doped Bi-2212. (a) The Fermi surface of Bi-2212 showing the possible electron-hole transitions that would contribute to the Fermi liquid charge response (image credit: Matteo Mitrano). (b) Plot of the expected charge response of Bi-2212 if it were a good Fermi liquid from [167]. (c) The measured M-EELS charge response function as a function of energy and momentum in Bi-2212. Notice that the spectra are dominated by a broad, nearly flat, continuum of fluctuations extending up to about 1 eV that is momentum independent above 0.1 r.l.u. Thus, unlike the Fermi liquid, the charge response of the strange metal is essentially featureless in both energy and momentum.
Figure 6.6: *Energy and momentum map of the strange metal continuum in Bi-2212*. For energies below about 1 eV, the charge response is constant as a function of energy and scales with momentum as $q^2$. Above 1 eV, the response decays approximately as $\omega^{-2}$. In both regimes one should notice that the charge response function factors into a function of energy times a function of momentum. For low momenta (hatched region), the response deviates from this separable form, which is expected and will be discussed in section 6.5.
Brillouin zone (apart from a trivial $q^2$ scaling), makes it the polar opposite of the well-defined dispersing plasmon expected of a Fermi liquid in Figure 6.4c. Several conclusions can be made here. First, the separable nature of the charge response is essentially a decoupling of momentum and energy, implying that the emergent length and energy scales associated with a Fermi surface play no role in shaping the strange metal charge fluctuations (i.e. particle-hole excitations of a Fermi surface cannot give rise to the observed strange metal continuum). 

**Said differently, strange metal charge fluctuations are localized in space, rather than in momentum as in the Fermi liquid.**

A second observation can be made by recalling that $\chi''(q,\omega)$ represents both charge fluctuations and charge correlations due to the fluctuation-dissipation theorem. For a Fermi liquid, the existence of a plasmon that is sharp in energy signifies that charge is only strongly-correlated on energy scales comparable to the plasma frequency $\omega_p$, while for $\omega \ll \omega_p$ they are screened and uncorrelated. On the other hand, the flat energy dependence of the strange metal continuum implies that charge carriers are as correlated at low energies as they are at the plasma frequency. In other words, the featureless nature of the strange metal response in energy implies that charge fluctuations are localized in time, unlike the Fermi liquid where they are localized in energy.

We now have a consistent picture of why Fermi liquid theory may break down in the strange metal due to strong correlations. In the Landau-Silin approach to charged Fermi liquids, it was necessary for some screening mechanism to push the singular part of the Coulomb interaction in the Landau function to high energy scales so that it can be treated separately, or even ignored (see Chapter 3). With the strong, singular part of electron-electron interactions out of the way, one can proceed by treating the system as a neutral Fermi liquid. On the other hand, in the strange metal, we do not have such a separation of energy scales because charge correlations are not limited to a sharply peaked region around $\omega_p$. We can therefore conclude that a core assumption for the applicability of the Landau-Silin theory of the Fermi liquid (at least within the RPA) is invalidated in the strange metal.
Let us now summarize what the M-EELS results in optimally doped Bi-2212 have shown by providing an explicit answer to question #1 posed in Chapter 1 and section 3.2.5:

**Question #1:** What is so strongly correlated about charge in the strange metal that distinguishes it from the Fermi liquid?

**Our Answer:** Charge correlations in the strange metal are manifested as a featureless continuum of fluctuations extending up to the plasma frequency and over 90% of the Brillouin zone. In the Fourier domain, charge correlations in the strange metal are therefore localized in time and space, rather than energy and momentum as in the Fermi liquid. The flat energy dependence of the strange metal means that charge carriers are as strongly correlated at low-energies as they are up at the plasma frequency. In comparison, charge in the Fermi liquid is only strongly-correlated in a very small window around the plasma frequency, leaving low-energy charge fluctuations screened and weakly-correlated.

### 6.3.1 Connections to the Marginal Fermi liquid

While the strange metal continuum cannot be produced by quasiparticles of a Fermi surface, it can certainly act as a decay channel for any quasiparticles that do exist. In fact, the energy- and momentum-independent nature of the strange metal continuum bears a resemblance to the postulated Marginal Fermi liquid (MFL) response [88] discussed in Chapter 2. Within the MFL hypothesis, one postulates a momentum- and energy-independent form for the dissipative part of the polarizability $\Pi''(q,\omega)$ except for energies below the thermal energy $k_B T$ where the response goes as $\Pi'' \sim \omega/k_B T$. We see that the measured charge response $\chi''$ does show the characteristic momentum- and energy-independence postulated by the MFL hypothesis. Crucially however, phonon contributions obscure the study of the low-energy $\omega/T$ scaling that is thought to be responsible for T-linear resistivity, so future studies are needed to disentangle the strange metal continuum at low energies from lattice excitations. Nonetheless, the MFL hypothesis of a flat charge response in energy and momentum qualitatively agrees with the M-EELS spectra shown in Figure 6.5c.
6.3.2 Isotropic strange metal continuum within the copper-oxide plane

It is worth discussing the possibility for anisotropy in the strange metal continuum. ARPES measurements show the Fermi surface of Bi-2212 is nearly absent along the nodal (1,0) direction, but has Fermi arcs along (1,-1) (see Figure 6.1b and [4]). Furthermore, the d-wave nature of the superconducting gap and the atomic orbitals themselves are also strongly anisotropic.

The M-EELS spectra on Bi-2212 in in Figure 6.5c was taken along the anti-nodal (1,-1) direction, so it is worth exploring the possibility of whether the response is quite different along the nodal direction (1,0). To test this, we measured M-EELS spectra along the (1,0) direction and compare them to those along (1,-1) at the same value of $q = |q|$ in Figure 6.7 at both 300 K and 23 K. What we find is that the response along the two directions is very similar when $q \geq 0.16$ r.l.u., confirming that the strange metal continuum is independent of both the magnitude and direction of momentum for about 90% of the Brillouin zone. Nonetheless, there are some differences between the M-EELS spectra for the two directions for $q < 0.16$ r.l.u., which suggests that while the strange metal response is local in space, it may retain some of the rotational symmetry of the underlying electrons and/or lattice.

6.3.3 Comparison between transmission and reflection EELS

Given that the M-EELS results shown here are obtained in the reflection geometry, surface and bulk excitations may both contribute to the measured spectra. It is important, then, to verify that the strange metal continuum discussed in the previous sections is a property of the bulk, rather than a surface effect. The most natural way to verify the bulk nature of the continuum is to perform the same measurement in Figure 6.5c but with transmission EELS. Such transmission EELS measurements were carried out on Bi-2212 over 30 years ago [171, 172], but had very poor energy resolution (500 - 1000 meV) and utilized various
Figure 6.7: **Nodal and anti-nodal strange metal response in Bi-2212.** (a) Cartoon showing the nodal (1,0) and anti-nodal (1,-1) directions in Bi-2212 relative to the Fermi surface. (b) Comparison of the charge response along the (gray) nodal (1,0) and (red) anti-nodal (1,-1) directions in OP91K Bi-2212 at 295 K and 23 K. The strange metal continuum is largely isotropic except for $q < 0.16$ r.l.u. where a sharper resonance is observed along the (1,0) direction compared to (1,-1). One concludes, therefore, that the strange metal response is largely isotropic in the ab-plane.
peak subtraction routines in an attempt to study the spectra below 2 eV. Moreover, these transmission EELS results are seemingly contradicted by later measurements that have improved energy resolution and do not utilize peak subtraction methods [173, 174]. To remedy this situation, we performed our own transmission EELS measurement on Bi-2212 using a modern Nion Scanning Transmission Electron Microscope (STEM-EELS) with much better energy resolution (≈7-10 meV) so that no peak subtraction is necessary. These STEM-EELS measurements were done in collaboration with Katia Marche and Christian Dwyer at Arizona State University (ASU).

The STEM-EELS instrument at ASU was tuned for 10 meV energy resolution at an incident electron energy of 60 keV. Samples of Bi-2212 for STEM-EELS were prepared by simply crushing a crystal of OP91K Bi-2212 in a mortar and pestle, and then dispersing the resulting crystallites onto a holey carbon TEM grid with ethanol. The adjustable beam spot size in STEM-EELS (0.1 to > 40 nm) allows one to simply hunt for a crystallite of Bi-2212 with the right orientation and high degree of crystallinity. Upon finding such a crystallite, an EELS spectrum was taken to compare with M-EELS, as shown in Figure 6.8. To remove the Bose factor, Figure 6.8 also shows the result of the STEM-EELS measurement after antisymmetrizing, in addition to the raw STEM-EELS spectrum. Figure 6.8 clearly shows that the strange metal continuum observed with reflection M-EELS is visible with a nearly identical shape in transmission STEM-EELS, thus confirming the bulk nature of these charge fluctuations. This agreement is remarkable, as the transmission STEM-EELS measurement uses electrons at a thousand times higher beam energy and probes a sample volume ≈10⁻⁹ times smaller than that of M-EELS.

It should be noted that the STEM-EELS instruments are designed to be performed in a converging-beam geometry (i.e. high spatial-resolution rather than momentum-resolution), with a convergence angle of 4 mrad in our case. Thus, the STEM-EELS measurements essentially integrate over the entire first Brillouin zone of Bi-2212 up to \( q \lesssim 0.63 \) r.l.u. This is not a serious problem however, as the M-EELS results show that the continuum
6.4 Fate of the strange metal continuum with doping and temperature

With a characterization of optimally doped Bi-2212 deep in the strange metal regime in hand, we turn now to understanding how the dynamic charge susceptibility changes as one leaves the strange metal regime with both doping and temperature. In other words, we will map the phase diagram of charge fluctuations in Bi-2212. Recalling the phase diagram in...
Figure 6.1, we roughly expect the strange metal continuum seen in Figure 6.5c to persist within a fan-like region centered around optimal doping. In the limit of large doping and low temperature, we expect some restoration of Fermi liquid behavior, while on the underdoped side we expect highly incoherent charge dynamics. Mapping out this phase diagram is not only useful for understanding how the strange metal arises in the context of its nearby phases, but is also a powerful method for determining which aspects the continuum of section 6.3 are solely properties of the strange metal regime. Work presented in this section has been published in [175].

To map out the strange metal phase diagram, we study four dopings described in section 6.2: UD50K, UD70K, OP91K, and OD50K. These samples formed the largest range of stable dopings available at the time of the experiment. For each doping, we measure the momentum-dependence for four momenta at 300 K and 100 K (or 115 K for OD50K) and the temperature-dependence at two momenta for 5-6 temperatures between 30 K and 300 K. For reference, these dopings and temperatures are shown in Figure 6.9. To normalize the spectra, we again apply the f-sum rule, but, rather than a fixed value of $N_{\text{eff}}$, we determine $N_{\text{eff}}$ from the optical loss function at the closest doping and temperature to the M-EELS data (i.e. $N_{\text{eff}} \rightarrow N_{\text{eff}}(x,T)$) from [116].

Before presenting the M-EELS measurements of $\chi''(q,\omega)$ throughout the phase diagram of Bi-2212, let us first consider how a Fermi liquid responds to changes in temperature and doping. The role of temperature in a Fermi liquid’s charge response is trivial, as temperature only enters by changing the occupation number of quasiparticles through the Fermi-Dirac distribution (see equation 3.12). Since the thermal energy $k_B T$ is much smaller than the Fermi energy $E_F$, all changes to the Fermi liquid’s charge response due to temperature are minute and at most give rise to tiny shifts in the plasma frequency $\omega'_p = \omega_p + k_B T$. On the other hand, doping causes more significant changes to the Fermi liquid charge response because the carrier density is changed by $N \rightarrow N + x$. This change in carrier density means that the plasma frequency $\omega_p \propto \sqrt{N}$ will increase in energy as the square root of the doping.
\( \omega'_p = \omega_p \sqrt{1 + x/N} \). In the case of Bi-2212, we would then expect the plasma frequency from UD50K to OD50K (or \( x = 0.08 \) to \( x = 0.23 \)) to increase by a factor of approximately 1.7. To summarize then, the effects of temperature and doping in a Fermi liquid are independent from each other, with temperature causing very small changes to the plasmon energy on the order of the thermal energy \( k_B T \), while doping rigidly shifts the plasma frequency to higher energy due to the change in carrier density.

Let us now turn to the momentum-dependence of \( \chi''(q, \omega) \) for the four dopings studied at room temperature (300 K) in Figure 6.10a-d. Surprisingly, the spectra for all dopings at 300 K are nearly identical as a function of momentum and energy. Thus, the featureless strange metal continuum of section 6.3 persists in the same form for all dopings studied. This behavior is at odds with what one expects from a Fermi liquid, as we are introducing 3x more carriers going from UD50K to OD50K, and yet the energy-dependence of the charge response remains unchanged. In fact, this observation agrees with the largely doping-independent plasma frequency reported in optical measurements[116].

At low temperature (100 K for UD50K, UD70K, OP91K and 115 K for OD50K), the situ-
ation changes completely. As shown in Figure 6.10, the energy-dependence becomes strongly doping-dependent, with an enhancement of spectral weight below \( \sim 0.5 \) eV when underdoped, no change at optimal doping, and a suppression of spectral weight below \( \sim 0.5 \) eV in the overdoped regime. It is remarkable here that the energy scale of this spectral weight change is much larger than the thermal energy \( k_B T \approx 0.01 \) eV, which is at odds with the Fermi liquid expectation. In contrast to the energy-dependence however, the momentum-independence of \( \chi''(q, \omega) \) remains unchanged, implying that the charge response is still localized in space.

### 6.4.1 Spectral weight transfer and the Coulomb energy

To build a more complete understanding of the spectral weight change shown in Figure 6.10, we performed a finer temperature-dependence at two fixed momenta \( q = 0.12 \) and 0.24 r.l.u. For simplicity we focus here just on \( q = 0.24 \) r.l.u., although \( q = 0.12 \) r.l.u. shows similar behavior (see Appendix C and Figure C.3). The resulting spectra are shown in Figure 6.11. These measurements now provide a more precise understanding of the spectral weight redistribution shown in Figure 6.10. Underdoped samples exhibit a rapid increase in spectral weight below 0.5 eV (roughly 30% change in intensity) at low temperatures. Overdoped samples show the opposite behavior, exhibiting a more gradual *suppression* of spectral weight below 0.5 eV with a nearly 50% change in intensity. Optimal doping sits in between these two regimes with no significant change in spectral weight down to 23 K.
Figure 6.10: **Doping and momentum dependence of the strange metal charge response.** Each panel plots the charge response function $\chi''(q, \omega)$ at a fixed momentum for the four dopings studied. (a-d) Charge response function at four momenta at room temperature (300 K) for the four dopings studied. Despite their differing nominal carrier concentration, the spectra all exhibit the same featureless continuum (e-h) Charge response at low temperature (LT) for the same momenta as (a-d). LT corresponds to 115 K for OD50K and 100 K for UD50K, UD70K, and OP91K. Unlike the response at 300 K, the spectra are now strongly doping dependent, with large spectral weight changes up to 0.5 eV. In particular, spectral weight is enhanced for UD50K and UD70K, suppressed for OD50K, and unchanged for OP91K. Nonetheless, there is little momentum dependence at both temperatures for any doping, suggesting charge fluctuations are local across the entire phase diagram of Bi-2212.
Figure 6.11: Temperature- and doping-dependent spectral weight transfer in the charge response of Bi-2212. (a-d) Temperature dependence of the charge response at \( q^* = 0.24 \) r.l.u. Note the use of a logarithmic x-axis scale to emphasize the low-energy region. At 300 K the spectra are similar among all dopings, but they exhibit very different behavior as temperature is lowered, UD50K (c) and UD70K (d) exhibit an enhancement of spectral weight at low temperature, OP91K (c) stays the same, and OD50K (d) exhibits a suppression of spectral weight. (e) Integrated spectral weight \( \xi \) of the charge response between 0.1 and 0.5 eV relative to the spectral weight of OP91K at 150 K of \( 12.94 \times 10^{-5} \) Å\(^{-3} \). The trends in the spectral weight with doping and temperature confirm our observation of enhanced weight on the underdoped side, suppressed weight when overdoped, and little to no spectral weight change at optimal doping.
We can now provide a quantitative measure of the spectral weight change $\xi$ by integrating the charge response between 0.1 and 0.5 eV. For reference, let us take OP91K at 150 K to be our baseline spectral weight. Then, we can define the (relative) spectral weight change $\xi(x, T)$ as

$$
\xi(x, T) = -\int_{0.1 \text{ eV}}^{0.5 \text{ eV}} [\chi''(q^*, \omega) - \chi''_{\text{ref.}}(q^*, \omega)] \, d\omega,
$$

(6.4)

where $q^* = 0.24 \text{ r.l.u.}$ and $\chi''_{\text{ref.}}(q^*, \omega)$ is the charge response for OP91K at 150 K. The quantity $\xi(x, T)$ measures the degree the M-EELS spectra deviate from the flat energy response at optimal doping which itself has an integrated weight of $12.94 \times 10^{-5} \text{ Å}^{-3}$. More physically, $\xi(x, T)$ is proportional to the change in Coulomb energy. The relationship to the Coulomb energy can be seen by considering the expectation value of the Coulomb energy for an arbitrary system\(^6\)

$$
\langle V_{\text{Coul.}} \rangle = \frac{1}{2\pi} \int dq \int d\omega \frac{4\pi e^2}{q^2} \langle \rho^\dagger(q, \omega) \rho(q, 0) \rangle
$$

(6.5)

$$
\propto -\int dq \int d\omega \frac{4\pi e^2}{q^2} \chi''(q, \omega). \quad (6.6)
$$

Thus, the differential Coulomb energy is proportional to the charge response function $\chi''(q, \omega)$

$$
\langle V(q, \omega) \rangle \propto -\frac{4\pi e^2}{q^2} \chi''(q, \omega).
$$

(6.7)

Returning to $\xi(x, T)$, a plot of this relative spectral weight change for all dopings and temperatures in shown in Figure 6.11. Confirming our previous observations, $\xi(x, T)$ clearly shows the enhancement of spectral weight (or Coulomb energy) in the underdoped regime, suppression of weight when overdoped, and a sign-reversal with no change as a function of

\(^6\)It is worth noting that, because of the virial theorem, $\langle V_{\text{Coul.}} \rangle = -2\langle \text{Kin. Energy} \rangle$. Then the total energy of a system $\langle U \rangle = \langle V_{\text{Coul.}} \rangle + \langle \text{Kin. Energy} \rangle$ is simply given by $\langle U \rangle = \frac{1}{2}\langle V_{\text{Coul.}} \rangle$. Thus, the quantity $\langle V_{\text{Coul.}} \rangle$ also represents the total energy of a system.
temperature at optimal doping.

One may wonder if the observed changes in Coulomb energy are related to the superconducting condensation energy, especially in light of the “Mid-infrared scenario” put forth in [176]. In this scenario, the energy saving required for superconductivity to occur in the cuprates come from changes in the Coulomb energy $\langle V(q, \omega) \rangle$ in the long-wavelength (i.e. $q \lesssim d^{-1}$ where $d$ is the spacing between layers) and mid-infrared energy regions (0.1 to 2 eV). This hypothesis is based on the observation that the superconducting transition temperature in a number cuprate families increases with the number of CuO$_2$ layers per unit cell and that most of the spectral weight in $\langle V(q, \omega) \rangle$ appears to be between $\sim 0.1$ and 2 eV. The essential logic here is that it is energetically favorable for the system to become a superconductor to facilitate better screening of charge carriers between different CuO$_2$ layers.\footnote{Note that this is the exact opposite perspective of approaches that seek out superconductivity from the Hubbard model which only retains short-ranged Coulomb interactions. If those approaches are correct, one would instead expect changes to $\langle V(q, \omega) \rangle$ at much larger momenta (e.g. comparable to the Cu-O-Cu bond distance, or perhaps the size of the $d_{x^2-y^2}$ orbital itself).}

While the M-EELS spectral weight shown in Figure 6.11 clearly do not have the $\sim 0.1$% level accuracy needed to make concrete statements on the condensation energy, they do exhibit parallel trends to ellipsometry results in [116] which probe the charge response at $q = 0$. In [116], the difference in the optically-determined Coulomb energy between the normal and superconducting state goes from negative on the overdoped side, through zero at optimal doping, and then becomes positive in the underdoped region. This trend qualitatively matches trends in $\xi(x, T)$ in Figure 6.11, but the M-EELS spectral weight change is orders of magnitude larger and occurs even above the superconducting transition. Moreover, the fact that the M-EELS spectral weight occurs over a broad range of momenta means that energetic changes within an individual CuO$_2$ plane also plays an important role. Future M-EELS studies with more efficient detection schemes are clearly needed to address the...
mid-infrared scenario\textsuperscript{8,9}.

6.4.2 A new phase diagram of the strange metal based on the charge susceptibility

We are now in a position to use the relative spectral weight change $\xi(x, T)$ of Figure 6.11e to construct a new phase diagram of the strange metal in Bi-2212 which is based on the dynamic charge response $\chi''(q, \omega)$. Figure 6.12 shows this phase diagram, and what we see is that the charge response is flat in energy within a fan-like region centered at optimal doping where the strange metal is thought to reside \cite{36}. Thus, we can confirm that the momentum-independent continuum seen originally in section 6.3 is part of the general phenomenology of the strange metal. This fan-like region itself resides between two regimes with opposing charge dynamics, with the underdoped side on one hand expressing enhanced charge fluctuations and the overdoped regime showing a strongly-suppressed charge response instead.

We now summarize our key observations:

1. The strange metal is tied to a charge susceptibility which is flat in energy (i.e. fluctuations localized in time), confirming the conclusions of section 6.3.

2. Upon leaving the strange metal regime, a dramatic redistribution of low-energy spectral weight occurs (up to at least 0.5 eV in Bi-2212), resulting in charge response that is no

\textsuperscript{8}It should be mentioned that analogous scattering measurements of the condensation energy for ordinary BCS superconductors have actually never been performed either. According to the very general arguments in \cite{177}, the condensation energy in BCS theory comes from a decrease in kinetic energy of the nuclei (not electrons!). In principle, this prediction could be tested by measuring changes in the nuclear form factor with ordinary neutron diffraction across $T_c$. The most promising system is likely elemental Niobium due to its simple BCC crystal structure, lack of optical phonons, relatively high $T_c$, and low incoherent cross section. I invite readers of this thesis to try and perform this experiment.

\textsuperscript{9}Another promising method to test the mid-infrared scenario is by engineering the dielectric environment between the CuO$_2$ layers. This seems to be possible in light of the recent discovery of superconductivity in a half-unit-cell thick film of Bi-2212 \cite{178}. An experiment where different substrates and film thicknesses are used may serve as a novel test of the mid-infrared scenario.
Figure 6.12: **Strange metal phase diagram in Bi-2212 based on the charge susceptibility.** Phase diagram constructed using the relative spectral weight $\xi(x, T)$ described in the main text from [175]. Here the color of each point indicates the value of $\xi$. The green, fan-like region schematically shows the portion of the phase diagram where $\xi \approx 0$ and the charge response most resembles the flat strange metal continuum observed at optimal doping. The phase diagram clearly shows three regions, the underdoped regime with larger spectral weight, the overdoped regime with suppressed spectral weight, and the strange metal regime above optimal doping that resides in between the two.
longer flat in energy. The sign of this spectral weight change depends on the direction in doping the strange metal regime is exited.

3. Having a momentum-independent (i.e. local) charge response is not unique to the strange metal regime. In the case of Bi-2212, a local response is observed across the entire phase diagram under study.

As we have already discussed the implications of the first observation in section 6.3, let us focus now on the second observation of spectral weight transfer across the strange metal phase diagram. Noting that the charge response \( \chi''(\mathbf{q}, \omega) \) directly contributes to the quasiparticle self-energy \( \Sigma''(\mathbf{k}, \omega) \) \([14, 108]\), the observed charge response and its spectral weight changes provide a very natural explanation for the observed quasiparticle lifetime. According to ARPES measurements \([4, 41]\), quasiparticle lifetimes are shortest in the underdoped region of the phase diagram at low temperature (but above \( T_c \)), which is precisely where \( \chi''(\mathbf{q}, \omega) \) exhibits enhanced spectral weight at low-energies (Figure 6.11a-b). In contrast, the quasiparticle lifetime is much longer in the overdoped regime at low temperatures, in line with the suppression of spectral weight in this region of the phase diagram. The strange metal region sits in between these two opposing regimes, with quasiparticle lifetimes exhibiting marginal scaling \([179]\) in agreement with the flat energy-dependence of \( \chi''(\mathbf{q}, \omega) \), as discussed in section 6.3.1.

The asymmetric temperature dependence of the spectral weight change also suggests a possible connection to the pseudogap. While the overdoped spectral weight in in Figure 6.11e appears to be steadily suppressed, the underdoped charge response exhibits a sudden enhancement of spectral weight at rather high temperatures (between 150-200 K for UD70K and 200-300 K for UD50K). This large temperature scale suggests the spectral weight enhancement may be related to the appearance of the pseudogap in the underdoped regime, which forms at similar temperature scales. This relationship can be tested in future experiments by looking for emergent anisotropy in the spectral weight enhancement, as the
The pseudogap is known to have d-wave symmetry.

Moving on to the third observation, the lack of momentum-dependence across the entire phase diagram means that the charge response is not generated by quasiparticles for any doping or temperature, at least within the RPA. If one insists on using quasiparticles to generate this continuum, then the origin of the momentum-independent charge response arises from contributions to the polarizability that go beyond the RPA (e.g., exchange, local field, and vertex correction effects). However, it is unclear what types of beyond-RPA effects are most important and how they can result in a momentum-independent charge response over a broad range of doping and temperature without fine-tuning. For example, it is certainly possible that if the band structure is fine-tuned, one may produce momentum-independent interband transitions in $\chi''(q,\omega)$. However, one would then need to explain why these bands are both temperature and doping dependent, along with why no such bands have been predicted from calculations or experimentally observed in Bi-2212 [180]. Alternatively, one may associate the charge response with the incoherent portion of the single particle spectral function rather than the coherent quasiparticles, as the incoherent weight dominates over the coherent quasiparticle weight $Z$ even in the overdoped regime [179]. Should this viewpoint be valid, it may be possible for one to obtain the observed $\chi''(q,\omega)$ by computing it within the RPA using the full fermion Green function $G(k,\omega)$ rather than just the coherent quasiparticle portion.

A more conceptually appealing explanation for the momentum-independent charge response is the presence of extreme disorder which breaks translation-symmetry so completely that $q$ simply becomes a bad quantum number. There are two problems with this interpretation. The first is that both ARPES and spectroscopic-STM observe dispersing quasiparticles in Bi-2212 with a Fermi surface in the same regions of the phase diagram where the charge response is momentum-independent, indicating that the system is still ordered. The second problem is that dispersing, momentum-dependent charge excitations have been observed in other transition metal oxide and dichalcogenide systems with similar degrees of disorder.
as well as in completely amorphous systems [27, 181, 182, 183, 184]. Thus, it is unlikely that structural disorder is the sole reason for the momentum-independent charge response. On the other hand, it is possible that some kind of emergent electronic disorder due to strong interactions could influence the charge response in a fundamentally different way that makes momentum irrelevant only in two-particle response functions, as suggested in [185].

Perhaps the most exotic explanation for the momentum-independent and separable form of $\chi''(q,\omega)$ is quantum criticality. Near the quantum critical point, the correlation lengths in time and space (or energy and momentum) are related by a critical exponent $z$ such that $\xi_{\text{time}} \sim \xi_{\text{space}}^z$ or $\omega \sim q^{-z}$. When $z = \infty$, space and time are decoupled and one obtains momentum-independent response functions. This scenario is known as local quantum criticality, and has been proposed to be the origin of the strange metal regime in the cuprates [186, 187]. The key problem with this interpretation is that the momentum-independence observed here with M-EELS extends beyond the strange metal regime (i.e. it extends beyond the purported quantum critical “fan” [91]) and instead holds across the full phase diagram. Moreover, there is no sign of a soft collective mode that becomes gapless at some critical doping, though it is possible that the relevant soft mode does not have charge character and so is invisible to M-EELS. Future M-EELS studies performed close to the proposed critical doping of $x \approx 0.19$ [96] are needed to address the role of quantum criticality in the charge response.

Let us now end this section by providing an explicit answer to the second question posed about the strange metal in Chapter 1 and section 3.2.5.

**Question #2:** How do the strong charge correlations of the strange metal evolve as one leaves the phase (e.g., through doping and temperature)?

**Our Answer:** The primary effect of leaving the strange metal regime with doping and temperature is a large redistribution of low-energy spectral weight (up to 0.5 eV in the case of Bi-2212). The sign of this spectral weight change depends on how one exits the
strange metal regime. If one exits towards a more Fermi liquid-like regime, a suppression of spectral weight is observed. On the other hand, if one exits towards an even more incoherent metal, spectral weight enhancement is observed. If one does not change doping at all but simply lowers the temperature of the strange metal, no significant change in spectral weight occurs on the energy scales probed here. These large spectral weight changes should be compared to a good Fermi liquid where the effects of temperature and doping are decoupled, with temperature playing an insignificant role and doping only acting to rigidly move the plasma frequency. Finally, in the case of Bi-2212, the momentum-independence of the charge response in the strange metal regime remains true regardless of doping and temperature.

A cartoon summary contrasting the strange metal and Fermi liquid is shown in Figure 6.13. We conclude that the charge fluctuations of the strange metal are localized in time and space, not energy and momentum as in the Fermi liquid (Figure 6.13a-b), and that the effects of doping and temperature are to add or remove low-energy spectral weight rather than rigidly shift the plasma frequency (Figure 6.13c-d).

### 6.5 The long-wavelength regime and the connection to optics

In this section we will discuss the deviation of the strange metal charge response from its featureless form as one approaches the long wavelength limit \((q \to 0)\) where it eventually must agree with optical measurements. This limit, known as the hydrodynamic regime \([15]\), is of relevance to hydrodynamic theories of the strange metal \([103, 104]\) as well as the mid-infrared scenario for high-temperature superconductivity \([176]\). Unfortunately, it is in precisely this limit of small momentum where our limited theoretical understanding of reflection M-EELS becomes apparent, as the theoretical form for the scattering matrix element diverges, but the physically measured signal stays finite.

To begin, recall that in section 6.3 we saw that the strange metal regime in Bi-2212
Figure 6.13: Cartoon comparison of the Fermi liquid and strange metal charge response. (a) Schematic Fermi liquid collective charge response in real space at a fixed time. The charge response exhibits propagating waves of charge (i.e. plasmons) with well-defined energy and momentum. (b) Same as (a) but for the strange metal. Unlike the Fermi liquid, the charge response of the strange metal is localized in space and quickly decays in time, indicating that its charge fluctuations are broad in both momentum and energy. (c) Impact of doping and temperature on the charge response of a Fermi liquid as a function of energy. Temperature has a negligible impact on the charge response, and doping acts to rigidly shift the plasmon peak in energy. (d) Same as (c) but for the strange metal. Doping and temperature are now deeply intertwined, and their impact is to deplete low-energy spectral weight for high values of doping and low temperatures.
Figure 6.14: Comparison of EELS and Ellipsometry in Bi-2212. Comparison of the (a) EELS charge response in Bi-2212 measured at low momentum $q = (0.05, 0)$ with M-EELS [167] as well as HR-EELS (Schulte) and transmission EELS (Nücker) [171, 188] with that of (b) ellipsometry measurements from [116]. Although both EELS and ellipsometry observe a broad plasmon peak at small momentum, the peak in ellipsometry is much sharper (by about 50%). Because the energy resolution of M-EELS is about 4 meV, this difference in linewidth most likely arises from $q = (0.05, 0)$ not being small enough for EELS and optics to be comparable rather than an issue of limited energy resolution.

exhibits a characteristic continuum of charge fluctuations that are momentum-independent over 90% of the Brillouin zone\textsuperscript{10}. In this regime, the charge susceptibility is a separable function of momentum and energy $\chi''(q, \omega) = q^2 g(\omega)$. However, for $q \lesssim 0.1$ r.l.u., the charge response starts to become momentum-dependent (see Figures 6.6 and 6.7). That the charge response is not a momentum-independent continuum as $q \to 0$ is completely physical, as the longitudinal susceptibility measured with M-EELS must eventually agree with the transverse susceptibility from ellipsometry\textsuperscript{11}, which observe a broad plasmon peak rather than a continuum [116].

Indeed, the spectra in Figure 6.6 and 6.7 show that a broad, peak-like structure develops in the M-EELS spectra below $q = 0.10$ r.l.u., and that this broad peak is sharper along

\textsuperscript{10}Aside from a mandatory $q^2$ prefactor needed to satisfy the f-sum rule.

\textsuperscript{11}The reason the longitudinal and transverse electromagnetic responses of a system must agree as $q \to 0$ is as follows. For sufficiently long wavelengths compared to the system’s size, the charges of the system cannot distinguish between a spatially varying electric field and one that is constant in space. Thus, whether the electric field is longitudinal ($q \times \mathbf{E} = 0$) or transverse ($q \cdot \mathbf{E} = 0$) becomes immaterial, and only the direction of $\mathbf{E}$ matters.
the (1,0) direction compared to (1,-1). The appearance of this broad peak qualitatively agrees with optical measurements from [116] at \( q = 0.05 \) r.l.u., as we show in Figure 6.14. However, despite the high energy-resolution of M-EELS (4 meV), the broad peak seen with M-EELS in Figure 6.14 is about 50% broader than that of ellipsometry. The most plausible reason for this discrepancy is that \( q = 0.05 \) r.l.u. is not small enough for the longitudinal and transverse responses to become equivalent. One would therefore like to understand the behavior of M-EELS down the lowest experimentally accessible momenta to look for agreement with ellipsometry.

At these low momenta, however, a problem occurs in the determination of \( \chi''(\mathbf{q},\omega) \) from the experimental M-EELS data. To understand this problem, first recall the M-EELS matrix element from equation 4.67

\[
|V_{\text{eff}}|^2 = \left| \frac{4\pi e^2}{q^2 + K^2} \right|^2 = \left| \frac{4\pi e^2}{q^2 + (k_{z i} + k_{z f})^2} \right|^2, \tag{6.8}
\]

where \( k_{z i} \) and \( k_{z f} \) are the initial and final momenta of the probe electron along the z-axis perpendicular to the sample surface. This matrix element formally diverges as \( q^{-4} \) at the specular condition, where \( q = 0 \) and \( k_{z i} + k_{z f} = 0 \). The divergent behavior of \( |V_{\text{eff}}|^2 \) is not a problem if the M-EELS intensity is measured by varying energy loss \( \omega \) with both \( q \) and \( k_{z i} + k_{z f} \) kept fixed. When \( q \) and \( k_{z i} + k_{z f} \) are kept fixed, \( |V_{\text{eff}}|^2 \) is simply an overall constant for each M-EELS energy scan and can be divided out. The problem arises at small \( q \), where it is kinematically infeasible to vary \( \omega \) without changing \( q \) and/or \( k_{z i} + k_{z f} \). The reason is simple, a free electron must necessarily lose momentum when it loses energy. So, for a given energy loss, there is a bare minimum momentum transfer of approximately \( Q_{\text{min}} \approx \omega/v \), where \( v \) is the velocity of the probe electron. If one is interested in energy and momenta such that \( v \gg \omega/q \), then the scattering angles can be adjusted so that an energy scan at constant
Figure 6.15: Coulomb matrix element effects at small momentum. (a) Raw M-EELS intensity as a function of momentum along (1,-1) in Bi-2212. Spectra are vertically offset for clarity. (b) The extracted charge response $\chi''(q, \omega)$ from the M-EELS intensity in (a) obtained by dividing out the Coulomb matrix element. Note that for $q < 0.05$ r.l.u. there are now features in $\chi''(q, \omega)$ that are nowhere visible in the raw intensity, thus making these features questionable in nature. For larger momentum ($q > 0.05$ r.l.u.) this matrix element distortion is minimal, and $\chi''(q, \omega)$ more closely resembles the raw M-EELS intensity. (c-d) Same as (a-b) but for Sr$_2$RuO$_4$. It is noteworthy that despite Bi-2212 and Sr$_2$RuO$_4$ being very different materials, they both show similar matrix element effects, indicating the problem goes beyond any one material family.

momentum transfer is possible. But for $\omega/q \sim v$, it is not possible to scan energy without varying momentum and so $V_{\text{eff}}$ effectively becomes energy-dependent. To summarize, the problem with extracting $\chi''(q, \omega)$ from M-EELS at small $q$ (i.e. $q \sim \omega/v$) is that the M-EELS Coulomb matrix element effectively becomes a rapidly-varying function of energy and diverges as $|V_{\text{eff}}|^2 \sim \omega^{-2}$.

Thus, for studying the continuum at around $\omega = 1$ eV with 50 eV electrons, we expect the rapidly varying Coulomb matrix element to be an issue when the momentum transfer is a few times $\omega/v$, or about 0.06 r.l.u.$^{12}$ To complicate matters further, the form of the effective M-EELS Coulomb matrix element is only an approximation (see Chapter 4), so any diverging behavior only amplifies the consequences of our ignorance.

To illustrate the consequences of the diverging matrix element, Figure 6.15 shows a

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$^{12}$On the other hand, if one was only interested in the phonons below 0.1 eV, kinematic constraints only become relevant at momenta smaller than 0.006 r.l.u., which is well beyond the q-resolution of M-EELS.
series of M-EELS spectra taken at low momenta on optimally doped Bi-2212 at fixed out of plane momentum transfer $q_z = k_i^z - k_f^z = 4.10 \ \text{Å}^{-1}$ before and after dividing out the Coulomb matrix element. Near $q \approx 0$, one expects the M-EELS response to resemble the optical loss function, which shows a plasmon peak, but what is observed instead is a largely featureless raw M-EELS spectra, likely due to the diverging behavior of the matrix element as roughly $\omega^{-2}$. However, upon dividing this featureless response by the diverging Coulomb matrix element, a peak-like structure appears in $\chi''(q, \omega)$ that is nowhere apparent in the raw M-EELS data. Because the M-EELS matrix element in reflection is only approximately known, it is therefore unclear how reliable this procedure is. Reassuringly, for larger momenta where $q > \omega/v$ (i.e. $q \gtrsim 0.05 \ \text{r.l.u}$), the effects of the varying Coulomb matrix element are suppressed and no longer causes significant change to the M-EELS spectra.

There are two important steps that need to be taken to establish a connection between reflection M-EELS and optical measurements in the hydrodynamic limit. The first, and most important, is that an improved theory of the reflection M-EELS scattering process is clearly needed to understand how $\chi''(q, \omega)$ should be extracted from the raw data at small momentum transfer. The second is that the actual form of the effective Coulomb matrix element must be experimentally verified. This verification can be done in a material-independent manner by measuring the M-EELS response at fixed $q$ for various combinations of the out-of-plane momentum $k_i^z + k_f^z$, or by comparing the M-EELS response at $+q$ with that of $-q$ at different out-of-plane momenta. We envision that meV- and momentum-resolved transmission EELS at low momenta will also provide a very valuable crosscheck for both of these steps in the near future as soon as transmission M-EELS instruments become available.
6.6 Summary and open future questions

Let us now summarize the main conclusions of this chapter regarding the strange metal and then provide some promising future directions for follow-up research.

We began by aiming to answer the question of what was so strongly correlated about charge in the strange metal compared to the Fermi liquid. By studying the charge correlations in the heart of the strange metal phase of Bi-2212, we saw in section 6.3 that a key signature of the strange metal is a featureless continuum of charge fluctuations up to a cutoff energy of \( \sim 1 \text{ eV} \) that is independent of momentum for 90% of the Brillouin zone apart from an overall \( q^2 \) scaling required to satisfy the f-sum rule. For comparison, an RPA calculation of the Fermi liquid response predicted a sharply-defined, dispersing plasmon. We concluded, therefore, that the strange metal is identified by charge fluctuations localized in time and space, rather than being well-defined in energy and momentum as in the Fermi liquid. Additional measurements verified that this strange metal continuum is a bulk property of Bi-2212 rather than a surface effect.

Then, in section 6.4, we moved on to address how the strong charge correlations in the strange metal regime of Bi-2212 evolve with doping and temperature. Three core observations were made. First, a flat charge response is observed in a fan-like region centered around optimal doping where the strange metal is known to exist from other measurements, thus confirming that a featureless continuum of charge fluctuations is a signature of the strange metal. Second, we observed that, as one leaves the strange metal regime, massive changes in the low-energy spectral weight occur below 0.5 eV, with the sign of the spectral weight change depending on how one exited the strange metal region. In particular, exiting towards the more incoherent metal on the underdoped side resulted in enhanced charge fluctuations below 0.5 eV, while exiting towards the more Fermi liquid-like overdoped side resulted in a suppression of charge fluctuations. The third and final observation was that the momentum-independent nature of the charge response remains intact regardless of doping.
and temperature, which can be interpreted to mean that it is a general materials property of Bi-2212.

While we have broken new ground in the understanding of the strange metal’s charge response, there are several outstanding questions that deserve future study.

1. **Strange metal response at low-energy (0 to 100 meV):** The most important follow-up to the work presented in this thesis would be a closer study of the strange metal response in the low-energy/phonon region between 0 and 100 meV. A key prediction of Marginal Fermi Liquid and quantum critical theories of the strange metal is the existence of $\omega/k_B T$ scaling of the strange metal charge fluctuations. Determining the behavior of the strange metal charge response below 100 meV would therefore be a major step forward for testing the validity of such theories in the cuprates. Distinguishing the strange metal response from the many optical phonons in this energy window is a major challenge, but this hurdle may be overcome by measuring the charge susceptibility across multiple Brillouin zones. Unlike the valence charge fluctuations which are essentially visible only in the first Brillouin zone due their delocalized form factor, phonons are highly local and are easily visible in higher-order Brillouin zones. Thus, it may be possible to isolate the strange metal response by comparing the density response in the first zone $\chi''(q,\omega)$, where valence fluctuations and phonons overlap, with that of higher-order zones $\chi''(q + G,\omega)$ where only phonons are present.

2. **Relationship with charge order:** A second area of future research is an examination of the interplay between the strange metal and charge order, as it is conceivable that the collective modes associated with charge ordering play some role in the strange metal regime. For addressing this question, LSCO or Bi-2201 may be preferable to Bi-2212 due to their much stronger charge order peaks [159].

3. **Comparison with electron-doped cuprates:** Finally, a study of the charge response of electron-doped cuprates, rather than hole-doped, will be highly illuminating, as electron-doped cuprates do not exhibit T-linear resistivity [52], are reported to have Fermi
liquid-like charge collective modes [113], but are still highly anomalous (i.e. non-Fermi liquid-like) in many other aspects [52].
Chapter 7

Coexisting strange metal and Fermi liquid excitations in Sr$_2$RuO$_4$

In this chapter we will explore the third and final question outlined in Chapter 1 – namely, are the collective charge excitations of the strange metal and Fermi liquid mutually exclusive, or can they simultaneously coexist? A model system for this purpose is the ruthenate Sr$_2$RuO$_4$, which behaves as a totally incoherent bad metal above 600 K, a robust Fermi liquid below $T_{FL} = 40$ K, and as a strange metal in the temperature regime between the two.

We will first present our M-EELS results on Sr$_2$RuO$_4$ at 300 K which exhibit a broad strange metal continuum up to about 1.2 eV and throughout most of the Brillouin zone, with clear similarities to the strange metal Bi-2212. Surprisingly, in addition to strange metal fluctuations, Sr$_2$RuO$_4$ also exhibits a well-defined dispersing Fermi liquid collective mode at low energies ($<80$ meV) and long-wavelengths ($<0.08$ r.l.u.). Upon cooling just below $T_{FL}$ to 30 K, the strange metal continuum undergoes suppression of spectral weight below $\sim 0.7$ eV, similar to overdoped Bi-2212, while the Fermi liquid collective mode’s dispersion becomes strongly renormalized with a $\sim 40\%$ reduction in mode velocity. These findings show that Sr$_2$RuO$_4$ exhibits strange metal fluctuations at high energies and short wavelengths, and a coherent Fermi liquid mode at low energies and long wavelengths. Our results therefore demonstrate that strange metal and Fermi liquid excitations can simultaneously coexist, and point towards Sr$_2$RuO$_4$ as an ideal testing bed for studying the interaction between the strange metal and Fermi liquid in a single system.
7.1 An experimental overview of $\text{Sr}_2\text{RuO}_4$

7.1.1 Why, of all materials, $\text{Sr}_2\text{RuO}_4$?

Before describing the properties and behavior of $\text{Sr}_2\text{RuO}_4$, let us first explain why this material was chosen for study in the first place. As we saw in Chapter 6, the cuprates are a powerful platform for studying the strange metal. However, cuprates are much less appealing for studying the interplay between the strange metal and Fermi liquid. The reason is the lack of a clear, well-accepted regime where they are Fermi liquids. Even in the overdoped regime, where cuprates are thought to be most Fermi liquid-like, there is evidence for non-Fermi liquid behavior [72, 189]. In contrast to the cuprates, the ruthenate $\text{Sr}_2\text{RuO}_4$, as well as its cousin $\text{Sr}_3\text{Ru}_2\text{O}_7$ [190], exhibits a very clean transition from a high temperature strange/bad metal to a low-temperature Fermi liquid [21, 191, 192, 193]. The microscopic reason for strange metal behavior in $\text{Sr}_2\text{RuO}_4$ is also quite different from the cuprates (Hund’s coupling versus Mott physics), enabling us to distinguish between material-dependent and material-independent physics. Finally, $\text{Sr}_2\text{RuO}_4$ is an extremely clean, stoichiometric compound, allowing us to rule out contributions from crystallographic disorder.

In the following section, we will provide a brief summary of the properties of $\text{Sr}_2\text{RuO}_4$, pointing out its commonalities and differences with respect to the cuprates along the way.

7.1.2 Properties of $\text{Sr}_2\text{RuO}_4$ in a nutshell

$\text{Sr}_2\text{RuO}_4$ is a highly two-dimensional metal ($\sigma_{ab}/\sigma_c$ of up to $\sim 10^3$) which exhibits a rich variety of different behavior as a function of temperature, as shown in Figure 7.1c. At high temperatures, $\text{Sr}_2\text{RuO}_4$ is a bad metal with resistivity much larger than the Mott-Ioffe-Regel bound (well over 1 m$\Omega$·cm with no signs of saturation) [40]. However, as one cools below about 40 K, $\text{Sr}_2\text{RuO}_4$ becomes a robust, strongly-correlated Fermi liquid, exhibiting the expected $T^2$ scaling of resistivity, optical relaxation rate of $\tau^{-1}(\omega) \sim \omega^2 + (2\pi k_B T)^2$, sharp
Figure 7.1: **General properties of Sr$_2$RuO$_4$.** (a) Fermi surface of Sr$_2$RuO$_4$ determined from ARPES measurements [194] showing three bands which arise from the $t_{2g}$ orbitals $d_{xy}, d_{xz}, d_{yz}$. (b) Crystal structure of Sr$_2$RuO$_4$ showing its tetragonal Ruddlesden-Popper structure. Conduction is highly two-dimensional and occurs within the RuO layers. (d) Temperature regimes of Sr$_2$RuO$_4$. Above 600 K, Sr$_2$RuO$_4$ is a totally incoherent bad metal that violates the MIR resistivity bound. Below about 40 K, Sr$_2$RuO$_4$ exhibits Fermi liquid behavior [21] and eventually superconductivity. In the intermediate temperature regime between 40 K and 600 K, Sr$_2$RuO$_4$ is a strange metal.
quasiparticle peaks in ARPES, and well-defined quantum oscillations of the expected period [21, 40, 42, 192]. Cooling even further, unconventional superconductivity occurs at 1.5 K with what has been thought to be exotic $p_x \pm ip_y$ pairing symmetry [195, 196, 197, 198], but more recently appears to be $d$-wave symmetry instead [199]. In the intermediate temperature regime between the high-temperature, totally incoherent bad metal and the low-temperature Fermi liquid, Sr$_2$RuO$_4$ behaves as a strange metal in that quasiparticles are poorly defined but not completely incoherent (see Figure 7.2b-c).

7.1.3 The “Hund’s metal” picture of Sr$_2$RuO$_4$

Although Sr$_2$RuO$_4$ is essentially isostructural to the La-based cuprates with a tetragonal Ruddlesden-Popper structure (see Figure 7.1), its microscopics are very different. Unlike the cuprates, the formal valence of ruthenium in Sr$_2$RuO$_4$ is Ru$^{4+}$, which leaves four electrons in its 4d orbitals, rather than just one. After accounting for the crystal-field of the O$^{2-}$ surrounding the Ruthenium atom, the four electrons mainly occupy three bands based on the Ru $t_{2g}$ orbitals ($d_{xy}, d_{yz}, d_{xz}$). Furthermore, due to how the in-plane oxygen atoms are situated, the $d_{xy}$ orbital can hop in both in-plane directions, while the $d_{yz}, d_{xz}$ orbitals are quasi-one dimensional. Therefore, the Fermi surface has three sheets: the roughly circular $\alpha$ band which is mostly of $d_{xy}$ character, and the $\beta, \gamma$ bands which have mixed $d_{yz}, d_{xz}$ character (see Figure 7.2). The net result is that, unlike the cuprates, Sr$_2$RuO$_4$ is a multiband system of 4d, rather than 3d, electrons. Because 4d orbitals are spatially more extended than 3d orbitals, the on-site Coulomb repulsion $U$ is smaller in Sr$_2$RuO$_4$ than in the cuprates. A smaller $U$ would naively suggest weaker correlations; however, the fact that multiple bands are present means that Coulomb repulsion between different orbitals (i.e. Hund’s coupling $J$) must be taken into account and that different orbitals may have different degrees of correlation.

Unlike electrons on the same orbital which have no choice but to form a spin singlet with energy cost $U$, electrons on different orbitals can reduce their Coulomb repulsion by
having parallel spins in accordance with the first rule of Hund’s coupling. Metals for which Hund’s coupling plays a crucial role in determining their strongly-correlated nature have been named “Hund’s” metals [200, 201].

A minimal model for understanding Hund’s metals is a simplified version of the Kanamori Hamiltonian [201, 203]

$$\mathcal{H} = \sum_{i \neq j, \mathbf{l}, \mathbf{m}, \sigma} d_{i\sigma}^\dagger d_{j\sigma} + U \sum_{\mathbf{l}} n_{\mathbf{l}\uparrow} n_{\mathbf{l}\downarrow} + U' \sum_{\mathbf{l} \neq \mathbf{m}} n_{\mathbf{l}\uparrow} n_{\mathbf{m}\downarrow} - J \sum_{\mathbf{l} < \mathbf{m}, \sigma} n_{\mathbf{l}\sigma} n_{\mathbf{m}\sigma}. \quad (7.1)$$

The first term in the Hamiltonian above is the kinetic energy term, the second is the Hubbard Coulomb repulsion for electrons on the same orbital, the third is the Coulomb repulsion for
electrons on different orbitals, and the fourth is the reduction in Coulomb repulsion for electrons on different orbitals with parallel spins (i.e. the ferromagnetic Hund’s coupling). Thus, Hund’s metals can be described by two types of terms: ordinary Mott charge repulsion ($U$ and $U’$) that only distinguishes between charge states (but not spin), and the ferromagnetic Hund’s coupling $J$ which reduces the Coulomb repulsion for parallel spins.

At its core, having multiple bands with sizable $J$ introduces different energy scales for charge/orbital fluctuations ($T_{\text{orb}}$) compared to spin fluctuations ($T_{\text{sp}}$), with $T_{\text{orb}} \gg T_{\text{sp}}$ in general [204]. For comparison, a system dominated by ordinary charge repulsion $U$ with insignificant $J$ has $T_{\text{orb}} \approx T_{\text{sp}}$ [204]. This separation of scales between orbital and spin degrees of freedom has led to a Kondo impurity picture of Hund’s metals largely based on Dynamical Mean Field Theory (DMFT) [86, 201, 204, 205]. DMFT is an impurity-solver method that maps a strongly-interacting system of electrons onto the behavior of a single atomic site self-consistently interacting with a complex effective medium (i.e. a complicated, dynamical version of the Weiss-effective field) [85, 201]. Due to its highly-local prescription, DMFT largely interprets phenomenology in terms of Kondo-like effects.

Within this Kondo-like picture of Hund’s metals, orbital fluctuations are suppressed and coherently screened below some large temperature scale $T_{\text{orb}} \sim 1000 \text{ K}$, at which point Hund’s coupling aligns the spins on each atomic site to produce large, local moments with fixed orbital occupation numbers (a so-called “frozen-spin” state [201]). Then, as one further cools below a spin-coherence temperature $T_{\text{sp}} = T_{\text{FL}}$, these local moments become coherently screened by itinerant charge carriers, just as in the Kondo effect, and a strongly-correlated Fermi liquid is formed. Although the Hund’s coupling $J$ is on the scale of 0.4 eV, the spin coherence temperature is massively reduced to about 25-40 K due to its exponential dependence on $J$ in the same way it is suppressed in the Kondo effect. This picture of spins being screened below $T_{\text{FL}}$ was originally proposed to explain measurements of the magnetic susceptibility of Sr$_2$RuO$_4$ which indicate local moments with Curie-Weiss paramagnetic behavior above $T_{\text{FL}}$ and Pauli paramagnetism (i.e. mobile, delocalized spins) below $T_{\text{FL}}$ [206].
It should be emphasized however, that impurity models of Hund’s metals like Sr$_2$RuO$_4$ intrinsically do not tell the full story, as the local moments and itinerant conduction electrons in Hund’s metals are fundamentally one and the same and cannot be separated. This situation is unlike the ordinary Kondo effect and heavy fermion systems where the local moments are physically distinct from the itinerant carriers. Nonetheless, it should be emphasized that this microscopic picture of Hund’s coupling-driven strong correlations in Sr$_2$RuO$_4$ is certainly quite different from the cuprates.

Taking Sr$_2$RuO$_4$ as a Hund’s metal, the picture of the strange metal regime above $T_{FL}$ is then roughly understood to arise from strong and not-yet-understood interactions between charge carriers and a lattice of large local moments that prevents coherent Fermi liquid quasiparticles from forming. An understanding of precisely how such interactions give rise to non-Fermi liquid behavior and the experimentally observed transport has been elusive and remains an open question [201]. However, recent renormalization group analyses have shown that approximating charge/orbital fluctuations as frozen out below $T_{orb}$ is too drastic [207, 208]. These works show that charge/orbital degrees of freedom need to be treated as fluctuating even for $T \ll T_{orb}$ in order to account for the strange metal properties because spin and orbital fluctuations cannot truly be decoupled [207, 208]. Currently, the role of the charge susceptibility $\chi''(q,\omega)$ in Hund’s metals such as Sr$_2$RuO$_4$ and its relation to strange metal behavior is an open theoretical question.

With the overall theoretical status of the strange metal in Sr$_2$RuO$_4$ in mind, we are in a position to ask: how exactly do the charge fluctuations of the strange metal regime give way to Fermi liquid collective excitations in Sr$_2$RuO$_4$? Do they give way abruptly, implying that strange metal and Fermi liquid physics are mutually exclusive, or is there coexistence between the two?
7.2 Sample characterization, experimental design, and fitting procedures

High-quality single crystals of Sr$_2$RuO$_4$ were grown by Chanchal Sow from the group of Yoshiteru Maeno at Kyoto University (batch #C430) using a floating-zone technique [209, 210]. The superconducting transition temperature in Sr$_2$RuO$_4$ is a highly-sensitive measure of crystal quality, with $T_c = 1.5$ K being observed only in very clean crystals. Accordingly, only high-quality samples with $T_c = 1.47$ K, as verified by measurements of the AC magnetic susceptibility at 3011 Hz, were used for our EELS experiments. Their structural crystallinity was further confirmed using x-ray diffraction.

As a matter of convention, we will use the tetragonal unit cell of Sr$_2$RuO$_4$ with $a = b = 3.873$ Å and $c = 12.732$ Å [211]. As before, we will report momenta in units of reciprocal lattice units of $2\pi/a$, meaning that the Brillouin zone boundary is located at $(0.5,0)$. The M-EELS electron beam was tuned up at 50 eV and corrected for aberrations (see section 5.4) achieving 6 meV energy resolution, 0.03 Å$^{-1}$ momentum resolution, and about 40 pA of beam current.

Samples of Sr$_2$RuO$_4$ were mounted on copper pucks and cleaved at 300 K in ultra-high vacuum as described previously (see section 6.2). Only crystals with sharp, single specular and Bragg reflections were measured. Cleaves with multiple specular reflections due to surface morphology were terminated to avoid misassignment of momentum transfer. For “good” cleaves, the elastic diffraction pattern taken with M-EELS was generally very high, with sharp, resolution-limited Bragg reflections clearly visible (see Figure 7.3). Normalization of the M-EELS charge susceptibility was done by applying the f-sum rule up to 2.5 eV

$$\int_0^{2.5\text{eV}} \omega \chi''(q, \omega) d\omega = -\pi \frac{q^2}{2m} N_{\text{eff}}, \quad (7.2)$$
with $N_{\text{eff}} = 3.21 \times 10^{-4} \text{Å}^{-3}$ obtained from the optical loss function in the same energy window \cite{21}.

It should be mentioned that other surface probes such as ARPES and STM report a $\sqrt{2} \times \sqrt{2}$ surface reconstruction in Sr$_2$RuO$_4$ due to a coordinated octahedral tilt that result in folded bands at the Fermi surface. We believe these bands are largely irrelevant to M-EELS measurements for two reasons. First, these surface states are easily passivated and leave essentially no trace in ARPES spectra by cleaving at room temperature \cite{212} and by exposure of the sample surface to residual carbon monoxide found in any ultra-high vacuum chamber \cite{194}. Secondly, in contrast to the surface states, bulk bands are entirely unaffected by this passivation and remain very sharp in both energy and momentum \cite{194}. Due to the fact that we cleave Sr$_2$RuO$_4$ at room temperature and the graphite-coated M-EELS spectrometer exposes the sample to residual carbon monoxide, we expect the surface-reconstructed bands are almost entirely passivated, leaving just the bulk bands. Note that this passivation does not disturb the bulk crystal quality, as seen in the sharp Bragg reflection in Figure 7.3.

Later in this chapter we will also present STEM-EELS measurements on Sr$_2$RuO$_4$ to confirm the reflection M-EELS results. These STEM-EELS measurements were performed with a Nion UltraSTEM microscope with Hongbin Yang and Philip Batson at Rutgers University. The primary beam energy was set to 60 keV with a 10 meV full-width at half-maximum and a convergence semi-angle of $\alpha = 30$ mrad was used (i.e. completely averaged over all of momentum space). Sr$_2$RuO$_4$ samples for the STEM-EELS measurements were prepared by cutting out a thin lamella oriented along the ab-plane using the FEI Scios 2 Focused Ion Beam instrument at the Illinois Materials Research Laboratory (see section 5.7 for details). Measurements were done in a region of the lamella that was approximately 45 nm thick, as determined by the transmission of the electron beam and calculated inelastic mean free path of 60 nm for 60 keV electrons (i.e. 80% of the electron beam transmitted through the sample elastically, implying $t = 0.80 \cdot 60\text{nm} = 45\text{nm}$). The STEM-EELS
Figure 7.3: **Crystallinity of Sr$_2$RuO$_4$ samples prepared for M-EELS** (a) Photograph of a Sr$_2$RuO$_4$ crystal used in M-EELS measurements (scale bar 5 mm) with the crystal axes determined by scanning the elastic M-EELS signal as a function of momentum. (b) Momentum scan of the M-EELS response of Sr$_2$RuO$_4$ at $\omega = 0$ revealing a very sharp specular reflection at $(0,0)$ and Bragg reflection at $(1,0)$. The full-width at half-maximum of the Bragg reflection is very sharp, at around 0.03 Å$^{-1}$.

spectra were acquired on a 2D CMOS gain-corrected image with an acceptance semi-angle of $\beta = 16$ mrad. The image was integrated along the non-energy-dispersive direction for higher statistics. To obtain the momentum-integrated STEM-EELS charge susceptibility $\chi''(\omega)$, the spectra were antisymmetrized to remove the Bose factor and the same f-sum rule integral described above for M-EELS was performed for the STEM-EELS data.

Finally, in our description of the Fermi liquid mode we fitted the mode to extract its peak position, full-width at half-maximum (FWHM), and peak intensity. This fit was done on the raw M-EELS intensity (measured in Hertz), not the charge susceptibility $\chi''(q,\omega)$. In particular, this fit was performed by fitting the quasi-elastic line to a pseudo-Voigt function (i.e. linear combination of a Gaussian and Lorentzian), the Fermi liquid mode to an antisymmetrized Lorentzian (i.e. a Lorentz oscillator), the 67 meV phonon to a Fano profile (based on previous works [150, 213]), and the optical phonons at 25, 35, and 50 meV to antisymmetrized Lorentzians when they are present in the M-EELS spectra. All errors
Figure 7.4: Example fits of the Fermi liquid collective mode for (a) \( q = 0.03 \) Å\(^{-1}\) along the (1,1) direction at 300 K, (b) \( q = 0.06 \) Å\(^{-1}\) along the (1,0) direction at 300 K and (c) \( q = 0.08 \) Å\(^{-1}\) along the (1,0) direction at 30 K. The quasi-elastic line is fitted by pseudo-Voigt (grey dashed line), Fermi liquid mode by an antisymmetrized Lorentzian (red line), and the optical phonon was fit to a Fano lineshape in accordance with studies of phonons in \( \text{Sr}_2\text{RuO}_4 \) [150, 213].

Bars shown combine the statistical fit errors with the Poisson noise related to the M-EELS counting statistics. Furthermore, as the phonons in \( \text{Sr}_2\text{RuO}_4 \) are very well-studied both theoretically and experimentally [150, 213], we only present the behavior of the Fermi liquid mode. Sample fits are shown in Figure 7.4.

For \( q < 0.02 \) r.l.u., the Fermi liquid mode merges with the quasi-elastic line and is no longer clearly visible within our resolution. Fitting in this momentum regime is thus subject to large systematic errors, so we simply provide an estimated upper bound of the mode energy in this range of momenta. This estimate was obtained by fitting the quasi-elastic peak to a pure Gaussian and then fitting its non-Gaussian tails according to two different schemes. In scheme A, the non-Gaussian tail is attributed purely to the Fermi liquid mode, while in scheme B it is attributed to the sum of the Fermi liquid mode and some unresolvable “scheme B mode”. The upper bound of the Fermi liquid mode energy was then set to higher of the two fitted energies. An example of this fitting procedure is shown for \( q = 0.00 \) r.l.u. in Figure 7.5.
Figure 7.5: **Upper bound estimate of the Fermi liquid mode energy.** For \( q < 0.02 \) r.l.u., the Fermi liquid mode in \( \text{Sr}_2\text{RuO}_4 \) merges with the quasi-elastic line and is not readily resolved. To place a rough upper bound on the Fermi liquid mode energy in this low-momentum region, we use two fitting schemes. Scheme A attributes the non-Gaussian tails of the quasi-elastic line to the Fermi liquid mode, while scheme B attributes this tail to a sum of the Fermi liquid mode and some unresolvable “Scheme B” mode. (a) Scheme A fit at \( q = 0.00 \) r.l.u. at 300 K. (b) Same as (a) but for the scheme B fit. (c-d) Same fitting as (a-b) but with the vertical axis zoomed out to show the large quasi-elastic line.

**7.3 Observation of a strange metal continuum in \( \text{Sr}_2\text{RuO}_4 \)**

Our starting point for M-EELS measurements in \( \text{Sr}_2\text{RuO}_4 \) is in the strange metal regime at 300 K, well above the Fermi liquid coherence temperature \( T_{FL} \approx 40 \) K. Following the conclusions of the M-EELS data in Bi-2212 from Chapter 6, we expect to see a largely flat continuum of charge fluctuations for a broad range of energies and momenta in \( \text{Sr}_2\text{RuO}_4 \), rather than a sharply defined dispersing plasmon.
Figure 7.6 shows the charge susceptibility of Sr$_2$RuO$_4$ measured up to 2.5 eV along the (1,0) direction for a range of momenta going up to the Brillouin zone boundary at (0.5,0). Remarkably, we see very similar phenomenology to that of Bi-2212 from Figure 6.5. In particular, there is a very broad peak at low momentum that likely connects to the optical loss function, but for $\sim$90% of the Brillouin zone there is a flat continuum of charge excitations which is momentum-independent aside from an $q^2$ scaling to satisfy the f-sum rule. Thus, Sr$_2$RuO$_4$ exhibits a strange metal continuum at 300 K. Considering that Sr$_2$RuO$_4$ has very different microscopic physics compared to Bi-2212, the results in Figure 7.6 further support our statement that a featureless continuum is a universal signature of the strange metal, rather than an anomalous property unique to the cuprates. Additionally, because Sr$_2$RuO$_4$ is a clean and stoichiometric compound, we are able to rule out crystallographic disorder as the primary origin for the non-dispersive nature of the strange metal continuum.

To prove the strange metal continuum in Sr$_2$RuO$_4$ is a bulk property, we also performed STEM-EELS measurements on Sr$_2$RuO$_4$ with our collaborators Hongbin Yang and Philip Batson at Rutgers University, as shown in Figure 7.6c. These (momentum-integrated) STEM-EELS measurements match extraordinarily well with the M-EELS spectra especially considering that they probe a sample volume which is $10^{-9}$ times smaller, use electrons at $>1000$ times higher beam energy, and were performed in transmission rather than reflection. Considering that STEM-EELS measurements on Bi-2212 also agreed with M-EELS in section 6.3.3, we conclude that the strange metal continuum is a bulk property of these materials.

### 7.3.1 Isotropic strange metal fluctuations

While we have shown that the strange metal continuum in Sr$_2$RuO$_4$ is largely independent of the magnitude of $q$, it is also important to assess the possibility for an anisotropic dependence on the direction of $q$. Because of Sr$_2$RuO$_4$’s tetragonal symmetry, we decided to measure the charge response along the (1,1) direction at $|q| = 0.5$ r.l.u. to compare to the response
Figure 7.6: **Strange metal continuum in Sr$_2$RuO$_4$.** (a) Energy scans of the charge response function $\chi''(q, \omega)$ as a function of momentum along the (1,0) direction at 300 K in Sr$_2$RuO$_4$. Each curve is normalized by $q^2$ and offset by multiples of 0.05 eV$^{-1}$ Å$^{-1}$ for visual clarity. These spectra reveal a highly damped peak below 0.16 r.l.u. that becomes a featureless strange metal continuum that is flat in energy and momentum independent for $q > 0.16$ r.l.u. over about 90% of the Brillouin zone. Thus, Sr$_2$RuO$_4$ is confirmed to have strange metal fluctuations with many similar qualities to Bi-2212. (b) Cartoon of the M-EELS scattering process. (c) Comparison between bulk-sensitive STEM-EELS and reflection M-EELS in Sr$_2$RuO$_4$. The spectra closely match one another and therefore demonstrate the bulk nature of the strange metal fluctuations in Sr$_2$RuO$_4$. 196
Figure 7.7: **Isotropic strange metal continuum in Sr$_2$RuO$_4$** Comparison of the M-EELS charge response of Sr$_2$RuO$_4$ along (1,0) (red) and (1,1) (grey) at $|q| = 0.5$ r.l.u. Although the (1,1) spectra is noisier due to its shorter acquisition time, the spectra show an overall agreement and demonstrate the strange metal continuum in Sr$_2$RuO$_4$ is isotropic in the ab-plane.

at (0.5,0). This comparison is shown in Figure 7.7. The data along (1,1) are noisier due to its shorter averaging time, but it is nonetheless clear that the strange metal continuum is nearly identical for the two directions. Thus, we conclude that the strange metal response in Sr$_2$RuO$_4$ is largely isotropic in-plane$^1$.

### 7.3.2 An aside: universal and non-universal aspects of the strange metal continuum

One important difference between the M-EELS spectra for Sr$_2$RuO$_4$ in Figure 7.6 and that of Bi-2212 in Figure 6.5 is the position of high-energy cutoff. While the rounding off of the strange metal fluctuations occurs at about 1 eV in Bi-2212, it is closer to 1.2 eV in Sr$_2$RuO$_4$.

$^1$It is still possible that the response at small momentum transfer is anisotropic, as in the case of Bi-2212. However, as Figure 7.7 shows, this anisotropy must disappear at larger momentum transfer.
This difference in cutoff indicates that the endpoint of the strange metal charge fluctuations is non-universal and material-dependent. At the most simplistic level, this difference in cutoff may be a reflection of the fact that Sr$_2$RuO$_4$ has a higher overall carrier density than Bi-2212 [21, 116].

To better understand the relationship between a strange metal and its cutoff energy, we measured the charge susceptibility of overdoped Bi-2201 with $T_c = 15$ K which was lead doped to suppress the superlattice. Bi-2201 is a close relative of Bi-2212, but has single copper oxide layers with insulating layers in between, rather than copper oxide bilayers as in Bi-2212. These crystals were generously provided by the group of Erik van Heumen at the University of Amsterdam who characterized the optical plasma frequency of OD12K Bi-2201 to be at 0.8 eV. This plasma frequency is significantly lower than Bi-2212, where it is around 1 eV instead [116], which is largely a result of having less conducting layers per unit volume. Thus, one might expect that at room temperature, OD12K Bi-2201 would show similar behavior to OD50K Bi-2212 (i.e. exhibiting a strange metal continuum in its charge response) but with a smaller cutoff around 0.8 eV instead.

Indeed, Figure 7.8 shows that OD12K Bi-2201 also shows a largely momentum-independent strange metal continuum, but with a cutoff closer to 0.75-0.80 eV as expected. As a final check, we also measured on two materials which are not strange metals: ordinary single-crystal graphite, and the Mott insulator Ca$_2$RuO$_4$. Single crystal graphite was purchased from Naturally Graphite™ who obtained them from natural graphite mines in Tanzania, while Ca$_2$RuO$_4$ was grown by Fumihiro Nakamura from the group of Yoshiteru Maeno at Kyoto University. A comparison of the charge susceptibilities of Sr$_2$RuO$_4$, Bi-2212, OD12K Bi-2201, graphite, and Ca$_2$RuO$_4$ at $q = 0.5$ r.l.u. (in their respective lattice units) is shown in Figure 7.9. This comparison clearly shows that the charge fluctuation continuum is universal and shared by three different strange metals, but is absent in ordinary materials which are not strange metals. On the other hand, the position of the cutoff energy is strongly material-dependent, and most likely reflects the non-universal carrier density among the
Figure 7.8: Strange metal cutoff in OD12K Bi-2201. M-EELS spectra on OD12K Bi-2201 at 300 K for three momenta. These spectra provide evidence for the strange metal continuum being present in Bi-2201 similar to Bi-2212, but with a reduced high-energy cutoff of 0.8 eV compared to about 1 eV in Bi2212. This difference in the high-energy cutoff likely reflects the lower carrier concentration in Bi-2201.

So far, we have seen that the charge response of Sr$_2$RuO$_4$ at 300 K is dominated by strange metal fluctuations extending up to $\sim$1.2 eV in energy and across the Brillouin zone in momentum. However, at lower energies and longer wavelengths, an entirely different kind of collective mode becomes visible in the M-EELS response. This collective mode exists for energies below 70 meV and momenta below 0.08 r.l.u. and is shown in Figure 7.10. Unlike the broad non-propagating strange metal continuum, this collective mode rapidly disperses on a scale of about 0.7 eV·Å. Such a large dispersion velocity implies that this mode must be electronic in nature, as the speed of sound for lattice excitations in Sr$_2$RuO$_4$ is nearly two

7.4 Fermi liquid collective mode at low energies and long wavelengths

strange metals studied.
Figure 7.9: **Universal strange metal continuum.** Comparison of the normalized charge response $\chi''(q, \omega)/q^2$ for three strange metals (OP91K Bi-2212, Sr$_2$RuO$_4$, and OD12K Bi-2201), an ordinary semi-metal (single crystal graphite), and a Mott insulator (Ca$_2$RuO$_4$). The spectra clearly show that all three strange metals exhibit a featureless continuum, but with a material-dependent endpoint of the charge fluctuations (0.8 eV for Bi-2201, 1 eV for Bi-2212, and 1.2 eV for Sr$_2$RuO$_4$). For comparison, graphite and Ca$_2$RuO$_4$ do not exhibit a continuum, as one expects. The spectra are taken at $q = 0.5$ r.l.u. (of their respective Brillouin zones) for all materials except Bi-2201 where the charge response was taken at $q = 0.27$ r.l.u. The normalization of these spectra is done with $N_{\text{eff}}$ obtained by integrating the optical conductivity from [57, 116, 214, 215, 216].
Figure 7.10: Fermi liquid collective mode in Sr$_2$RuO$_4$ at 300 K. Color plot of the M-EELS intensity as a function of energy and momentum in Sr$_2$RuO$_4$. Each energy cut is normalized by its integrated intensity above 5 meV and is put in arbitrary units. Unlike the strange metal continuum, this mode is well-defined in energy and rapidly disperses with momentum on the scale of $\sim 0.7$ eV·Å. This velocity is close to the mean Fermi velocity and thus implies this excitation is a collective mode of the Fermi liquid in Sr$_2$RuO$_4$.

orders of magnitude smaller at $\sim 0.008$ eV·Å [213]. Moreover, in addition to being electronic in origin, the approximate velocity of this collective mode of 0.7 eV·Å is remarkably close to the mean Fermi velocity in Sr$_2$RuO$_4$ of about 0.56 eV·Å [20, 194], clearly demonstrating that this collective excitation is fundamentally Fermi liquid-like in nature. We will see later that, unlike the isotropic strange metal continuum, this Fermi liquid mode is also anisotropic, with a higher velocity of $\sim 0.85$ eV·Å along (1,1) compared to $\sim 0.7$ eV·Å along (1,0).

We conclude, therefore, that Sr$_2$RuO$_4$ exhibits coexisting strange metal and Fermi liquid excitations, with featureless, non-propagating strange metal fluctuations.
Figure 7.11: Map of coexisting Fermi liquid and strange metal excitations in Sr$_2$RuO$_4$. Cartoon map of the charge response of Sr$_2$RuO$_4$ which exhibits both broad strange metal fluctuations at high energy (up to about 1.2 eV) and short wavelengths, as well as a coherent, dispersing Fermi liquid-like collective mode at low energies and long wavelengths.

dominating at high energies and short wavelengths, and a propagating Fermi liquid collective mode at low energies and long wavelengths. A schematic summary of this coexistence is shown in Figure 7.11 which shows a map of the charge response of Sr$_2$RuO$_4$ as a function of energy and momentum. That the Fermi liquid mode is visible at 300 K is an indication that Fermi liquid quasiparticles are resilient and survive above the nominal $T_{\text{FL}}$ where $T^2$ resistivity is observed, in agreement with theoretical DMFT calculations [205].

A careful reader will notice that the Fermi liquid collective mode also appears to be gapless, unlike the ordinarily gapped zero sound mode (i.e. plasmon) found in most Fermi
liquids. Indeed, we will discuss possible origins of this Fermi liquid collective mode in the next section. But to set the stage for that discussion, let us first report how the Fermi liquid and strange metal excitations in Sr$_2$RuO$_4$ respond to cooling below $T_{FL}$.

7.5 Fate of the strange metal and Fermi liquid excitations below $T_{FL}$

So far, we have seen that Sr$_2$RuO$_4$ exhibits excitations of both the strange metal and Fermi liquid at 300 K in different regimes of momentum and energy. Let us now study the charge response at 30 K, which lies below the Fermi liquid coherence temperature $T_{FL}= 40$ K.

7.5.1 Spectral weight suppression of the strange metal continuum

Starting with the strange metal excitations, Figure 7.12 shows a comparison between the strange metal continuum at 300 K and at 30 K in Sr$_2$RuO$_4$. What is observed is a small, but non-negligible spectral weight suppression below 0.9 eV for almost all momenta that shifts spectral weight to higher energies above 1 eV. This spectral weight suppression shows parallels to the behavior of the strange metal continuum in overdoped Bi-2212 which, upon cooling, exhibited a large spectral weight suppression below 0.5 eV (see section 6.4). A comparison of Sr$_2$RuO$_4$ and OD50K Bi2212 in this respect is shown in Figure 7.12b-c. That relatively less spectral weight is suppressed in Sr$_2$RuO$_4$ may be due to the much lower Fermi liquid coherence temperature of 25 K to 40 K in Sr$_2$RuO$_4$ compared to over 200 K in overdoped Bi-2212 [217]. It is possible, therefore, that more spectral weight suppression will be observed if one were to measure the charge response as temperatures much lower than 30 K. Nonetheless, our observations suggest that spectral weight suppression is a general mechanism for Fermi liquid-like behavior to form out of the strange metal. Furthermore,
these findings show that development of Fermi liquid coherence does not require a total loss of strange metal fluctuations. Instead, Fermi liquid coherence can be established by pushing low-energy strange metal fluctuations up to higher energies where their impact on low-frequency properties, such as resistivity or quasiparticle lifetimes, are suppressed.

From a more microscopic perspective, the observation of spectral weight suppression in the charge sector calls for revisiting the microscopic Hund’s metal picture of Sr$_2$RuO$_4$ described at the beginning of this chapter. Recall that the predominant view [86, 201, 205] of the Hund’s metal was that orbital fluctuations, which are present in the charge response because multipole excitations are allowed at non-zero $q$, can be projected out of the problem below the large orbital coherence temperature $T_{\text{orb}} \sim 1000$ K, leaving just local spin moments at each site. The fact that charge fluctuations exhibit spectral weight changes down to the $T_{\text{FL}}$ implies that orbital fluctuations are not nearly as inactive as previously expected. Indeed, more recent renormalization group approaches to the Hund’s metal show that orbital fluctuations cause changes to the spin fluctuations and vice-versa even down to $T_{\text{FL}}$ which is well below $T_{\text{orb}}$ [207, 208]. Furthermore, the separation of spin and orbital degrees of freedom is explicitly broken by the small, but non-negligible spin-orbit coupling in Sr$_2$RuO$_4$ of about 0.1 eV [218].

It is also interesting to note that the observation of local strange metal fluctuations and non-local Fermi liquid collective modes in the charge sector parallels the behavior of the spin sector. In particular, inelastic neutron scattering observes two key features in Sr$_2$RuO$_4$: local, quasi-ferromagnetic spin fluctuations that are very broad in momentum, and delocalized incommensurate spin fluctuations with peaks around $(H \pm 0.3, K \pm 0.3)$ [219, 220]. Thus, future theoretical studies aimed at calculating the dynamic charge density response in Sr$_2$RuO$_4$ will be very valuable for understanding the relationship between spin and charge degrees of freedom in Hund’s metals.
Figure 7.12: Strange metal fluctuations in Sr$_2$RuO$_4$ above and below the Fermi liquid coherence temperature $T_{FL}$ (a) Comparison of the charge response in Sr$_2$RuO$_4$ at 300 K (red) and at 30 K (blue). One notices a small, but non-negligible spectral weight suppression for energies below about 0.9 eV and subsequent increase in spectral weight to above 1 eV. This behavior parallels that of overdoped Bi-2212. (b-c) Comparison of the spectral weight change of (b) Sr$_2$RuO$_4$ at $q = 0.24$ r.l.u. with that of (c) OD50K Bi2212. Both Sr$_2$RuO$_4$ and Bi-2212 show a spectral weight suppression in the strange metal continuum, but with different magnitudes. This difference in magnitude likely arises from the much smaller $T_{FL}$ of Sr$_2$RuO$_4$ which is about 25 K to 40 K [21] compared to over 200 K in OD50K Bi-2212 [217].
7.5.2 Renormalized Fermi liquid collective mode dispersion

Let us turn now to the Fermi liquid mode at low energy and momenta. Figure 7.13a-b shows a comparison between the Fermi liquid collective mode at 300 K and 30 K along (1,0), and Figure 7.13c shows the fitted peak positions. Raw linecuts are also presented for reference in Figures 7.14a-b. Surprisingly, the Fermi liquid mode’s dispersion, as roughly estimated by the slope between $q = 0.04$ and 0.08 r.l.u., is strongly renormalized from $\sim 0.7$ eV·Å at 300 K to about 0.5 eV·Å at 30 K, reflecting a 40% change in the mode’s velocity between the two temperatures. Given that the Fermi surface volume does not change with temperature (i.e. $k_F$ and the nominal carrier density are constant), this change in dispersion can be attributed to strongly renormalized quasiparticles. Remarkably, the quasiparticle effective mass is known to increase by a factor of 1.4 upon cooling to below $T_{FL}$ (see Figure SM5 of [21]). Translating the change in effective mass to a change in (average) Fermi velocity, the reduction in the Fermi liquid mode dispersion can therefore be quantitatively accounted for by the temperature-dependent $v_F$ in Sr$_2$RuO$_4$.

At first sight, one may be surprised that the Fermi liquid mode becomes slower below $T_{FL}$ despite the suppression of strange metal fluctuations and the overall increased quasiparticle coherency. This change in effective mass becomes more understandable if one accepts the Kondo-like Hund’s metal picture of Fermi liquid coherence in Sr$_2$RuO$_4$. In this picture, like in the ordinary Kondo effect or heavy fermion systems, the local moments that drive strange metal behavior become coherently screened below $T_{FL}$. However, their effects do not completely go away and they give rise to dressed, “heavy” quasiparticles with a large effective mass and slow Fermi velocity. From the opposite point of view, if one were to heat up the system up from below $T_{FL}$, quasiparticles become increasingly “undressed” allowing them to propagate with masses closer to the free electron mass.

In addition to having a renormalized dispersion, the Fermi liquid mode’s lifetime is slightly increased at low temperature. This is seen in the fitted full-width at half-maximum
Figure 7.13: **Renormalized Fermi liquid collective mode below $T_{FL}$**. Comparison of the Fermi liquid mode in Sr$_2$RuO$_4$ observed with M-EELS along (1,0) at (a) 300 K and (b) 30 K. As before, each energy cut is normalized by its integrated intensity above 5 meV and is put in arbitrary units. One can immediately see that the Fermi liquid mode undergoes a very significant renormalization, with a $\sim$40% reduction in mode velocity at 30 K compared to 300 K. (c) Fits to the peak positions of the Fermi liquid mode at 300 K along (1,1) (green), at 300 K and (1,0) (red), and at 30 K along (1,0) (blue). (d) Directions of the data points in (c) overlaid onto the Fermi surface of Sr$_2$RuO$_4$ for reference.
Figure 7.14: Linecuts of the Fermi liquid collective mode in Sr$_2$RuO$_4$. (a) M-EELS spectra on Sr$_2$RuO$_4$ along (1,0) at 30 K (blue) and 300 K (red). These data are the same as that of Figure 7.13a-b. One can clearly see the change in dispersion going from 30 K to 300 K. (b) Same as (a) but for the M-EELS response along (1,1) at 300 K. For clarity, the spectra in (a-b) are normalized to their value at 90 meV and offset vertically.
Figure 7.15: **Full-width at half-maximum (FWHM) of the Fermi liquid collective mode.** Plot of the fitted FWHM of the Fermi liquid mode of Figures 7.10, 7.13, 7.14. For $q \leq 0.02$ r.l.u. the Fermi liquid mode is no longer clearly identifiable, a fact which indicate by using broken lines. Statistical fit error bars are smaller than the size of the markers. One should note that the width of the peaks is smeared by up to 25 meV due to the finite momentum resolution of M-EELS and the rapid dispersion of the Fermi liquid collective modes. Nonetheless, the modes become increasingly damped at higher momentum indicating that true decay mechanisms are present. Eventually the modes disappear altogether above 0.08 r.l.u., which is consistent with the expected onset of Landau damping in Sr$_2$RuO$_4$ (see main text). The linewidth of the Fermi liquid mode at 30 K is also sharper than that of 300 K which may indicate suppression of decay channels below $T_{FL}$. 
Figure 7.16: **Fitted peak intensity of the Fermi liquid collective mode in the raw M-EELS spectra.** The peak intensity roughly decays as $q^{-2}$ as one might expect considering the Coulomb matrix element. As stated previously, for $q \leq 0.02$ r.l.u. the Fermi liquid mode is no longer clearly identifiable, and we indicate this region by using a broken line for $q \leq 0.02$ r.l.u.

of the mode shown in Figure 7.15, which is overall slightly smaller at 30 K compared to 300 K. It should be noted however, that the rapid dispersion of the Fermi liquid mode combined with the finite M-EELS momentum resolution of $\sim 0.03 \text{Å}^{-1}$ introduces a “smearing” of the spectra by up to 25 meV depending on how quickly the mode disperses. Eventually however, the linewidth of the mode becomes 40 meV at around 0.07 r.l.u., indicating that true decay channels are also present. At higher momentum of about 0.08 r.l.u., the Fermi liquid mode quickly damps away and is no longer visible. This disappearance can be understood as the onset of Landau damping, and a rough calculation using the experimental values of $m^*$ and $v_F$ from [221] confirms$^2$ that the Fermi liquid particle-hole continuum onset at $q = 0.08$ r.l.u. is approximately 70 meV.

For completeness, the fitted peak intensity of the Fermi liquid mode in Hertz is given in Figure 7.16 and roughly goes as $q^{-2}$, which likely reflects the M-EELS Coulomb matrix element.

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$^2$The onset of the particle-hole continuum goes as $E_{onset} = h^2q^2/2m^* + hv_F q$, and using $hv_F = 0.4$ eV·Å (the slower of the bands) and $m^* \approx 2.4m$ from [221] gives about 70 meV at $q = 0.08$ r.l.u., which is the right order of magnitude to damp out the Fermi liquid mode.
7.5.3 Possible origins of the Fermi liquid collective mode

A very curious property of the Fermi liquid mode observed in Sr$_2$RuO$_4$ is that it appears to be gapless within the resolution of M-EELS. In fact, optical measurements do not report any electronic modes between 0 and 15 meV in Sr$_2$RuO$_4$ [21], implying that this Fermi liquid mode is truly gapless.

The gapless nature of the Fermi liquid mode is unexpected, as the long-range Coulomb interaction usually lifts the zero sound mode of charged Fermi liquids to finite frequency and gives rise to the usual gapped plasmon at the plasma frequency. The most obvious explanation then is that the Fermi liquid collective mode we observe is a surface plasmon, as the Coulomb interaction in semi-infinite and 2D systems results in a gapless plasmon. This is not entirely satisfying however, as surface plasmons usually have a $\sqrt{q}$ dispersion [147, 222], while the mode we observe has a linear (or possibly quadratic) dispersion according to Figure 7.13c. Still, it is possible that a more careful calculation of a surface plasmon dispersion that takes the band structure of Sr$_2$RuO$_4$ into account may reproduce the observed dispersion.

There is also a more exotic category of explanations for the observed Fermi liquid mode in terms of a zero sound-like mode. While zero sound is usually gapped due to the long-ranged Coulomb interaction, it is possible that the high-energy strange metal charge response provides the screening needed for the low-energy Fermi liquid mode to behave as a neutral excitation. Supporting this scenario is the fact that the strange metal fluctuations shows a more peaked plasmon-like behavior in the same range of momentum where the Fermi liquid collective mode exists. Thus, there is at least some finite region of energy and momentum where the Fermi liquid mode is screened and does not readily decay into strange metal fluctuations.

The smoking-gun evidence needed to decide between the surface plasmon and zero sound explanations for the Fermi liquid mode is a bulk-sensitive measurement, such as momentum-resolved transmission EELS or Resonant Inelastic X-ray Scattering. If the Fermi liquid mode
is a bulk excitation, one can rule out the surface plasmon and should take the zero sound explanation more seriously. On the other hand, if the mode is a property of the surface, the surface plasmon is the simplest to accept.

Regardless of its origin, it is worth putting some context around just how strongly renormalized the dispersion of the Fermi liquid mode becomes at low temperature. In general, the speed of propagation for gapless acoustic excitations goes as \( v = \sqrt{\kappa/\rho} \), where \( \kappa \) is the compressibility and \( \rho \) is the density of the medium. Thus, one should realize that a 40% change in velocity for ordinary acoustic sound is enormous, as it would require the density or compressibility to change by a factor of two (e.g., a change in density from steel to lead!). Similarly, in systems with surface plasmons such as graphene, the only method for appreciably changing the surface plasmon velocity is by altering the carrier concentration through brute-force electrostatic gating and/or using carefully chosen substrates [223]. For ordinary metals, both of these methods are highly impractical, which makes it all the more extraordinary that metallic \( \text{Sr}_2\text{RuO}_4 \) renormalizes its collective mode dispersion on its own simply by changing the temperature. Of course, it is doubtful that the Fermi liquid mode in \( \text{Sr}_2\text{RuO}_4 \) will ever have any practical use, but the principle of using strong correlations to influence the dispersion of charge collective modes is certainly worth investigating further.

7.6 Summary and future steps for bridging the divide between the Fermi liquid and strange metal

Let us now summarize the main conclusions of our M-EELS work on \( \text{Sr}_2\text{RuO}_4 \) and then provide an explicit answer to the final question we set out to address in Chapter 1.

At room temperature, we observed that \( \text{Sr}_2\text{RuO}_4 \) exhibits coexisting strange metal and Fermi liquid collective excitations, with local strange metal fluctuations at high energies and momenta and a propagating Fermi liquid mode at low energies and long wavelengths. Upon cooling below \( T_{\text{FL}} \) to 30 K, strange metal fluctuations are suppressed below 0.9 eV and the
Fermi liquid collective mode’s dispersion is strongly renormalized, with a reduction in mode velocity of about 40% at 30 K compared to 300 K. These results imply that strange metal and Fermi liquid collective excitations can simultaneously coexist. Furthermore, we found that the development of Fermi liquid coherence only requires shifting strange metal excitations to higher energy, and not a total transmutation of incoherent strange metal fluctuations into coherent Fermi liquid modes.

Let us now provide an explicit answer to question #3 of Chapter 1 and section 3.2.5

**Question #3:** In what sense, if any, can a Fermi liquid and strange metal coexist? Does one cross over from one regime to the other smoothly, or is there a phase transition?

**Our Answer:** The Fermi liquid and strange metal can simultaneously coexist in the sense that their collective excitations can both be present at the same time. In the case of Sr\textsubscript{2}RuO\textsubscript{4}, this coexistence happens with the strange metal and Fermi liquid occupying different sectors of energy and momentum space, with local strange metal fluctuations persisting over high \((q,\omega)\) and propagating Fermi liquid modes at low \((q,\omega)\). Furthermore, the strange metal and low-temperature Fermi liquid are connected by a crossover, rather than a true phase transition. The manifestation of this crossover to a more Fermi liquid-like state is the gradual suppression of low-energy strange metal fluctuations and their redistribution to high energies where they have weaker impact on low-frequency probes such as resistivity.

Our study of coexisting Fermi liquid and strange metal excitations in Sr\textsubscript{2}RuO\textsubscript{4} also motivate us to pose several important followup questions that are open for future experimentalists to solve.

1. **Strange metal fluctuations in the hydrodynamic regime:** Just as in Bi-2212, the hydrodynamic regime \((qv_f \ll \omega)\) of the high-energy strange metal excitations up to 2.5 eV is obscured by kinematic restrictions and the diverging Coulomb matrix element (see section 6.5). It would be very useful to understand precisely how the broad plasmon in optics connects with the M-EELS strange metal continuum in more detail, especially above and below \(T_{FL}\). Figure 7.12 suggests that significant changes occur in the strange metal
response in the hydrodynamic regime, but more detailed work is needed to clarify this.

2. **Bulk versus surface character of the Fermi liquid mode**: Because M-EELS is sensitive to both bulk and surface excitations, further work is needed to pinpoint the nature of the Fermi liquid mode. If the mode is a surface excitation, does that imply Sr$_2$RuO$_4$ exhibits a 2D Fermi liquid coupled to a 3D strange metal? On the other hand, if the mode is a bulk excitation, why is it gapless?

3. **Incoherent high-temperature regime**: Theoretical studies [205] suggest that the quasiparticle weight in Sr$_2$RuO$_4$ eventually vanishes at around 600 K where T-linear resistivity sets in. How do the Fermi liquid and strange metal collective excitations reflect this behavior?

4. **Charge fluctuations as $T_{FL} \to 0$**: The Fermi liquid coherence temperature can be suppressed to below that of Sr$_2$RuO$_4$ by substituting strontium with calcium in Ca$_{2-x}$Sr$_x$RuO$_4$ [224], examining related compounds such as Sr$_3$Ru$_2$O$_7$ [190, 225], or possibly by applying external fields such as strain. An important question is whether there are clear trends as the Fermi liquid coherence temperature is suppressed. For example, does the charge response Sr$_2$RuO$_4$ and related compounds eventually resemble that of the cuprates at optimal doping as $T_{FL} \to 0$?
In this thesis we set out to understand the nature of charge correlations in the strange metal. In particular, we formulated three questions in Chapter 1 and section 3.2.5:

1. What is so strongly correlated about charge in the strange metal that distinguishes it from the Fermi liquid?

2. How do the strong charge correlations of the strange metal evolve as one leaves the phase (e.g., though doping and temperature)?

3. In what sense, if any, can a Fermi liquid and strange metal coexist? Does one cross over from one regime to the other smoothly, or is there a phase transition?

In our M-EELS study of optimally doped Bi-2212 in Chapter 6 we were able to address question #1. What we found is that the strongly correlated nature of the strange metal is reflected in a continuum of charge fluctuations which is essentially momentum independent. This observation led us to the conclusion that the strange metal is characterized by charge fluctuations that are localized in space and time, unlike the Fermi liquid where charge excitations have well-defined momentum and energy instead.

We then moved on to understand question #2 by mapping the charge response of Bi-2212 across its doping-temperature phase diagram. There, we saw that the primary mechanism by which one enters or leaves the strange metal regime with regards to charge correlations was by redistributing the low-energy spectral weight of the charge response. As one moved from the strange metal to a more incoherent metal in underdoped Bi-2212, there was an
accumulation of spectral weight at low energies. On the other hand, as one went from the strange metal to a more coherent Fermi liquid-like state, low-energy spectral weight was depleted.

Finally, question #3 was addressed in Chapter 7 where we studied Sr$_2$RuO$_4$ with M-EELS. At room temperature, we observed both strange metal collective excitations at high energies and momenta, and a propagating Fermi liquid collective mode at much lower energies and longer wavelengths. Upon cooling below the Fermi liquid coherence temperature $T_{\text{FL}}$, the low-energy spectral weight was depleted from the strange metal continuum and the dispersion of the Fermi liquid collective was strongly renormalized. These results led to the conclusion that strange metal and Fermi liquid excitations can simultaneously coexist. Furthermore, we concluded that the development of coherent Fermi liquid quasiparticles does not necessitate a replacement of all strange metal fluctuations with Fermi liquid modes. Instead, quasiparticle coherence can come about by pushing the strange metal fluctuations to higher energies where they become less relevant to low-energy properties such as transport.

The story does not end here, however. While our M-EELS measurements have revealed the nature of strong correlations in strange metals, they certainly do not pinpoint any theory for describing the circumstances under which those strong correlations come about. Future work is therefore needed to compare the experimentally-determined strange metal charge response to predictions from theory before a consensus on the nature of the strange metal can be reached.
## Appendix A: Common experimental techniques and their corresponding response functions

<table>
<thead>
<tr>
<th>Technique</th>
<th>Correlation/Response Function</th>
<th>Energy Scale of Measurement Process</th>
<th>Length Scale of Interaction</th>
<th>Restrictions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity</td>
<td>Current-current</td>
<td>&lt;0.5 neV</td>
<td>mm - cm</td>
<td>Essentially None</td>
</tr>
<tr>
<td>Hall Effect</td>
<td>(Off diagonal) current-current</td>
<td>&lt;0.5 neV</td>
<td>mm - cm</td>
<td>Essentially None</td>
</tr>
<tr>
<td>SQUID Magnetometry</td>
<td>Magnetization-Magnetization</td>
<td>&lt;0.5 neV</td>
<td>mm - cm</td>
<td>B-field not arbitrary</td>
</tr>
<tr>
<td>NMR</td>
<td>(nuclear) spin-spin</td>
<td>&lt;1 meV</td>
<td>Å (local atomic environment)</td>
<td>B-field not arbitrary</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>Heat current-heat current</td>
<td>μeV to meV</td>
<td>mm - cm</td>
<td>Increasingly difficult at low temp.</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>Energy-Energy</td>
<td>μeV to meV</td>
<td>mm – cm</td>
<td>Increasingly difficult at low temp.</td>
</tr>
<tr>
<td>μSR</td>
<td>(local) Magnetization-Magnetization</td>
<td>neV - meV</td>
<td>Å (local atomic environment)</td>
<td>Low Flux</td>
</tr>
<tr>
<td>Neutron Diffraction</td>
<td>(nuclear) position-position</td>
<td>&lt;1 neV</td>
<td>0.01 –300 Å</td>
<td>Large samples</td>
</tr>
<tr>
<td>Inelastic Neutron Scattering</td>
<td>(nuclear) position-position</td>
<td>neV – 1000 meV</td>
<td>0.01 –300 Å</td>
<td>Large samples, small cross-section</td>
</tr>
<tr>
<td>Magnetic Neutron Scattering</td>
<td>spin-spin (or total J=L+½)</td>
<td>neV – 1000 meV</td>
<td>0.01 – 300 Å</td>
<td>See above</td>
</tr>
<tr>
<td>X-ray Scattering</td>
<td>(electron) density-density</td>
<td>&lt;1 neV</td>
<td>0.01 – 300 Å</td>
<td>Insensitive to light elements</td>
</tr>
<tr>
<td>Inelastic X-ray Scattering</td>
<td>(electron) density-density</td>
<td>1 meV – 2 keV</td>
<td>0.5 – 300 Å</td>
<td>Insensitive to light elements</td>
</tr>
<tr>
<td>Resonant Inelastic X-ray Scattering</td>
<td>Various (spin, charge, orbital)</td>
<td>20 meV – 3 eV</td>
<td>5 – 300 Å</td>
<td>Resonant to atomic core transitions</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Technique</th>
<th>Correlation/Response Function</th>
<th>Energy Scale of Measurement Process</th>
<th>Length Scale of Interaction</th>
<th>Restrictions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Reflectivity (FIR)</td>
<td>Current-current</td>
<td>0.6 meV – 20 eV</td>
<td>500nm - mm</td>
<td>Need gold reference</td>
</tr>
<tr>
<td>Ellipsometry</td>
<td>Current-current</td>
<td>10 meV – 10 eV</td>
<td>500nm - mm</td>
<td>Difficulty in dealing with anisotropy</td>
</tr>
<tr>
<td>THz spectroscopy</td>
<td>Current-current</td>
<td>0.1 –50 meV</td>
<td>mm</td>
<td>Transmission requires thin films</td>
</tr>
<tr>
<td>Dielectric spectroscopy</td>
<td>Current-current (or polarization-polarization)</td>
<td>neV – meV</td>
<td>cm</td>
<td>Sensitive to contributions</td>
</tr>
<tr>
<td>XAS/XES/XANES/XAFS/XESF/XANE</td>
<td>Current-current</td>
<td>100 meV – 20 keV</td>
<td>&lt;0.5 Å, but performed with broad beam</td>
<td>Self-absorption limits contrast</td>
</tr>
<tr>
<td>SHG</td>
<td>Second order current susceptibility</td>
<td>100 meV – 5 eV</td>
<td>500nm - mm</td>
<td>Precise control of pulse shape needed for spectroscopic use</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>Third-order current susceptibility</td>
<td>0.1 meV – 1 eV</td>
<td>500nm at best</td>
<td>Clean conditions, can contain complex contributions</td>
</tr>
<tr>
<td>ARPES</td>
<td>Fermion Green function J (eV)</td>
<td>0.5 meV – 10 eV</td>
<td>2 - 300 Å</td>
<td>Surface-sensitive, needs Ultra-high vacuum</td>
</tr>
<tr>
<td>X-ray Photoemission</td>
<td>Fermion Green function J (eV)</td>
<td>100 meV – 1000 eV</td>
<td>&lt;2 Å, but performed with broad beam</td>
<td>Surface-sensitive, needs high vacuum</td>
</tr>
<tr>
<td>Spectroscopic STM</td>
<td>(Local) Fermion Green function DOS J (eV)</td>
<td>0.01 meV – 1 eV</td>
<td>0.1 – 800 Å</td>
<td>Surface-sensitive, needs Ultra-high vacuum</td>
</tr>
<tr>
<td>Auger Electron Spectroscopy</td>
<td>3rd order charge-charge</td>
<td>100 meV – 1 keV</td>
<td>&lt;1 Å, but performed with broad beam</td>
<td>Surface-sensitive, needs high vacuum</td>
</tr>
<tr>
<td>EELS</td>
<td>Charge-charge</td>
<td>0.5 meV – 20 keV</td>
<td>0.5 - 400 Å</td>
<td>High vacuum needed</td>
</tr>
<tr>
<td>Electron Diffraction</td>
<td>Charge-charge</td>
<td>&lt;1 keV</td>
<td>0.01 – 400 Å</td>
<td>High vacuum needed</td>
</tr>
</tbody>
</table>

Figure A.1: Extended table of common experimental techniques and their associated correlation/response functions. Note that many experiments are sensitive to multiple correlation functions, so this table should be taken as a rough approximation.
Appendix B: Spin, magnetic, and relativistic contributions to the M-EELS cross section

Although the dominant interaction between a probe electron and system of charges is via the instantaneous Coulomb interaction (i.e. electric-field driven), accounting for the spin and magnetic field of the probe electron opens up the possibilities for other novel scattering channels that probe quantities distinct from the dynamic charge response. In particular, exchange scattering, where the probe electron “swaps” places with an electron in a material but still only interacts through the Coulomb potential, allows the measurement of the dynamic spin susceptibility, similar to Inelastic Neutron Scattering. Furthermore, diamagnetic coupling between the vector potential and magnetic field of the probe electron and currents in a material uniquely permit a measurement of the current-current response function at momentum transfers that are not limited to the light cone (i.e. $q \neq \omega/c$), unlike in optical methods. In this section, we will very briefly sketch out derivations for the spin and magnetic contributions to the M-EELS cross section following references [119, 226, 227] and then describe the regimes where they are most accessible in experiment.

B.1 Exchange scattering and spin-resolved M-EELS (SPEELS)

So far, our derivations of the M-EELS cross section have tacitly assumed that the probe electron and system electrons are distinguishable by writing the initial and final states as tensor products of the form
\[ |\Psi_i\rangle = |k_i\rangle \otimes |i\rangle \] \hspace{1cm} (B.1)
\[ |\Psi_f\rangle = |k_f\rangle \otimes |f\rangle . \] \hspace{1cm} (B.2)

Granted, while the probe and system electrons are clearly distinguishable before the scattering process, it is impossible to distinguish whether the scattered electron arriving at the detector is the same electron that was prepared initially, or if it originally belonged to the sample. To account for this indistinguishability, the final state of the combined probe-material system must be fully anti-symmetric as mandated for a system of identical fermions. Thus, written in terms of wave functions, the initial and final wavefunctions for M-EELS are

\[ \Psi_i(r, \sigma_0, r_1, \sigma_1; \ldots; r_n, \sigma_n) = e^{i k_0 \cdot r} \chi_i(\sigma_0) \phi_i(r_1, \sigma_1; \ldots; r_n, \sigma_n) \] \hspace{1cm} (B.3)
\[ \Psi_f(r, \sigma_0, r_1, \sigma_1; \ldots; r_n, \sigma_n) = e^{i k_f \cdot r} \chi_f(\sigma_0) \phi_f(r_1, \sigma_1; \ldots; r_n, \sigma_n) \] \hspace{1cm} (B.4)
\[ - \sum_{k=1}^{n} e^{i k_f \cdot r_k} \chi_f(\sigma_k) \phi_f(\ldots r_{k-1}, \sigma_{k-1}; r, \sigma_0; r_{k+1}, \sigma_{k+1}; \ldots). \] \hspace{1cm} (B.5)

Here, \( r \) is the spatial coordinate of the probe electron and \( r_1 \cdots r_n \) are those of the material. Similarly, \( \sigma_0 \) is the initial spin state of the probe, while \( \sigma_1 \cdots \sigma_n \) are those of the material. The initial state of the probe is that of a plane wave with momentum \( k_0 \), and likewise \( k_f \) for the final state of the detected electron\(^1\). The spin wavefunctions are denoted by \( \chi(\sigma) \). One can see that the summation in equation B.5 represents all possible exchange terms where the probe electron swaps places with a sample electron. Let us now compute the modified Coulomb matrix element with the antisymmetrized final state wavefunction of equation B.5.

Noting that the Coulomb interaction is then given by,

\(^1\)In this section, we will neglect the fact that the surface wavefunction depends non-trivially on the out-of-plane coordinate \( z \) as it is cumbersome and does not add much to the discussion here.
\[
V(\mathbf{r}) = \sum_j \frac{e^2}{|\mathbf{r} - \mathbf{r}_j|},
\]

we can see that the matrix element will separate into two terms. The first represents ordinary Coulomb scattering which we have seen previously

\[
\mathcal{M}_{\text{Coul.}} = \chi_f^\dagger(\sigma_0) \cdot \chi_i(\sigma_0) \int d\mathbf{r} d\mathbf{r}_{1\ldots n} e^{i\mathbf{q} \cdot \mathbf{r}} V(\mathbf{r}) \phi_f^*(\mathbf{r}_{1\ldots n}, \sigma_{1\ldots n}) \phi_i(\mathbf{r}_{1\ldots n}, \sigma_{1\ldots n})
\]

\[
= \delta_{\sigma_f, \sigma_0} V(q) \langle f | \rho(\mathbf{q}) | i \rangle,
\]

where the transition does not change the spin of the probe electron and the matrix element squared is proportional to the dynamic charge response \( \chi''(\mathbf{q}, \omega) \). The second term however, involves exchange processes and is given by

\[
\mathcal{M}_{\text{exch.}} = -\sum_{k,j} \chi_f^\dagger(\sigma_k) \cdot \chi_i(\sigma_0) \int d\mathbf{r} d\mathbf{r}_{1\ldots n} e^{i\mathbf{k_0} \cdot \mathbf{r}_i} e^{-i\mathbf{k}_j \cdot \mathbf{r}_k} V(|\mathbf{r} - \mathbf{r}_j|)
\]

\[
\times \phi_f^*(\cdots \mathbf{r}_{k-1}, \sigma_{k-1}; \mathbf{r}, \sigma_0; \mathbf{r}_{k+1}, \sigma_{k+1}; \cdots) \phi_i(\mathbf{r}_{1\ldots n}, \sigma_{1\ldots n}).
\]

This expression for \( \mathcal{M}_{\text{exch.}} \) can be largely simplified by noting that terms where \( k \neq j \) are virtually zero. To see why this is the case, let us note that the integral for a term where \( k \neq j \) can be written as

\[
\int d\mathbf{r} \prod_{i \neq k} d\mathbf{r}_i e^{i\mathbf{k}_0 \cdot \mathbf{r}_i} V(|\mathbf{r} - \mathbf{r}_j|) \phi_f^*(\cdots \mathbf{r}_{k-1}, \sigma_{k-1}; \mathbf{r}, \sigma_0; \mathbf{r}_{k+1}, \sigma_{k+1}; \cdots)
\]

\[
\times \left( \int d\mathbf{r}_k e^{-i\mathbf{k}_j \cdot \mathbf{r}_k} \phi_i(\mathbf{r}_{1\ldots n}, \sigma_{1\ldots n}) \right).
\]
The last integral in parentheses over \( r_k \) denotes the overlap between the initial wavefunction of the sample \( \phi_i \) and that of a free-electron plane wave \( e^{-ik_f \cdot r_k} \). Since \( k_f \) is comparatively large and sits well above the Fermi energy, this overlap integral is virtually zero because any electron with a sizable overlap with \( e^{-ik_f \cdot r_k} \) would be able to spontaneously escape the sample. Thus, the only terms which contribute to \( M_{\text{exch.}} \) are those where \( k = j \) which have the form

\[
M_{\text{exch.}} = -\frac{1}{n} \sum_j \chi_j^\dagger(\sigma_j) \cdot \chi_i(\sigma_0) \int d\mathbf{r} d\mathbf{r}_{1...n} e^{i k_0 \cdot \mathbf{r}} e^{-i k_f \cdot r_j} V(|\mathbf{r} - \mathbf{r}_j|) \int d\mathbf{r}_1 ... d\mathbf{r}_n \]

\[
\times \phi^*_f(\cdots \mathbf{r}_{j-1}; \mathbf{r}, \sigma_0; \mathbf{r}_{j+1}, \sigma_{j+1}; \cdots \cdot \phi_i(\mathbf{r}_{1...n}, \sigma_{1...n}).
\]

(B.14)

It is worth re-expressing \( M_{\text{exch.}} \) in terms of electron field operators \( \psi^\dagger \) and \( \psi \). To do this, note that the wavefunctions \( \phi_i, \phi_f \) can be written as\(^2\)

\[
\phi_i(\mathbf{r}_{1...n}, \sigma_{1...n}) = \langle \mathbf{r}_{1...n}, \sigma_{1...n}|i\rangle
\]

(B.15)

\[
\phi_f(\cdots \mathbf{r}_{j-1}, \sigma_{j-1}; \mathbf{r}, \sigma_0; \mathbf{r}_{j+1}, \sigma_{j+1}; \cdots |f) = \langle \cdots \mathbf{r}_{j-1}, \sigma_{j-1}; \mathbf{r}, \sigma_0; \mathbf{r}_{j+1}, \sigma_{j+1}; \cdots |f\rangle
\]

(B.16)

\[
= \frac{1}{n} \langle \mathbf{r}_{1...n}, \sigma_{1...n}|\psi^\dagger_{\sigma_0} (\mathbf{r}) \psi_{\sigma_j} (\mathbf{r}_j)|f\rangle.
\]

(B.17)

Thus, \( M_{\text{exch.}} \) can be written as

\[
M_{\text{exch.}} = -\frac{1}{n} \sum_j \chi_j^\dagger(\sigma_j) \cdot \chi_i(\sigma_0) \int d\mathbf{r} d\mathbf{r}_{1...n} e^{i k_0 \cdot \mathbf{r}} e^{-i k_f \cdot r_j} V(|\mathbf{r} - \mathbf{r}_j|) \int d\mathbf{r}_1 ... d\mathbf{r}_n \]

\[
\times \langle f|\psi^\dagger_{\sigma_0} (\mathbf{r}) \psi_{\sigma_j} (\mathbf{r}_j)|\mathbf{r}_{1...n}, \sigma_{1...n}\rangle \langle \mathbf{r}_{1...n}, \sigma_{1...n}|i\rangle,
\]

(B.18)

\(^2\)Note the factor of \( \frac{1}{n} \) in equation B.17 which arises how field operators are normalized in second quantization.
which reduces to

\[ M_{\text{exch.}} = -\frac{1}{n} \sum \int dr_je^{i\mathbf{k}_0 \cdot \mathbf{r}}e^{-i\mathbf{k}_f \cdot \mathbf{r}_j}V(|\mathbf{r} - \mathbf{r}_j|) \langle f|\psi_{\sigma_0=\sigma_f}^\dagger(\mathbf{r})\psi_{\sigma_j=\sigma_f}(\mathbf{r})|i \rangle \]  

(B.20)

\[ = -\int dr' e^{i\mathbf{k}_0 \cdot \mathbf{r}}e^{-i\mathbf{k}_f \cdot \mathbf{r}'V(|\mathbf{r} - \mathbf{r}'|) \langle f|\psi_{\sigma_0}^\dagger(\mathbf{r})\psi_{\sigma_f}(\mathbf{r}')|i \rangle \]  

(B.21)

This exchange transition process thus represents the replacement of a sample electron in spin state \( \sigma_f \) by the probe electron with spin state \( \sigma_0 \). Unlike the ordinary Coulomb scattering process however, this exchange channel allows the spin state of the probe to change from \( \sigma_0 \) to \( \sigma_f \), provided there is a pre-existing electron in the sample with spin \( \sigma_f \). Let us now write \( M_{\text{exch.}} \) in momentum-space as (up to overall constant prefactors)

\[ M_{\text{exch.}} = -\int d\mathbf{k} d\mathbf{k}' \int d\mathbf{r} d\mathbf{r}' e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}}e^{i(\mathbf{k}' - \mathbf{k}_f) \cdot \mathbf{r}'}V(|\mathbf{r} - \mathbf{r}'|) \langle f|\psi_{\sigma_0}^\dagger(\mathbf{k})\psi_{\sigma_f}(\mathbf{k}')|i \rangle \]  

(B.22)

\[ = -\int d\mathbf{k} d\mathbf{k}' \frac{4\pi e^2}{|\mathbf{k}_0 - \mathbf{k}|^2} e^{i(\mathbf{k}_0 - \mathbf{k}) \cdot \mathbf{r}}e^{i(\mathbf{k}' - \mathbf{k}_f) \cdot \mathbf{r}'} \langle f|\psi_{\sigma_0}^\dagger(\mathbf{k})\psi_{\sigma_f}(\mathbf{k}')|i \rangle \]  

(B.23)

\[ = -\int d\mathbf{k} d\mathbf{k}' \frac{4\pi e^2}{|\mathbf{k}_0 - \mathbf{k}|^2} \langle f|\psi_{\sigma_0}^\dagger(\mathbf{k} + \mathbf{q})\psi_{\sigma_f}(\mathbf{k})|i \rangle \]  

(B.24)

\[ = -\int d\mathbf{k} \frac{4\pi e^2}{|\mathbf{k}_0 - \mathbf{k}|^2} \langle f|\psi_{\sigma_0}^\dagger(\mathbf{k} + \mathbf{q})\psi_{\sigma_f}(\mathbf{k})|i \rangle , \]  

(B.25)

where \( \mathbf{q} \equiv \mathbf{k}_0 - \mathbf{k}_f \) is the momentum transfer. A final simplification is possible when the incident electron momentum is much larger than those of the material’s electrons so that \( k_0 \gg k \) and \( V(\mathbf{k}_0 - \mathbf{k}) \approx V(\mathbf{k}_0) \). In this limit, \( M_{\text{exch.}} \) goes as

\[ M_{\text{exch.}} = -\frac{4\pi e^2}{k_0^2} \int d\mathbf{k} \langle f|\psi_{\sigma_0}^\dagger(\mathbf{k} + \mathbf{q})\psi_{\sigma_f}(\mathbf{k})|i \rangle . \]  

(B.26)

We can now see that while the ordinary Coulomb cross section both grows rapidly as \( q \to 0 \)
and is independent of $k_0$, the exchange scattering cross section is independent of $q$ (in the limit where $k_0 \gg q$) and decreases rapidly for increasing incident energy as $k_0^{-4}$ (or equivalently $E^{-2}$). Therefore, exchange scattering is a relatively small contribution to the overall M-EELS cross section for energies above about 25 eV (i.e. wavelengths shorter 2.5 Å, which is smaller than most lattice parameters). The core reason for exchange scattering being small is the large momentum transfer needed for a high-energy probe electron to swap places with a low-energy electron in a material. Because the Coulomb interaction favors small momentum transfer, the probability for exchange processes rapidly decreases with incident beam energy. However, if one had a method to discriminate between spin-preserving and spin-flip scattering, the exchange cross section could be disentangled from the ordinary Coulomb channel because spin-flip events only occur in the former. Focusing then on the spin-flip case where $\sigma_0 = \downarrow$ and $\sigma_f = \uparrow$, the exchange scattering matrix element is given by

$$M_{\text{exch.}} = \frac{-4\pi e^2}{k_0^2} \int dk \langle f | \psi_\uparrow^+(k + q) \psi_\downarrow(k) | i \rangle$$ (B.27)

$$= \frac{-4\pi e^2}{k_0^2} \langle f | \hat{S}_-(q) | i \rangle,$$ (B.28)

where $\hat{S}_-$ is the spin lowering operator. The total scattering cross section for spin-flip exchange scattering can then be written as

$$\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS \ exchange}} = \frac{\pi m^2}{2e^2 \hbar^4} \frac{k_f}{k_0} V(k_0)^2 \langle \hat{S}_+ \hat{S}_- \rangle(q, \omega)$$ (B.29)

$$= -\frac{m^2}{2e^2 \hbar^4} \frac{k_f}{k_0} V(k_0)^2 n(\omega) \chi''_{\pm}(q, \omega),$$ (B.30)

where $n(\omega)$ is the Bose factor and $\chi''_{\pm}(q, \omega)$ is the transverse dynamic spin susceptibility. Thus, a measurement of the spin-flip scattering in M-EELS gives the transverse spin response function, which is directly tied to what is measured with
magnetic Inelastic Neutron Scattering.

Experimentally, the primary method for extracting spin-flip contributions to M-EELS is through the use of a spin-polarized high-energy electron beam combined with a spin-discriminating detector (e.g., using Mott or VLEED detectors [228]). The principle challenge of this approach is threefold: (1) the low flux inherent to spin-polarized electron beams with the meV energy resolution, (2) the low efficiency of electron spin detectors, and (3) the small overall exchange cross section for energies significantly above 25 eV. Thus, spin-resolved EELS (SPEELS) suffers from very low overall count rates. To increase the overall signal, SPEELS has been successfully implemented [229] by using lower beam energies on the order of 7 eV. At these low energies, the exchange cross section becomes strongly enhanced as $k_0$ approaches the Fermi momentum $k_f$ in the system and the Coulomb matrix element in equation B.25 becomes very large. Such low-energy SPEELS experiments have successfully been able to measure the dispersion of magnons in magnetic thin films [230].

While SPEELS methods have become increasingly more efficient in time [229], they have not seen widespread use due to the specialized equipment needed. As a poor-man’s approach, we propose an alternative method for observing spin excitations with M-EELS that does not require the use spin-polarized beams or electron spin detectors, but instead only requires the ability to smoothly change the incident beam energy. Because the exchange cross section strongly depends on the incident beam energy (it is enhanced when $k_0$ is of the order of the Fermi momentum $k_f$) but the ordinary Coulomb contribution remains largely unaffected, one can extract the spin excitations in M-EELS by taking a series of spectra as a function of the incident beam energy at fixed energy loss and momentum transfer. Excitations that only appear at “resonant” energies can be identified as spin excitations, while those that are not are identified as charge excitations. One does not require particularly high signal-to-noise

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3Note that the M-EELS exchange cross section at these low energies is no longer exactly proportional to a dynamic spin susceptibility, but weighs spin excitations slightly differently due to the presence of $V(k_0 - k)$ in equation B.25. One consequence of this is that uninteresting Stoner single spin-flip excitations become slightly enhanced compared to the more interesting collective spin dynamics [226].
with this approach, as the exchange cross section can be stronger than the ordinary Coulomb channel at low energies [230]. Thus, we envision that such a resonant M-EELS instrument may find wider usage the traditional SPEELS setups, although purpose-built electron optics will be needed as the Ibach-style HR-EELS design does not permit smoothly changing beam energy without altering the beam focus.

### B.2 Relativistic and magnetic scattering channels

Complementing exchange scattering at low beam energies, relativistic and magnetic contributions to M-EELS become important at high incident beam energies. When the beam energy is on the order of 100 keV and above, scattering from magnetic fields can be significant. In particular, the dominant magnetic contribution to M-EELS is through diamagnetic coupling between the probe and system. This coupling allows the measurement of dynamic current-current response function. To describe these scattering channels, let us start with the Dirac Hamiltonian for the probe electron in the presence of both a vector and scalar potential

\[ H = c \alpha \cdot (p - eA) + mc^2 \beta - e\phi, \quad (B.31) \]

where \( \alpha, \beta \) are related to the gamma matrices by \( \alpha_i = \gamma^0 \gamma^i \) and \( \beta = \gamma^0 \). To obtain the non-relativistic Pauli limit, one can perform a perturbative expansion using a canonical transformation (i.e. the Foldy-Wouthuysen transformation) with \( H' = e^{iS}He^{-iS} \) using \( S = -\frac{i}{2mc} \beta \alpha \cdot (p - eA) \). Following reference [231] and ignoring negative energy states, one then obtains
\[ H' = mc^2 + \frac{1}{2m}(p - eA)^2 - \frac{e\phi}{c} - \frac{e\hbar}{2m}\sigma \cdot B \]

\[ + \frac{e\hbar}{8m^2c^2}\sigma \cdot (p \times E) - \frac{e\hbar}{4m^2c^2}\sigma \cdot (E \times p) + \frac{i\hbar}{8m^2c^2}p \cdot E + O(p^4) \]

In addition to the familiar kinetic energy and Coulomb terms, there is a Zeeman coupling of spin to magnetic field \((\approx 10^{-4}\) eV), spin-orbit coupling \((\approx 10^{-5} - 10^{-2}\) eV), and a Darwin term \((\approx 10^{-3}\) eV). While there are certain situations where spin-orbit scattering can occur (e.g., Mott scattering from high-Z materials like gold [228], or spin-dependent electron reflectivity from the surface of W(100) [232]), the generically dominant relativistic contribution to M-EELS is through the vector potential in the kinetic energy term as the other terms are, in general, orders of magnitude smaller.

Let us now focus on scattering due to the \(\frac{1}{2m}(p - eA)^2\) term. The interaction Hamiltonian for the probe electron is now given by

\[ H_{\text{int}} = j \cdot A_{\text{ext}} + j_{\text{ext}} \cdot A + O(A^2), \]

where \(j\) is the current operator for the material. It is worth noticing at this point that the coupling caused by the \(j \cdot A\) term is bidirectional, the current of the probe \(j_{\text{ext}}\) couples to the vector potential (or magnetic field) of the material, \(A\), and the vector potential of the probe \(A_{\text{ext}}\) couples to currents in the material, \(j\). Let us first examine the term \(j \cdot A_{\text{ext}}\), which we will see allows M-EELS to measure the current-current response function.

To describe the vector potential of the probe electron moving at velocity \(v\), it is most simple to work in the Lorentz gauge where the scalar potential of the probe satisfies [233]

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\(^{4}\)Note that the first term \(p \times E\) is identically zero for a static electric field, so that only the usual spin-orbit term \(E \times p\) contributes when considering the case of a central Coulomb potential.
\[
\left(-\nabla^2 + \frac{1}{c^2} \partial_{tt}\right) \phi(r, t) = 4\pi \rho = -4\pi e \delta(r - vt) \quad (B.35)
\]

\[
\left(q^2 + \frac{1}{c^2} \partial_{tt}\right) \phi(q, t) = -4\pi ee^{i q \cdot v t} \quad (B.36)
\]

\[
\left(q^2 - \frac{\omega^2}{c^2}\right) \phi(q, \omega) = -4\pi e \delta(\omega - q \cdot v) \quad (B.37)
\]

\[
\Rightarrow \phi(q, \omega) = \frac{-4\pi e}{q^2 - \omega^2/c^2} \delta(\omega - q \cdot v). \quad (B.38)
\]

This form can be compared to the usual instantaneous Coulomb potential for a moving charge which has the form \(\phi(q, \omega) = -\frac{4\pi e}{q^2} \delta(\omega - q \cdot v)\). Furthermore, the vector potential is given by \(A_{ext} = \frac{v}{c^2} \phi\), so the the interaction Hamiltonian can be written as

\[
\mathcal{H}_{int} = j \cdot A_{ext} = -e \phi \cdot \left(\frac{-j \cdot v}{ec^2}\right) \quad (B.39)
\]

Thus, apart from a factor of \((\frac{-j \cdot v}{ec^2})\) and the replacement of \(q^2\) in \(\phi\) by \(q^2 - \omega^2/c^2\), this interaction term is the essentially the same as the usual Coulomb interaction used to derive the M-EELS cross section in Chapter 4. The overall contribution of the \(j \cdot A_{ext}\) term to the M-EELS cross section can then be written as
\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} = \frac{2\pi \gamma^2 m^2 k_f}{\hbar^4 k_0} \sum_n |\langle k_f; n | \mathcal{H}_{\text{int}} | k_i; i \rangle|^2
\]

\[
= \frac{\pi \gamma^2 m^2 k_f}{2e^4 c^2 \hbar^4 k_0} \left( \frac{4\pi e^2}{q^2 - \omega^2/c^2} \right)^2 \sum_n |\langle n | \hat{j}(q) \cdot \frac{v}{c} | i \rangle|^2 \delta(\omega - \omega_{ni})
\]

\[
= \beta^2 \frac{\pi \gamma^2 m^2 k_f k_f}{2e^4 c^2 \hbar^4 k_0} \left( \frac{4\pi e^2}{q^2 - \omega^2/c^2} \right)^2 \langle j_z j_z \rangle(q, \omega)
\]

\[
\equiv \beta^2 \frac{\pi \gamma^2 m^2 k_f}{2e^4 c^2 \hbar^4 k_0} \left( \frac{4\pi e^2}{q^2 - \omega^2/c^2} \right)^2 S_{j_z j_z}(q, \omega)
\]

\[
= -\beta^2 \frac{\gamma^2 m^2 k_f}{2e^4 c^2 \hbar^4 k_0} \left( \frac{4\pi e^2}{q^2 - \omega^2/c^2} \right)^2 n(\omega) \chi''_{j_z j_z}(q, \omega),
\]

where \( \gamma = (1 - v^2/c^2)^{1/2} \) is the Lorentz factor, \( \beta = v/c, \hat{j}_z \) is the current operator aligned parallel to \( v \) (i.e. the z-axis), \( n(\omega) \) is the Bose factor, \( S_{j_z j_z}(q, \omega) \) is the current-current correlation function, and \( \chi''_{j_z j_z}(q, \omega) \) is the current-current response function. The factors of \( \gamma \) are included in the cross section to account for the relativistic density of states (or equivalently the relativistic mass). Equation B.44 shows that M-EELS in the relativistic regime can measure the current-current response function at arbitrary momentum transfer and energies, unlike photon-based techniques which are limited to the light-cone. The appearance of a \( \beta^2 \) factor however, shows that this contribution is suppressed in the non-relativistic limit where the M-EELS cross section reduces to the charge-charge response function.

Signatures of the current response are regularly observed with M-EELS within transmission electron microscopes \([129, 227]\), which operate at beam energies comparable to the electron rest mass, in the form of anisotropies and so-called “magic-angles”. The essential point here is that the current-current response only induces transition parallel to the electron trajectory, while the ordinary charge-charge response is isotropic. To date, most studies of the current response have focused on core electron transitions, and relatively little has been done to explore the current response in the energy and momentum regime of relevance to condensed matter. The primary challenge here is the need for a procedure to disentangle the
charge and current contributions to the M-EELS cross section. Perhaps the most straightforward method to do so would be to acquire M-EELS spectra at various incident beam energies (e.g., 100 keV, 200 keV, 300 keV) because the current response is scales roughly as the kinetic energy over the electron rest mass, while the charge contribution on the other hand remains unchanged\(^5\).

Finally, let us examine the \(j_{\text{ext}} \cdot A\) interaction term which describes the coupling of the probe current to the material’s vector potential. We will show that this term measures the dynamic magnetic fluctuations of the system. Because we wish to describe the vector potential of the material, it is useful now to work in the Coulomb gauge where \(\nabla \cdot A = 0\) so that the vector potential can be written in terms of the instantaneous magnetic field as

\[
A(r, t) = \nabla \times \frac{1}{4\pi} \int d\mathbf{r}' \frac{\mathbf{B}(r', t)}{|\mathbf{r} - \mathbf{r}'|} \tag{B.45}
\]

\[
A(q, t) = i q \times \frac{1}{q^2} \mathbf{B}(q, t) \tag{B.46}
\]

\[
\Rightarrow A(q, \omega) = i q \times \frac{1}{q^2} \mathbf{B}(q, \omega). \tag{B.47}
\]

Thus, we can write the matrix element as

\[
\mathcal{M} = \langle k_f; f | j_{\text{ext}} \cdot A | k_i; i \rangle \tag{B.48}
\]

\[
= \frac{i}{q^2} \langle f |-e\mathbf{v} \cdot \mathbf{q} \times \mathbf{B}(q)|i \rangle \tag{B.49}
\]

\[
= -\frac{i \hbar e}{m q^2} \langle f | \mathbf{B}(q) \cdot \mathbf{k}_0 \times \mathbf{q}|i \rangle \tag{B.50}
\]

So that the total cross section is given by

\(^5\)The factor of \(\gamma^2\) in equation B.44 occurs in both the charge and current cross sections, so its scaling with energy is not important.
\[
\left( \frac{\partial \sigma}{\partial \Omega \partial \omega} \right)_{\text{M-EELS}} = \frac{2\pi m^2 k_f}{h^4 k_0} \sum_n \left| \langle k_f; n | H_{\text{int}} | k_i; i \rangle \right|^2 (B.51)
\]

\[
= \frac{2\pi e^2 k_f}{h^2 k_0} \left( \frac{k_0^2}{q^2} \right) \sum_n |\langle n | B(q) \cdot k_0 \times q | i \rangle|^2 \delta(\omega - \omega_m) (B.52)
\]

\[
= \frac{2\pi e^2 k_f}{h^2 k_0} \left( \frac{k_0^2}{q^2} \right) \langle B_\perp B_\perp \rangle(q, \omega) (B.53)
\]

\[
\equiv \frac{2\pi e^2 k_f}{h^2 k_0} \left( \frac{k_0^2}{q^2} \right) S_{B_\perp B_\perp}(q, \omega) (B.54)
\]

\[
= - \frac{2e^2 k_f}{h^2 k_0} \left( \frac{k_0^2}{q^2} \right) n(\omega) \chi''_{B_\perp B_\perp}(q, \omega), (B.55)
\]

where \( B_\perp \) is the magnetic field oriented perpendicular to both the incident beam momentum \( k_0 \) and the momentum transfer \( q \). Thus, the \( j_{\text{ext}} \cdot A \) interaction allows M-EELS to measure a magnetic field-field correlation function or, equivalently, the dynamic magnetic response function\(^6\). Strictly speaking, measuring this field-field response with M-EELS does not require relativistic electrons, as it essentially describes the impact of the Lorentz force on the probe electron. Nonetheless, this contribution to the M-EELS cross section is small in general compared to the charge response, as even a local magnetic field several Tesla in strength has an energy scale on the order of 0.2 meV.

Currently, there is no straightforward way to extract the field-field response function \( \chi''_{B_\perp B_\perp}(q, \omega) \) from M-EELS spectra in general. The most favorable conditions to cleanly observe \( \chi''_{B_\perp B_\perp}(q, \omega) \) is in insulating magnetic materials where charge and current excitations are largely gapped (with the exception of lattice excitations). In fact, signatures of \( \chi''_{B_\perp B_\perp}(q, \omega) \) have been experimentally observed using (energy-integrated) electron diffraction from the antiferromagnetic insulator NiO \[235\]. There, antiferromagnetic Bragg reflections with the same intensity predicted by theory (about 0.01% of the direct beam) were readily observed in as short as a 0.24 second exposure.

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\( ^6 \)In the absence of time-varying electric fields in the sample, the magnetic field-field response function is equivalent to the current-current response function by Maxwell’s equations.
Appendix C: Supplemental M-EELS spectra taken on Bi-2212

Figure C.1: Momentum dependence of the M-EELS response in the phonon energy region of Bi-2212. Plot of the charge response in OD50K Bi-2212 at 115 K showing the behavior of the phonons as a function of momentum. The spectrum at $q = 0.00$ is anomalous because of the diverging Coulomb matrix element at $q \sim 0$. 

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Figure C.2: Temperature dependence of the M-EELS phonon energy region in Bi-2212 across dopings at a fixed momentum transfer of 0.24 r.l.u. Future work is needed to determine if anything of interest occurs in this region within the resolution limits of M-EELS.

Figure C.3: Temperature dependence of the M-EELS response across dopings in Bi-2212 at $q = 0.10$ r.l.u. These spectra show the same qualitative behavior as in Figure 6.11.
References


