Electronic States of Heavy Fermion Materials

by

Aaron B. Sutton

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Physics
University of Toronto

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Abstract

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The de Haas-van Alphen (dHvA) effect is one of the most powerful and straightforward methods of determining the electronic structure of metals, knowledge of which is essential to understanding the observed physical properties such as resistivity, magnetic structure, and specific heat. Of interest in the field of condensed matter physics are the so-called heavy fermion materials: compounds involving rare earth metals in which strong correlation effects cause the electrons to behave as if they are orders of magnitude heavier than a bare electron.

To enable measurement of these materials, I maintained our in-house data collection system known as DAVIES. Long standing issues in network communication between the involved computers have been mitigated or solved, improving the overall ease of measurement.

Using DAVIES and our $^3$He/$^4$He dilution refrigerator, I completed field modulation dHvA measurements on samples of YbRh$_2$Si$_2$ for field sweeps of 16-13 T and sample rotations from (100)-(110), (100)-(001), and (110)-(001). This yielded the first observation of an orbit that could be attributed to the J-sheet of the Fermi surface. The rotation measurements were compared against basic band structure calculations, which I completed, and more advanced band structure calculations. The calculations are in good agreement with the experimental results, though the ad hoc fitting method requires a more thorough examination to better understand the origin of this agreement.

I also conducted field modulation dHvA measurements on one sample of PrOs$_4$Sb$_{12}$ for sweeps of 10-7 and 6-3 T at temperatures from about 25-2800 mK. A novel technique, which examines the phase of the quantum oscillations, was utilized to explore the occupancy of the Pr crystal field levels and the lower antiferroquadrupolar (AFQ) phase boundary. These results were compared against mean field calculations, which took into account nearest neighbor quadrupolar coupling and the hyperfine interaction in the Hamiltonian. We obtained good
agreement of the theoretical and experimental phase boundary, except at the lowest tempera-
tures, in which a tail was predicted by calculations but not observed by experiment. This lead to the conclusion that further refinement of our mean field theory would be an interesting pursuit for future research into this material.
This thesis is dedicated to my parents. Without their steadfast support and belief in my abilities over the past three decades, none of this would have been possible.
Acknowledgements

At the outset of my PhD, I had two clear and definitive projects set before me. The first, was the completion of a Superconducting QUantum Interference Device (SQUID) based noise thermometer, a project I had begun as an undergraduate research assistant in the summer of 2006. The second, was to improve the recent de Haas-van Alphen (dHvA) quantum oscillation measurements made by another graduate student, Patrick Rourke, on the heavy fermion (HF) material YbRh$_2$Si$_2$. I assumed that these projects would be the beginning of my graduate career, and would eventually transition into different but related measurements on a variety of materials. What I suppose I underestimated was both the difficulty of these measurements, and the depth to which one could study a single material. Every measurement on YbRh$_2$Si$_2$ uncovered another aspect of a complex story, that didn’t always seem to make sense, but through persistence, repeated experimentation, head scratching, and dedication, has come to provide a clear picture of the electronic structure of a heavily studied system, that agrees extremely well with theoretical calculations based on Density Functional Theory (DFT) but only if they are modified in a way that is difficult to justify.

I believe that the narrative arc of my PhD experience has many elements in common with the present day theory of condensed matter physics, and scientific discovery on the whole in that the more we unearthed about the material we were studying, the more complicated the picture appeared to be.

I could probably write another entire book dedicated to exploring the countless ways in which numerous people have supported me in the completion of my thesis. I will try my best to give credit where credit is due.

Without question, the first acknowledgement has to go to my supervisor, Dr. Stephen Julian. He took me into his lab as an undergraduate researcher in the summer of 2006 and has guided me ever since. His extensive knowledge of experimental low temperature physics, combined with a deep understanding of the theory required to explain our observations makes him the best scientist I’ve ever had the pleasure of working with. Perhaps most importantly, Stephen also has an intuitive feeling of the physical underpinnings of our work that I believe surpasses his peers. His ability to describe challenging physical concepts in a straightforward and interesting manner makes him an incredible teacher and mentor. It has been an absolute pleasure working with him.

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He encouraged me to continue working when things were hard and to believe in myself when I was full of self doubt. I am endlessly grateful for everything he has done for me.

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Contents

1 Introduction
   1.1 Strongly Correlated Electron Systems ............................................. 3
       1.1.1 Theory of the Fermi Liquid .................................................. 4
           Drude Model ........................................................................... 5
           Sommerfeld Theory ................................................................. 6
           The Landau Fermi Liquid ......................................................... 11
       1.1.2 Non-Fermi Liquids ................................................................. 13
           Quantum Criticality .................................................................... 14
       1.1.3 Density Functional Theory ....................................................... 15
   1.2 Multipole Moments ........................................................................... 22
   1.3 The de Haas-van Alphen Effect ....................................................... 23
       1.3.1 Zero Temperature Theoretical Explanation ................................ 24
           Onsager Relation ....................................................................... 24
           Lifshitz-Kosevich Formula without Damping ............................... 28
       1.3.2 T>0 and Other Real World Issues ............................................ 29
           Temperature Damping Factor, $R_T$ ............................................ 29
           Dingle Factor, $R_D$ .................................................................. 30
           Electron Spin Factor, $R_S$ ......................................................... 31
       1.3.3 Experimental Observation ......................................................... 33
           Applications of Oscillation Phase vs. Temperature .................... 37
           Magnetic Breakdown .................................................................. 38
           True Frequency ......................................................................... 40

2 Instrumentation and Analysis Software ........................................... 42
   2.1 Equipment ....................................................................................... 43
       2.1.1 Dilution Refrigerator ................................................................. 43
       2.1.2 dHvA Equipment .................................................................... 44
       2.1.3 Data Collection ...................................................................... 50
           Overview .................................................................................. 52
           DAVIES Data Collection Backend .............................................. 53
Route 66 Error ................................................................. 54
2.1.4 Data Analysis ........................................................ 56
Python Data Analysis Software ........................................ 56

3 YbRh$_2$Si$_2$ .............................................................. 63
3.1 Introduction ............................................................ 63
3.2 Experiment ............................................................. 65
3.3 Calculations ........................................................... 73
3.4 Results ................................................................. 77
3.4.1 Orientation Issue ............................................... 78
3.4.2 Measurements .................................................... 78
3.4.3 Analysis of Harmonics ........................................... 89
3.5 Conclusions .......................................................... 91

4 PrOs$_4$Sb$_{12}$ ............................................................. 92
4.1 Introduction ........................................................... 92
4.2 Experiment .......................................................... 102
4.3 Calculations .......................................................... 106
4.4 Results ................................................................. 111
4.5 The $H_{c1}$ Quantum Critical Point .............................. 117
4.5.1 Comparison to LiHoF$_4$ ........................................ 127
4.6 Conclusions .......................................................... 129

5 Summary ................................................................. 131
5.1 Data Collection ........................................................ 131
5.2 YbRh$_2$Si$_2$ ............................................................ 132
5.3 PrOs$_4$Sb$_{12}$ .......................................................... 132

A Crystal Field Levels in PrOs$_4$Sb$_{12}$ ......................... 134

B SQUIDs ................................................................. 137
B.1 Introduction .......................................................... 137
B.2 Background .......................................................... 137
  B.2.1 Josephson Junctions .......................................... 138
B.3 DC SQUIDs .......................................................... 141
B.4 Noise Thermometry ................................................ 143
  B.4.1 Realization of the Noise Thermometer .................... 144

Bibliography .............................................................. 145
## List of Figures

1.1 Fermi surface of sodium metal ........................................... 9  
1.2 APW solution regions ..................................................... 21  
1.3 Breakdown orbit ......................................................... 41  

2.1 Coil schematic ............................................................. 46  
2.2 Graphite rotation mechanism ........................................... 48  
2.3 Rotation drive ............................................................ 49  
2.5 Experimental setup ...................................................... 57  
2.6 Comparison of dHvA analysis software ................................. 62  

3.1 YbRh$_2$Si$_2$ Crystal structure .......................................... 66  
3.2 YbRh$_2$Si$_2$ Phase diagram ............................................ 67  
3.3 X-ray diffraction for YbRh$_2$Si$_2$ “A” sample ........................ 68  
3.4 YbRh$_2$Si$_2$ “A” sample orientation ................................... 68  
3.5 YbRh$_2$Si$_2$ sample A coil ............................................. 69  
3.6 YbRh$_2$Si$_2$ sample B ................................................... 70  
3.7 Example Lifshitz-Kosevich fit for mass ................................ 73  
3.8 YbRh$_2$Si$_2$ “small” vs. “large” Fermi surface ....................... 75  
3.9 Calculated “large” Fermi surface of YbRh$_2$Si$_2$ ..................... 76  
3.10 Renormalized band structure surface of YbRh$_2$Si$_2$ ............... 77  
3.11 Original observation of new frequency in YbRh$_2$Si$_2$ ............. 79  
3.12 Original angle rotation study of YbRh$_2$Si$_2$ ....................... 81  
3.13 Example YbRh$_2$Si$_2$ oscillations .................................... 82  
3.14 2D cross section of YbRh$_2$Si$_2$ FS .................................. 84  
3.15 Recent dHvA rotation study of YbRh$_2$Si$_2$ ......................... 86  
3.16 Bessel function fit of YbRh$_2$Si$_2$ .................................... 90  

4.1 Phase diagram of PrOs$_4$Sb$_{12}$ .......................................... 94  
4.2 PrOs$_4$Sb$_{12}$ crystal electric fields ................................... 95  
4.3 PrOs$_4$Sb$_{12}$ crystal structure ........................................ 96  
4.4 PrOs$_4$Sb$_{12}$ crystal structure ........................................ 97  
4.5 Fermi surface of PrOs$_4$Sb$_{12}$ ......................................... 98
4.6 Raw dHvA data for PrOs$_4$Sb$_{12}$ from McCollam et al. ........................................... 100
4.7 Bessel function for PrOs$_4$Sb$_{12}$ ................................................................. 103
4.8 Example dHvA trace and FFT for PrOs$_4$Sb$_{12}$ ............................................. 104
4.9 Comparison of phase in PrOs$_4$Sb$_{12}$ at two temperatures ....................... 105
4.10 Percentage occupation of crystal field levels ................................................. 110
4.11 Raw dHvA traces for PrOs$_4$Sb$_{12}$ for sweeps of 10^{-7} T ......................... 112
4.12 Filtered dHvA traces for PrOs$_4$Sb$_{12}$ for sweeps of 10^{-7} T .................... 113
4.13 Filtered dHvA traces for PrOs$_4$Sb$_{12}$ for sweeps of 6-3 T ......................... 114
4.14 Comparison $\Delta \phi$ Plot for PrOs$_4$Sb$_{12}$ .................................................. 115
4.15 Expanded low temperature $\Delta \phi$ vs. T plots ............................................. 118
4.16 Quadrupole moment calculation ................................................................. 119
4.17 Calculation of AFQ transition ................................................................. 120
4.18 Triplet dispersion ................................................................. 122
4.19 Phase vs. temperature Fit ................................................................. 124
4.20 Frequency vs. field fit ................................................................. 125
4.21 Phase boundary ................................................................. 126
4.22 Phase diagram of LiHoF$_4$ ................................................................. 129
B.1 Josephson junction ................................................................. 138
B.2 DC SQUID ................................................................. 141
B.3 DC SQUID characteristics ................................................................. 143
B.4 Noise thermometer ................................................................. 144
B.5 Noise thermometer sensor ................................................................. 145
Chapter 1

Introduction

“An expert is a person who has found out by his own painful experience all the mistakes that one can make in a very narrow field.”

– Niels Bohr, as quoted by Edward Teller in *LIFE* magazine, (6 September 1954), p. 62

Most people seem to believe that what we, as experimental condensed matter physicists, do on a day-to-day basis is totally unrelatable, esoteric scientific research for the sake of progressing human knowledge. They fail to see that they, in fact, have extensive experience with the types of materials we study. Whether it be through fridge magnets holding pictures to a fridge, or pots and pans of different materials, some of which seem to heat food more quickly and evenly. The inquisitive person among us may even wonder, “what makes one metal a better pot than another?” It is this type of wonder in everyday things (though at the time certainly not pots and pans) that lead ancient humans to begin creating stories and explanations for how our universe worked. Before science, we naïvely believed that the nature of our universe could be explained by the inclusion of a magical sky wizard, whose omnipotence, omniscience, and benevolence, crafted a world specifically for us, and created all things in this world with a specific purpose, even if this purpose was unclear. As we learned more about our world, we began to be able to make predictions about what we would observe based on past experience and eventually, using the language and power of mathematics. Ancient scientists wanted to understand what everything was made of, leading Democritus to create the idea the atom. Generation upon generation added to our body of scientific knowledge and improved our understanding of the
atom. John Dalton built upon Democritus’ idea of the atom by imagining it as a small, circular, indivisible entity. As our experimental equipment and resolution improved, so did our understanding of the atom. Everything changed after the discovery of the electron at the Cavendish Laboratory in Cambridge, UK in 1897 by J.J. Thomson [1], and through further exploration we arrived at Ernest Rutherford’s model of the atom (also from Cavendish Labs) [2], followed by improvements by Niels Bohr [3], and the discovery of the neutron in 1932 by James Chadwick [4]. Alongside the development of the theory of the atom, physicists such as Louis Victor de Broglie, Max Born, Erwin Schrödinger, Werner Heisenberg, Albert Einstein, and Paul Dirac (amongst others) were laying down the fundamentals of quantum theory, which would allow us a much more complete (as of present) understanding of the atom. The speed at which these discoveries were made is absolutely astonishing.

The rigorous/mathematical understanding of the properties of metals sprung forth after the discovery of the electron. As an interesting aside, the governing equations of electromagnetism, known as Maxwell’s equations, were derived by James Clerk Maxwell between 1861 and 1862 [5], before the electron had been discovered! Early theoretical descriptions of the properties of metals, specifically that of Paul Drude in 1900 [6, 7], sought to explain electrical conduction, and even without a knowledge of electron interactions and quantum theory, did a remarkably good job of explaining and predicting properties such as AC/DC conductivity, and thermal conductivity but grossly miscalculated things, such as heat capacity, in a variety of materials. The Drude theory of metals, as it came to be known, was significantly improved upon by the inclusion of Fermi-Dirac statistics by Arnold Sommerfeld [8] and the effect of the periodic lattice on the electron wave function by Felix Bloch [9]. A major step forward in the theory of metals was published by Lev Davidovich Landau between 1956–1958 in what is now called Fermi liquid theory [10–12]. Landau’s theory not only corrected many of the issues present in the Drude-Sommerfeld theory, but also showed why this old model had proven so successful.

At the same time that Landau was developing his theory of metals, John Bardeen, Leon Cooper, and John Schrieffer (BCS) solved a problem that had remained unanswered since its discovery in 1911. Heike Kamerlingh Onnes first observed superconductivity in pure metals in 1911, but it was not until the BCS theory of 1957 that the origins of this phenomenon were understood [13]. This ignited excitement in condensed matter physics, with extensive theore-
ical and experimental work being conducted. In the mid-1960s, Hohenberg, Kohn, and Sham developed what’s now known as Density Functional Theory (DFT) [14, 15], which built upon the Thomas-Fermi model [16, 17], and allowed for theoretical computation of the band structure of real metals, a technique used in chapter 3 of this thesis. Throughout the rest of the 20th century, many exotic materials were explored with new and exciting properties, such as the cuprate high temperature superconductors discovered in 1986 [18]. Of particular importance to this thesis was the discovery of the Heavy fermion (HF) material CeAl$_3$ in 1975 by Andres et al. [19], which kicked off a vast amount of research into HF physics. Additionally, the discovery in 1991 of heavy fermion materials whose properties differed from those predicted by Landau’s Fermi liquid theory by Seaman et al. in Y$_{1-x}$U$_x$Pd$_3$ garnered additional excitement for condensed matter physics [20]. The interest in these non-Fermi liquid HF materials was also stoked by the discovery of the unconventional superconductor CeCu$_2$Si$_2$ by Frank Steglich in 1979 [21], and the discovery of a Quantum Critical Point (QCP) in a HF material by von Löhneysen in 1995 [22]. QCPs are discussed further in section 1.1.2. The interest in HF materials, though beginning to slow down at present, led me to carry on the work of Patrick Rourke on YbRh$_2$Si$_2$, discussed in chapter 3 using the de Haas-van Alphen effect, discussed in section 1.3, and as well to carry out measurements on PrOs$_4$Sb$_{12}$, chapter 4. These measurements were carried out at low temperature in our Oxford Instruments Kelvinox 400MX dilution refrigerator with analysis completed using software I designed, described in section 2.1.4.

1.1 Strongly Correlated Electron Systems

This section attempts to provide the reader with a semi-comprehensive overview of the theoretical/mathematical background required for an understanding of the measurements and analysis performed throughout my thesis. Those unfamiliar with, or just getting into condensed matter physics would benefit from a chapter that starts from a basic, classical picture, and builds upon this, showing the logical progression that took place in developing the more modern theory of interacting electrons. The following will not provide the reader with the basics of electromagnetism and the Maxwell equations [5], but the results of this fundamental work will be used throughout, when treating electrons moving in electric or magnetic fields. Also, I will inter-
changeably use the symbols $B$ and $H$ for magnetic field: $B$ being the magnetic flux density, in units of Tesla, and $H$ often called the magnetic field strength, in units of A/m. $B$ and $H$ are related to each other through the relation,

$$B = \mu_0 (H + M) = \mu_0 (1 + \chi_v) H = \mu H,$$

where $\mu_0$ is a fundamental constant, the permeability of free space with units T·m/A, $\chi_v$ is the volume susceptibility of the material in question, and $\mu$ is the resulting relative permeability of the material. The unit quoted in our dHvA measurements is kT (kilotesla). I will first discuss the developments in interacting fermions, which will lead naturally to a discussion of the effect used as a measurement technique in this work. Technical considerations will be discussed in chapter 2.

In general, strongly correlated electron systems are ones in which the interactions of the electrons produce new and exotic properties or states of matter, not easily predicted from the basic quantum mechanics of the system. One such type of system are the so-called heavy fermion materials, in which the electrons or quasiparticles appear to have a mass much larger (often 1000 times or more) the bare electron mass. Such systems have been shown to exhibit interesting forms of magnetism and superconductivity, such as in UPt$_3$, URu$_2$Si$_2$ and CeCu$_2$Si$_2$ [21, 23–25]. Normally, these materials are well described by Fermi liquid theory, which stems from the understanding of the non-superfluid properties of $^3$He. Additionally, Fermi liquid theory is able to account for many of the differences between theory and experiment of metals other than the simple, alkali metals, which tend to be adequately described by the Sommerfeld theory.

1.1.1 Theory of the Fermi Liquid

The theory of Strongly Correlated Electron Systems (SCES) is one that finds its true mathematical origins in the work of a number of scientists in the late 19th and early 20th century. It was not, however, until the middle of the 20th century that we were given the rigorous mathematical model of systems of interacting fermions in the normal state that we still use today. This theory, known as Fermi liquid (FL) theory, was the work of Lev Davidovich Landau [10–
12], and was published originally in the Soviet Journal of Physics (JETP) and a few years later was translated into English. This is discussed in the Landau section below. Landau’s work built upon a non-interacting, classical picture of electrons moving in a solid, known as the Drude Model [6, 7], which is discussed in the following section, and the work of Sommerfeld and Bloch [8, 9], known as the Sommerfeld theory of metals, discussed in the Sommerfeld section below. A surprising result of the classical picture, and likely a mathematical accident, is its ability to make accurate predictions of various properties of metals even without utilizing the quantum mechanical properties of the system.

**Drude Model**

Developed at the turn of the century by Paul Drude, his theory attempted to explain the transport properties of materials, mainly metals, using the kinetic theory of gases as the basis. The full detail can be found in the “bible” of condensed matter physics, Ashcroft & Mermin [26], though one could also attempt to read Drude’s original papers in their full German glory, as a direct translation does not seem to exist [6, 7]. The specific tenets of the Drude theory are:

1. Valence electrons move freely throughout the material until they collide with something, and the negative charge of the electron is compensated by positive charges which are stationary.

2. Between collisions, the electrons do not interact with the positive ionic background. This is known as the **free electron assumption** [26].

3. Likewise, the electrons do not interact with each other and collisions occur between ions and electrons, not electrons and other electrons. This is called the **independent electron assumption** [26].

4. Collisions occur instantaneously and with a probability per unit time of $1/\tau$ where $\tau$ is the average time between collisions. So, the probability of a collision occurring during a time interval $dt$ is $dt/\tau$ [26].
While there are certainly other aspects to the theory, these are taken to be the key few. From this, Drude calculated a variety of metallic properties. His simple picture, without any knowledge of quantum theory, did an excellent job of predicting both AC and DC conductivity in metals, including plasmons and predicting that radiation with frequency greater than some critical frequency (plasma frequency) could propagate through the material, rendering it effectively transparent, which has been demonstrated in the alkali metals [26]. Additionally, it could explain the Hall effect, though the positive charge carriers, observed in many systems, could not be accounted for. Impressively, as well, Drude was able to theoretically derive the Wiedemann-Franz law, which predicted that the ratio of the thermal conductivity, $\kappa$, to electrical conductivity, $\sigma$, was a constant times the temperature, specifically,

$$\frac{\kappa}{\sigma} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2 T,$$

and thus the constant had a value of about $1.11 \times 10^{-8}$ watt-ohm/K$^2$. As Ashcroft and Mermin point out, in his original calculation Drude made a factor of two error and arrived at a value of $2.22 \times 10^{-8}$ watt-ohm/K$^2$, which was in excellent agreement with the experimental value [26].

Despite the enormous success of the Drude model, it failed to explain a number of properties, including magnetoresistance, and many low temperature properties, and greatly overestimated the impact of the electronic contribution to the specific heat at room temperature. In fact, the great success was in part due to the cancellation of two errors, namely that the average electronic speed was about a factor of 100 too small, and the electronic specific heat a factor of 100 too large [26].

**Sommerfeld Theory**

Even if the Drude model suffered from a number of theoretical and conceptual issues, its fantastic agreement with theory sparked huge interest in the field. Following the development of quantum theory, Arnold Sommerfeld built upon the Drude model through the inclusion of Fermi-Dirac statistics for the electron, developed by Enrico Fermi [27] and Paul Dirac [28], and by utilizing the periodic background created by the positive ions as a weak perturbation, thus modifying what was known above as the **free electron assumption** into what is called
the **nearly free electron assumption**. Electron-electron interactions are still ignored in the Sommerfeld theory of metals [26].

Building upon developments in the electronic structure of atoms, Wolfgang Pauli was able to explain the stability and electronic groupings of the Bohr model of the atom through the use of the, later named, Pauli exclusion principle. In its simplest form it states that no two electrons can occupy the exact same quantum state (be defined by the same quantum numbers) [29]. This led to the development of Fermi-Dirac statistics, which instead of assuming all electrons in the ground state to be adequately described by the Maxwell-Boltzmann distribution that originated in using the ideal gas as an analogy for the electron gas, assumed that the electronic energy distribution was modified by the Pauli exclusion principle. The Fermi-Dirac distribution is given as,

\[
f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}, \tag{1.3}\]

where \(\mu\) is the chemical potential, which to 2nd order in \(T\) is,

\[
\mu \simeq \epsilon_F \left[ 1 - \frac{1}{3} \left( \frac{\pi k_B T}{2 \epsilon_F} \right)^2 \right], \tag{1.4}\]

where \(\epsilon_F\) is known as the Fermi energy. The Fermi energy is of critical importance to this thesis, as it defines the maximum occupied energy level occupied by the electrons at zero temperature. As is seen in equation 1.4, it is equal to the chemical potential at zero temperature.

As Ashcroft & Mermin point out, the fundamental contribution of the Sommerfeld model was simply assuming a Fermi-Dirac distribution for the electrons instead of the Maxwell-Boltzmann distribution [26]. Thus, before discussing the **nearly free electron assumption**, we can already see the implication of this modification. Solving the time independent Schrödinger equation for a free electron yields so-called plane wave solutions for the wave functions, where

\[
\psi_k(r) = \frac{1}{\sqrt{V}} e^{i \mathbf{k} \cdot \mathbf{r}}, \tag{1.5}\]

where \(\mathbf{k}\) is the wave vector, \(\mathbf{r}\) is the position vector, and the bold typeface is used to indicate a
vector quantity. This gives a resultant electronic kinetic energy of,

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m}$$  \hspace{1cm} (1.6)

Electrons are placed in energy levels in momentum or k-space (in 3D), with each point being occupied by electrons of both up and down spin. The energy levels are filled until all electrons have been placed. This yields a spherical Fermi surface for the parabolic band given in equation 1.6. By then introducing the periodicity of the crystal lattice, as was done by Felix Bloch [9], we obtain the nearly free electron model, in which the wave function of the freely itinerant electrons is modified by a weak potential provided by the ions which have been screened by both the core electrons, which are assumed bound to the atom, and the conduction electrons. The full Bloch wave function for the electron is written as,

$$\psi_k(r) = u_k(r) e^{i k \cdot r},$$  \hspace{1cm} (1.7)

where $u_k(r)$ has the periodicity of the lattice. This yields an energy band structure with the periodicity of the lattice and allows for more complex Fermi surfaces than the simple quadratic energy band of the free electron. This notion of bands, which are modified by the interactions of the electrons and their environment, forms the basis of fermiology or the study of the energy topology of electrons in crystal structures. Much more complex band structures are computed, in modern times, using a variety of numerical methods, as is described in section 1.1.3. The weak interaction of the nearly free electrons with the ions causes the system to lift the degeneracy of the bands at specific high symmetry points, the Brillouin zone (BZ) boundaries, yielding a spacing between bands, known as a band gap. In the simplest terms, materials that have a Fermi surface, i.e. the Fermi energy falls within a band, are conductors. Those materials that have a filled band as the highest occupied energy level are band insulators.

Besides the introduction of the concepts of the band theory of materials, the Sommerfeld model was successful in predicting the electronic contribution to the specific heat, thanks
Figure 1.1: The near perfectly spherical Fermi surface of sodium metal, calculated using Wien2k.
to the inclusion of Fermi-Dirac statistics, and was given as,

\[ c_v = \frac{\pi^2}{2} \left( \frac{k_B T}{\epsilon_F} \right) n k_B. \]  

(1.8)

Where \( \epsilon_F \) is the Fermi energy, and \( n \) is the conduction electron density of states at \( \epsilon_F \). The inclusion of a \( T \)-linear term in the specific heat due to the electrons was an enormous step in the right direction, and would eventually show why the effect of the electrons on the room temperature specific heat was so unimportant (phonons contribute a \( T^3 \) term). The contribution linear in \( T \) can be understood from the fact that only electrons within \( \sim k_B T \) of the Fermi energy are excited above the Fermi energy upon increasing the temperature; there are limited available states within \( k_B T \) for electrons deep below the FS to move into [26]. From this, Sommerfeld derived a new version of the theoretical understanding of the Wiedemann-Franz law, which agreed closely with that predicted by Drude, but without the erroneous cancellation of terms \( O(k_B T) \).

The Sommerfeld model, through the inclusion of Fermi-Dirac statistics, pushed us into a new era of understanding the properties of materials, however, it was unable to give insight into a number of outstanding issues including the origin of \( T^3 \) term in the specific heat (predicted by Debye, involving lattice collective excitations that were later called phonons [30]), magnetoresistance, and the Hall coefficients of some metals, to name a few. In discussing the Sommerfeld theory, a number of other extremely important results were combined or utilized without derivation in order to accelerate this discussion. Specifically, the inclusion of Bloch functions, the considerations of the periodicity of the lattice to form the nearly free electron model, and the idea of fermiology and band gaps were simply taken as \( a \ priori \) notions, eliminating the need for a separate section on the more quantum theory of electrons in metals. Both theories were completed in quick succession, with the Bloch theory flowing naturally from the Sommerfeld one. The Bloch theory gave us band structures, a new picture with which to see the possible properties of the materials, and through the application of theoretical atomic potentials, such as the tight-biding model or the nearly free electron model, we were given the numerical tools through which to compare our experimental results.
The Landau Fermi Liquid

Building upon this brief introduction to the theory of many body physics, we are now able to begin to discuss the modern basis of systems of interacting fermions. The so-called Landau Fermi Liquid (FL) theory was developed by Lev Davidovich Landau in a series of papers \cite{10–12} published in the Soviet Journal of Physics (JTEP) between 1956–1958. Originally intended to explain the low temperature properties of liquid $^3$He, the theory was also applied to electrons in crystal structures. It builds upon the Sommerfeld theory of metals through the inclusion of electron-electron interactions using a mean-field type approach. The central feature is the renormalization of the bare electrons into so-called quasiparticles, which retain a one-to-one correspondence with the original electrons. Great summaries are provided by Abrikosov \cite{31}, Neilson \cite{32}, and the textbook of Pines & Nozières \cite{33}.

Landau took a high density system of strongly interacting fermions, living near the Fermi surface, and mapped these electrons onto a low density liquid of fermionic excitations called “quasiparticles” \cite{10}. The low-lying quasiparticle excitations in the vicinity of the Fermi surface are prevented from scattering due to phase space constraints, making the quasiparticle states long lived \cite{32}. Following the discussion in Ashcroft & Mermin, if we begin with a filled Fermi sphere plus one electron at energy, $\epsilon_1$, we consider the ways in which it can scatter. It must interact with an electron at energy $\epsilon_2$ which is necessarily less than $\epsilon_F$, since no other occupied states exist at $T = 0$. The energies to which these electrons scatter, $\epsilon_3$ and $\epsilon_4$, must be above $\epsilon_F$. Energy conservation requires that,

$$\epsilon_1 + \epsilon_2 = \epsilon_3 + \epsilon_4.$$  \hspace{1cm} (1.9)

Satisfying all these conditions for $\epsilon_1 = \epsilon_F$ gives

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon_F \hspace{1cm} (1.10)$$

and so there is zero volume into which the electron can scatter and so the lifetime is theoretically infinite. Increasing $\epsilon_1$ slightly yields a small amount of phase space of width $|\epsilon_1 - \epsilon_F|^2$ for scattering, and so the quasiparticle is long lived. The interaction between the non-interacting
fermions is turned on very slowly, and such that by \( t = 0 \), the interaction is at full strength. From all this, a new excited state energy of the system is calculated as,

\[
\delta E = \sum_{k\sigma} \epsilon_0(k\sigma) \delta n(k\sigma) + \frac{1}{2} \sum_{k\sigma, k'\sigma'} f(k\sigma, k'\sigma') \delta n(k\sigma) \delta n(k'\sigma'),
\]

where,

\[
\delta n(k\sigma) = n(k\sigma) - n_0(k\sigma)
\]
represents the change in occupation from the \( T = 0 \) K equilibrium distribution, \( n_0(k\sigma) \), and the excited state, \( n(k\sigma) \), and,

\[
f(k\sigma, k'\sigma') = \frac{\delta^2 E}{\delta n(k\sigma) \delta n(k'\sigma')},
\]

which describes the interaction between quasiparticles. We then define the velocity of the quasiparticle as,

\[
v_k = \frac{1}{\hbar} \nabla \epsilon_{k\sigma} = \frac{\hbar k}{m^*},
\]

where \( m^* \) is the quasiparticle effective mass \[32\]. The strength of Fermi liquid theory is that it is a powerful microscopic theoretical treatment, yet it provides a number of measurable quantities to compare to, specifically, the electronic contribution to the resistivity, specific heat, and susceptibility of the system, whereby

\[
\rho \propto AT^2.
\]

\[
c_v \propto \gamma T
\]

\[
\frac{1}{\chi_M} = \frac{\pi^2}{\mu_B^2 m^* k_F} \left[ 1 + F_{a0} \right],
\]

where \( F_{a0} \) is a Landau parameter \[32, 34\]. From Ashcroft and Mermin eq. 17.66, the scattering rate of carriers in a Fermi liquid goes as \[26\],

\[
\frac{1}{\tau} = A_0 \frac{1}{\hbar} \frac{(k_BT)^2}{\epsilon_F},
\]
which follows from electrons occupying a thermally excited shell in k-space of width $k_B T$, and thus area of $O (k_B T)^2$. Then, substituting in

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m^*}$$

(1.19)

and

$$\rho = \frac{m^*}{ne^2} \frac{1}{\tau},$$

(1.20)

we obtain the expression for $A$,

$$A = A_0 \frac{2m^*k_B^2}{ne^2\hbar^3 k_F^2}$$

(1.21)

where $A_0$ is a constant that can be related to $f(k\sigma,k'\sigma')$. Importantly for heavy fermion materials, the ratio of the $T^2$ coefficient of resistivity to the square of the T-linear specific heat coefficient, $\frac{A}{\gamma}$ is approximately a constant, $1.0 \times 10^{-5} \, \mu\Omega \text{cm} \, (\text{mol K/mJ})^2$. This is known as the Kadowaki-Woods ratio [35]. As well, the Sommerfeld-Wilson ratio, $R_W = \frac{\pi^2 k_B^2 \chi}{3\mu_{\text{eff}}^2 \gamma}$, should be of order unity. $\chi$ is the Pauli susceptibility, and $\mu_{\text{eff}}$ is the effective quasiparticle magnetic moment [36].

### 1.1.2 Non-Fermi Liquids

While the above theory of Fermi liquids explains a number of normal metals, and $^3$He, there are, of course, exceptions to the rule. Many of the exotic materials that condensed matter physicists are interested in researching are so-called non-Fermi liquid materials (nFLs). Examples of such materials are the high-temperature superconductors and some heavy fermion materials, including YbRh$_2$Si$_2$ which was the material of my primary focus, discussed in chapter 3. In many of these $f$-electron heavy fermion materials, the temperature dependent properties deviate from their expected Fermi liquid values, specifically they follow different power laws where [37],

$$\rho \propto T^{1+\epsilon}, \quad \epsilon \sim 0 - 0.6$$

(1.22)

$$\gamma(T) = \frac{C_v(T)}{T} = \gamma_0 \log \left[ \frac{T_0}{T} \right]$$

(1.23)
\[
\frac{1}{\chi(T)} = \frac{1}{\chi_0} + cT^a,
\]
where \(a < 1\) \hfill (1.24)

For example, YbRh$_2$Si$_2$ exhibits a \(T^{1+\epsilon}\) resistivity, with \(0 \leq \epsilon \leq 0.5\), in the vicinity of the antiferromagnetic (AFM) quantum critical point (QCP, discussed in the next section) [38].

**Quantum Criticality**

As was mentioned above, there a number of different materials that exhibit nFL behaviour. Often, with the heavy fermion materials, this is found in the vicinity of what’s known as a quantum critical point (QCP), where a second order phase transition, often antiferromagnetic, is tuned to zero temperature by some tuning parameter, such as chemical doping, pressure, or application of a magnetic field. At this point, quantum fluctuations dominate, and new physics is often observed. Some materials, such as CeCu$_2$Si$_2$ exhibit superconductivity in the vicinity of the QCP, and some materials, like YbRh$_2$Si$_2$ do not and instead become FL-like heavy fermion paramagnets. In these materials, the competition between two different mechanisms, one which promotes magnetism (the Ruderman-Kittel-Kasuya-Yosida interaction [39–41]), and one which kills magnetism (the Kondo effect [42], also responsible for a non-Fermi liquid like upturn in resistivity at low temperature), can cause new and unexpected properties to occur.

The Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, is a conduction electron mediated local moment spin-spin interaction, which can promote either ferromagnetism (FM) or AFM. In contrast, in the Kondo interaction the local moments are screened by the conduction electrons, killing the magnetic state [43]. An effective Hamiltonian for the system is written as [44],

\[
H = \sum_{ij} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ij} I_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i J_K \mathbf{S}_i \cdot \frac{c_{i\uparrow}^\dagger c_{i\downarrow}}{2} c_i \hfill (1.25)
\]

where the spin-1/2 \(f\)-electron local moments at each site, \(i\), hybridize with a sea of conduction electron, \(c_{i\sigma}\). \(t_{ij}\) represents the hopping matrix of the conduction electrons, \(I_{ij}\) is the strength of the RKKY exchange interaction, and \(J_K\) is the strength of the Kondo exchange interaction. The competition between the Kondo and RKKY interactions is tuned using the parameter \(\delta\), which as mentioned above, can be chemical doping, magnetic field, or pressure, and is captured
in the equation,
\[ \delta \equiv \frac{T_0^0}{T} \]  
where \( T_0^0 \) is the Kondo temperature and is taken to be,
\[ T_0^0 \approx \frac{1}{\rho_0} e^{-1/\rho_0 J_K} \]  
where \( \rho_0 \) is the conduction electron density of states at the Fermi level. By application of a magnetic field, the interactions can be tuned towards AFM or a Kondo screened state. Low fields reduce the Kondo scale, \( T_0^0 \), quadratically in \( H \) but couple to the AFM interaction linearly, which modifies the ratio of the tuning parameter, \( \delta \) \[44\].

Being able to tune the relative interaction strengths between the magnetic and non-magnetic state through a variety of parameters provides a vast landscape for the understanding of heavy fermion materials. The often unexpected results, such as magnetically mediated superconductivity, made heavy fermion condensed matter physics an extremely popular field of research towards the end of the twentieth century, which has continued, albeit with slightly lower voracity, to today.

1.1.3 Density Functional Theory

I will now review density functional theory (DFT), as this forms the basis of Wien2k, the program I used to calculate the band structure of YbRh\(_2\)Si\(_2\). DFT is seemingly the most popular technique for calculating electronic structures, with one of its creators, Walter Kohn, receiving the 1998 Nobel Prize in chemistry. I will restrict my discussion of DFT to only that which is relevant to an understanding of the calculations I personally completed. A nice introduction is provided in the documentation of the Wien2k software \[45\], the textbook of Cottenier \[46\], and an excellent introductory lecture by Cuevas \[47\]. This section summarizes the main results of DFT following the Cuevas lecture notes and generally uses the same notation, with a few slight modifications.

In simplest terms, DFT is a computational method that allows one to determine the ground state of a system from the electron density, instead of working with all of the electrons separately.
It finds its origins in the variational principle for the ground state which states that the ground state energy of the system for an assumed wave function, \( \psi \), gives an upper limit of the actual ground state energy, \( E_0 \). By minimizing the energy of the N-electron energy functional, \( E(\psi) \), one obtains \( E_0 \) and the exact ground state wave function, \( \psi_0 \) [47]. An early attempt at this type of functional solution was provided by the Hartree-Fock approximation or self-consistent field method, in which the many body ground state wave function of the system could be approximated by the Slater determinant of the one electron wave functions. Minimizing the energy of this system using the approximate wave function yields the Hartree-Fock energy of the system, \( E_{HF} \).

\[
\psi_0 \approx \psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(x_1) & \psi_2(x_1) & \ldots & \psi_N(x_1) \\
\psi_1(x_2) & \psi_2(x_2) & \ldots & \psi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(x_N) & \psi_2(x_N) & \ldots & \psi_N(x_N)
\end{vmatrix},
\]

(1.28)

\[
\langle E_{HF} \rangle = \langle \psi_{HF} | \hat{H} | \psi_{HF}^* \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}),
\]

(1.29)

\[
H_i \equiv \int \psi_i^*(x) \left[ -\frac{1}{2} \nabla^2 - V_{ext}(x) \right] \psi_i(x) \, dx,
\]

(1.30)

\[
J_{ij} = \iint \psi_i(x_1) \psi_i^*(x_1) \frac{1}{r_{12}} \psi_j(x_2) \psi_j^*(x_2) \, dx_1 \, dx_2,
\]

(1.31)

\[
K_{ij} = \iint \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{12}} \psi_j^*(x_2) \psi_i(x_2) \, dx_1 \, dx_2,
\]

(1.32)

where \( H_i \) is the one electron Hamiltonian, \( J_{ij} \) is the Coulomb interaction, and \( K_{ij} \) is the exchange interaction. While this allowed theoretical calculations of the electronic state of the system, the N equations had to be solved self-consistently and required proper selection of the electron orbitals [47].

The first real DFT type computation was provided in the Thomas-Fermi model [16, 17], which eliminated the need for knowledge of the wave function of the system and instead per-
formed the calculation with the electronic density, $\rho (r)$. In fact, the kinetic energy and total ground state energy of the atom were derived as functionals of only the electron density, given as,

$$T_{TF} [\rho (r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3} (r) \, d\mathbf{r}$$

$$E_{TF} [\rho (r)] = \frac{3}{10} (3\pi^2)^{2/3} \int \rho^{5/3} (r) \, d\mathbf{r} - Z \int \frac{\rho (r)}{r} \, d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho (r_1) \rho (r_2)}{r_{12}} \, d\mathbf{r}_1 d\mathbf{r}_2,$$

where $Z$ is the atomic number of the element [47–49]. The energy of the system was minimized for the constraint that $\int \rho(r) \, d\mathbf{r} = N$. It, however, was shown to have limited accuracy due to its approximation of the kinetic energy, amongst other issues, and it needed to be improved upon [15, 47].

The modern version of DFT builds upon its predecessors and creates a rigorous mathematical framework from which the properties of the system can be calculated. The Hohenberg-Kohn theories set the tenets of DFT, whereby, the first theorem asserts that the external potential (i.e. the effective potential created by the positive nuclei), $V_{ext} (r)$, is, to within a constant, a unique functional of the electron density, $\rho (r)$ [47]. Thus, $\rho (r)$, defines the ground state properties of the system and allows us to write the total energy as,

$$E [\rho] = E_{Ne} [\rho] + T [\rho] + E_{ee} [\rho] = \int \rho (r) V_{Ne} (r) \, d\mathbf{r} + F_{HK} [\rho] \quad (1.35)$$

The functional, $F_{HK} [\rho]$, is the key element of DFT. It allows us to write down the kinetic and electron-electron interaction energies,

$$F_{HK} [\rho] = T [\rho] + E_{ee}, \quad (1.36)$$

and the electron-electron functional can be written as,

$$E_{ee} [\rho] = J [\rho] + E_{nc} [\rho], \quad (1.37)$$
Chapter 1. Introduction

where \( J[\rho] \) is the Coulomb term. Figuring out this functional, \( F_{HK} \), and specifically the kinetic energy and non-classical terms is one of the biggest challenges in DFT. The second rule of DFT is that the functional, \( F_{HK}[\rho] \), only yields the lowest ground state energy if the density used is the true density of the ground state. I won’t go through the mathematical proof of these theories, and refer the reader to the review lecture [47]. Thus if we could minimize the total energy of the system with the exact interaction expressions and our choice of \( \rho(r) \), we would be assured that our density is that of the true system.

As was mentioned earlier, one of the big issues with the Thomas-Fermi model was its poor determination of the kinetic energy. Kohn and Sham suggested that the way to determine the kinetic energy, was to calculate it for a non-interacting reference system with the identical electronic density to our real system and to modify the DFT functional with an extra term, known as the exchange-correlation energy, \( E_{XC}[\rho] \) [15], thus the kinetic energy of the non-interacting (ni) system is,

\[
T_{ni} = -\frac{1}{2} \sum_i^N \langle \psi_i \big| \nabla^2 \big| \psi_i \rangle ,
\]

\[
\rho_{ni}(r) = \sum_i^N \sum_s |\psi_i(r,s)|^2 = \rho(r),
\]

where the ni subscript is used to indicate the non-interacting case. Therefore, we can write the total functional of the system as,

\[
F[\rho] = T_{ni}[\rho] + J[\rho] + E_{XC}[\rho]
\]

and the exchange-correlation is defined as,

\[
E_{XC}[\rho] \equiv (T[\rho] - T_{ni}[\rho]) + (E_{ee}[\rho] - J[\rho]).
\]

Finally, we are able to write the total energy of the system as a sum of the different energies.
defined above, specifically,


\[ = -\frac{1}{2} \sum_{i}^{N} \langle \psi_{i} | \nabla^{2} | \psi_{i} \rangle + \frac{1}{2} \sum_{i}^{N} \sum_{j}^{N} \iint |\psi_{i}(r_{1})|^{2} \frac{1}{r_{12}^{2}} |\psi_{j}(r_{2})|^{2} d\mathbf{r}_{1} d\mathbf{r}_{2} \]

\[ + E_{XC}[\rho] - \sum_{i}^{N} \int \sum_{A}^{M} Z_{A} r_{1A} |\psi_{i}(r_{1})|^{2} d\mathbf{r}_{1} \]  

(1.42)

It’s clear now that in this Kohn-Sham treatment we’re still missing something extremely important, a definition of the exchange-correlation energy. This is the central issue of DFT, choice of this energy. The final Kohn-Sham equations, which re-write the Schrödinger equation using the variational principle are,

\[ H_{KS}\phi_{i} = \left( \frac{1}{2} \nabla^{2} + V_{S}(\mathbf{r}_{1}) \right) \phi_{i} = \epsilon_{i}\phi_{i} \]  

(1.43)

and,

\[ V_{S}(\mathbf{r}_{1}) = \int \frac{\rho(\mathbf{r}_{2})}{r_{12}} d\mathbf{r}_{2} + V_{XC}(\mathbf{r}_{1}) - \sum_{A}^{M} \frac{Z_{A}}{r_{1A}}. \]  

(1.44)

\( H_{KS} \) is the Kohn-Sham Hamiltonian, and \( V_{XC} \) is the exchange-correlation potential, which is the functional derivative of the exchange-correlation energy with respect to the electron density, \( V_{XC} = \delta E_{XC}/\delta \rho \) [15]. The procedure for solving this equation is, pick a starting density, define \( V_{S} \) using \( \rho(\mathbf{r}) \) and obtain the Hamiltonian, solve for the eigenfunctions and eigenvalues, compute a new density, and repeat until \( \rho(\mathbf{r}) \) doesn’t change between iterations [46].

Wien2k makes use of the local density approximation (LDA) to write down a form for the exchange-correlation energy, where the electrons are taken as a uniform gas moving in a positive potential, with the sum total of the charge being zero. The exchange-correlation energy can then be written as,

\[ E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r}) [\epsilon_{X}(\rho(\mathbf{r})) + \epsilon_{C}(\rho(\mathbf{r}))] d\mathbf{r}. \]  

(1.45)

\( \epsilon_{X}(\rho(\mathbf{r})) \) is the exchange energy for an electron gas, which has been computed exactly, and the trouble comes down to determining \( \epsilon_{C}(\rho(\mathbf{r})) \), which is done using Monte-Carlo simulations [47]. While normally LDA does a good job of determining the properties of materials, it’s
known to have issues dealing with materials such as heavy fermions (this is problematic since this thesis is focused on HF systems) where correlation effects are extremely important [50]. In the chapter on YbRh$_2$Si$_2$ (3), where band structure calculations are compared to experimental results, it will be seen that even though there exist known issues in calculations with the HFs, the calculations are very helpful in building our understanding of the electronic structure of the material, and can even be useful in comparisons with the experimental data.

Building upon LDA, Wien2k also makes use of something called the generalized gradient approximation or GGA, where in addition to specifying the local electron density, we also specify the gradient of the density, $\nabla \rho (\mathbf{r})$, so that the exchange-correlation energy can be written as,

$$
E_{XC}^{GGA}[n_\uparrow, n_\downarrow] = \int d\mathbf{r} f (n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow).
$$

(1.46)

Throughout this thesis, the Perdew-Burke-Ernzerhof GGA approximation of 1996 is used in all Wien2k calculations [51].

One last important thing to mention before concluding this section is that Wien2k uses augmented plane-wave plus local orbital (APW + lo) type solutions for the Kohn-Sham equations. The unit cell is broken up into spherical regions surrounding the atoms, with a local orbital solution consisting of spherical harmonics, and plane-wave solutions in the intermediate areas between the atoms. Originally, the set of equations was solved to ensure that the wave functions solutions matched in both value and slope at the boundary between the two regions (called the full linear augmented plane-wave + local orbital, FLAPW, method), this however, was not efficient, and it was determined that the APW + lo saved a significant amount of computational time [52]. Thus the wave functions used are,

$$
\phi_{\mathbf{k}_n} = \sum_{lm} [A_{lm,k_n} u_l (r, E_l)] Y_{lm} (\hat{r}),
$$

(1.47)

inside the atomic sphere $t$, of radius $R_t$, and where $Y_{lm}$ are the spherical harmonics and $u_l (r, E_l)$ is the solution of the radial Schrödinger equation for energy $E_l$. In the intermediate region, the
plane-wave solutions are written as,

\[ \phi_{k_n} = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_n \cdot \mathbf{r}} \]  

(1.48)

where \( k_n = k + \mathbf{K}_n \), and \( \mathbf{K}_n \) is a reciprocal lattice vector. Lastly, the so-called local orbital solutions are added in to enable treatment of the semicore and valence states together in a single energy window, and to improve linearization [53].

\[ \phi_{lm}^{lo} = [A_{lm} u_l (r, E_{1,l}) + B_{lm} \dot{u}_l (r, E_{1,l})] Y_{lm} (\hat{r}) , \]  

(1.49)

where \( \dot{u}_l \) is the energy derivative of the original spherical Schrödinger equation solutions. The requirement on the local orbitals, is that they go exactly to zero at the edge of the atomic sphere, thus causing a discontinuity not present in the FLAPW solutions, and requiring surface terms in the Hamiltonian, but which significantly reduce the computational requirements. The reader is referred to the Wien2k manual for further details [45].

![Figure 1.2: Cartoon picture of the different regions for LAPW (APW) calculations. Region I corresponds to the wave function solutions with spherical harmonics. Region II is the interstitial region where solutions are plane-waves. Adapted from the Wien2k manual [45].](Image)
1.2 Multipole Moments

Important to the discussion of PrOs$_4$Sb$_{12}$, a material which exhibits a form of hidden order, known as antiferroquadrupolar (AFQ) ordering, is an understanding of the origin of the electric quadrupole moment arising from the electrostatic potential. This discussion follows from chapter 3 of the elementary textbook on the subject by Griffiths [54].

For an arbitrary charge distribution, the resulting electric potential can be written as,

$$V(r) = \frac{1}{4\pi\epsilon_0} \int \rho(r') \frac{d^3r'}{|r-r'|}. \quad (1.50)$$

Now, rewriting the denominator inside the integral we obtain,

$$\frac{1}{|r-r'|} = \sqrt{r^2 + r'^2 - 2rr'\cos\theta'} \quad (1.51)$$

$$\implies \frac{1}{|r-r'|} = \frac{1}{r} \frac{1}{\sqrt{1 + \frac{r'^2}{r^2} - 2\frac{r'}{r}\cos\theta'}} \quad (1.52)$$

This final term can be expanded in the Legendre polynomials, $P_n$, so,

$$\frac{1}{r} \frac{1}{\sqrt{1 + \frac{r'^2}{r^2} - 2\frac{r'}{r}\cos\theta'}} = \sum_{n=0}^{\infty} P_n(\cos\theta') \left(\frac{r'}{r}\right)^n \quad (1.53)$$

Plugging this back into our original equation for the electrostatic potential yields,

$$V(r) = \frac{1}{4\pi\epsilon_0} \int \rho(r') \sum_{n=0}^{\infty} P_n(\cos\theta') \left(\frac{r'}{r}\right)^n d^3r' \quad (1.54)$$

$$= \frac{1}{4\pi\epsilon_0} \sum_{n=0}^{\infty} \frac{1}{r^{n+1}} \int \rho(r') P_n(\cos\theta') r^n d^3r' \quad (1.55)$$

In this expansion, $n = 0$ is the monopole term, $n = 1$ is the dipole term, $n = 2$ is the quadrupole term, and $n = 3$ is the octupole term. Focusing in on the quadrupolar term, which is central to the discussion of PrOs$_4$Sb$_{12}$, we can rewrite it in a more convenient form. From eq. 1.54,

$$\frac{1}{4\pi\epsilon_0 r^3} \int r'^2 P_2(\cos\theta') \rho(r') d^3r' = \frac{1}{4\pi\epsilon_0 r^3} \int r'^2 \left(\frac{3}{2}\cos^2\theta' - \frac{1}{2}\right) \rho(r') d^3r', \quad (1.56)$$
Substituting $r' \cos \theta' = r' \cdot \hat{r}$, we get,

$$V_Q = \frac{1}{4\pi \epsilon_0} \frac{1}{2r^3} \int \left( 3 \left( r' \cdot \hat{r} \right)^2 - r' r' \right) \rho (r') \, d^3r'$$  \hspace{1cm} (1.57)

Skipping a couple of steps and expanding,

$$V_Q \equiv \frac{1}{4\pi \epsilon_0} \frac{1}{2r^3} \sum_{i,j=1}^{3} \hat{r}_i \hat{r}_j Q_{ij}$$  \hspace{1cm} (1.58)

$Q_{ij}$ is called the quadrupole moment, where,

$$Q_{ij} \equiv \int \left( 3r'_i r'_j - (r'_i)^2 \delta_{ij} \right) \rho (r') \, d^3r';$$  \hspace{1cm} (1.59)

and $\delta_{ij}$ is the Kronecker delta. The quadrupole is a tensor, represented by a 3x3 matrix. A static alternating direction of the quadrupole moment on adjacent lattice sites in PrOs$_4$Sb$_{12}$ defines the onset of the AFQ phase, and the interaction of these quadrupole moments is an essential contribution to the interesting physics of PrOs$_4$Sb$_{12}$.

### 1.3 The de Haas-van Alphen Effect

The de Haas-van Alphen effect, named after W.J. de Haas and P.M. van Alphen is the primary technique used to explore HF materials throughout this thesis. de Haas and van Alphen discovered oscillations in the magnetic susceptibility of samples of bismuth at low temperatures in 1930 [55], and this was quickly followed by the discovery of oscillations in the resistivity as well, now known as the Schubnikov-de Haas effect [56]. Besides dHvA and SdH, oscillations can be seen in any quantity which depends on the density of states at the Fermi level. The de Haas-van Alphen (and related) effects, are not the only means of directly measuring the Fermi surface of a material, another popular technique is called Angle Resolved Photo Emission Spectroscopy (ARPES), but they are the only ones at present that can (and must) be used high field. The following section attempts to briefly introduce the origin of quantum oscillatory phenomena and does so from an idealized theory of free electrons as described in Sec. 1.1.1, and only deviates from this where absolutely relevant to the rest of the thesis. I will use B as the symbol for
magnetic field throughout this section, as the oscillations are periodic in \(1/B\), and thus their frequency is quoted in units of \(kT\) (thousand Tesla). A complete overview of the topic can be had in the book by Shoenberg \[57\], an excellent review article by Bergemann et al. \[58\], and the book chapter written by my supervisor, Stephen Julian \[59\]. This section is based mainly on these sources, with nice clarifications obtained in Patrick Rourke’s thesis \[60\].

### 1.3.1 Zero Temperature Theoretical Explanation

**Onsager Relation**

A theoretical understanding of the origins of the observed oscillations was provided by Lars Onsager in 1952 \[61\]. Beginning with electrons moving with crystal momentum \(\hbar \mathbf{k}\), a magnetic field, \(B\), is switched on in the \(\hat{z}\)-direction. The electron motion in \(\hat{z}\) remains unchanged, while the motion perpendicular to the field is altered by the Lorentz force, \(\mathbf{F} = e\mathbf{v} \times \mathbf{B}\), where \(e\) is the electronic charge. This causes the electron to enter into a so-called cyclotron orbit, with frequency written as, \(\omega_c = \frac{eB}{m^*}\). I introduce \(m^*\) instead of the bare electron mass in order to take care of the mass renormalization in the presence of interactions and modifications caused by the band theory. The semiclassical radius of the orbit is inversely proportional to the magnetic field, i.e.

\[
v = r\omega_c = \frac{eB}{m^*}r \tag{1.60}
\]

Or written another way, the centripetal force balances the force exerted by the field,

\[
\frac{m^*v^2}{r} = evB \tag{1.61}
\]

\[
\frac{v}{r} = \frac{eB}{m^*} \tag{1.62}
\]

and relating this result to the crystal momentum from the semi-classical equations of motion,

\[
\mathbf{v} = \frac{1}{\hbar} \nabla \epsilon(\mathbf{k}) \tag{1.63}
\]

\[
\hbar \mathbf{k} = -ev \times \mathbf{B} \tag{1.64}
\]
Thus,
\[ \hbar \frac{d\mathbf{k}}{dt} = -e \frac{d\mathbf{r}}{dt} \times \mathbf{B} \]
\[ \therefore \frac{d\mathbf{k}}{dt} = \frac{e}{\hbar} \mathbf{r} \times \mathbf{B} \] (1.65)

Also we see from the semi-classical equations that the path of the electron travels in the magnetic field is one of constant energy. Taking the dot product of eq. 1.63 with \( \dot{\mathbf{k}} \),
\[ \dot{\mathbf{k}} \cdot \mathbf{v} = \frac{1}{\hbar} \dot{\mathbf{k}} \cdot \nabla \epsilon(\mathbf{k}) \] (1.66)

We know from eq. 1.64 that \( \dot{\mathbf{k}} \) is perpendicular to \( \mathbf{v} \), thus
\[ \frac{1}{\hbar} \left( \frac{dk_x}{dt} \frac{d\epsilon(\mathbf{k})}{dk_x} + \frac{dk_y}{dt} \frac{d\epsilon(\mathbf{k})}{dk_y} + \frac{dk_z}{dt} \frac{d\epsilon(\mathbf{k})}{dk_z} \right) = 0 \]
\[ \frac{1}{\hbar} \frac{d\epsilon}{dt} = 0 \] (1.67)

If we left it at this, in the semi-classical picture we would see that the electron energies exist in a continuum, and no such dHvA effect would be observed. However, applying the Bohr-Sommerfeld quantization rule to the electron motion, given as,
\[ \oint p \cdot d\mathbf{r} = (n + \gamma) 2\pi \hbar \] (1.68)

which for our electron yields,
\[ \oint (\hbar \mathbf{k} - e\mathbf{A}) \cdot d\mathbf{r} = (n + \gamma) 2\pi \hbar, \] (1.69)

when we work through this integral using Stokes’s theorem, we arrive at,
\[ \Phi = B\alpha_r = (n + \gamma) \frac{2\pi \hbar}{e} = (n + \gamma) \Phi_0 \] (1.70)

where \( \Phi_0 \) is known as the flux quantum, so the flux through the area of the orbit in real space, \( \alpha \), must be quantized in units of the flux quantum. We relate the area of the orbit in real space
about some central point, \( r_0 \), to the area of the \( k \)-space orbit through the conversion factor, \( \eta \). which comes from eq. 1.65. Thus,

\[
a_r = \pi (r - r_0)^2 = \pi r^2 \quad (1.71)
\]

\[
\therefore a_k = \pi \left( \frac{eB}{\hbar} r \right)^2 \quad (1.72)
\]

so,

\[
\frac{a_k}{a_r} = \left( \frac{eB}{\hbar} \right)^2 = \eta^2 \quad (1.73)
\]

Finally, using eq. 1.73 in eq. 1.70 and solving for \( a_k \), we obtain,

\[
a_{kn} = (n + \gamma) \frac{2\pi eB}{\hbar} \quad (1.74)
\]

This is the original form of what’s now called the Onsager relation [61]. I will also use \( a_n \) to denote the area of the \( n \)th multiply degenerate Landau level in \( k \)-space. What we see is that the orbit increases in area in \( k \)-space proportional to the magnetic field, or in other words \( k_n \propto \sqrt{B} \), as the cyclotron orbit becomes smaller in real space. In a real material, \( a_k \) can vary depending on the particular sheet of the Fermi surface we’re examining, and as well has variation along the \( k_z \) direction in 3D. Here we ignore this complication and look at the simpler one band free electron picture. The electrons orbits in \( k \)-space are separated from each other by,

\[
a_{n+1} - a_n = \frac{2\pi eB}{\hbar} \quad (1.75)
\]

More generally (for the non-spherical FS case), looking at a slice through a Landau tube, electrons follow orbits of constant energy, perpendicular to the magnetic field, and not necessarily circles. Imagining now that the \( n \)th Landau tube has reached the Fermi surface with applied magnetic field, \( B_1 \), the \((n - 1)\)th tube will cross the FS at magnetic field \( B_2 \). The area of these two orbits is equal. \( A \) represents such an orbit. Thus,

\[
A = (n + \gamma) \frac{2\pi B_1}{\hbar} = (n - 1 + \gamma) \frac{2\pi B_2}{\hbar} \quad (1.76)
\]
Rearranging eq. 1.76,

\[ n = \frac{\hbar A}{2\pi e B_1} - \gamma = \frac{\hbar A}{2\pi e B_2} - \gamma + 1 \]  

(1.77)

Thus,

\[ T = \frac{1}{B_1} - \frac{1}{B_2} = \Delta \left( \frac{1}{B} \right) = \frac{2\pi e}{\hbar A} \]  

(1.78)

where \( T \) is the period, which is inversely proportional to the field. Phenomenologically, as the electrons (or quasiparticles) of the \( n \)th Landau tube reach the FS, they cannot go beyond the FS (as this would require their energy to have increased beyond the \( T=0 \) maximum) and they quickly depopulate to a different, lower Landau level. This oscillation in the density of states at the Fermi level can be seen in many different measurements, including susceptibility, resistivity, and specific heat. More commonly, this relation is conveniently written as,

\[ F = \frac{\hbar}{2\pi e A}, \]  

(1.79)

where \( F \) is the frequency of the oscillation (generally given in units of \( kT \)) [57]. This directly relates the frequency of the observed oscillations to the area of an extremal orbit of the FS.

As was mentioned, the measured oscillatory phenomena arise from a variation in the density of states at the FS, so it’s therefore important to define the density of states \( D \) for each Landau level. For a free electron gas, the density of states per unit volume of \( k \)-space is \( 2V/(2\pi)^3 = V/4\pi^3 \) [26]. Multiplying this by a volume of \( k \)-space, \( \Omega \), which in this case is a slice through the Landau tube perpendicular to the applied field \( \hat{k}_z \) multiplied by the spacing between adjacent levels, \( \Delta a \), with all electrons of energy between the \( n \) and \( n+1 \) level becoming a part of the \( n+1 \) level. Thus,

\[ D = \Delta a \frac{V}{4\pi^3} = \frac{eBV dk_z}{2\pi^2 \hbar} \]  

(1.80)

Importantly we see that density of states is independent of \( n \) and is proportional to \( B \). This result is rigorously true, regardless of whether we are looking at the free electron spherical FS or that of a real material [62, 63]. A large number of Landau levels are required to hold all of the electrons in a given material. For typical metals, the value of \( n \) is \( \sim 10^4 - 10^5 \).
From eq. 1.79, we can write the oscillations of any physical quantity that depends on the DOS at the Fermi level in the form,

$$Q(B) = \sum_p A_p \cos \left( \frac{2\pi p F}{B} + \phi \right)$$

(1.81)

where $p$ is the harmonic number and $A_p$ is the Fourier series amplitude of the particular harmonic [34, 58]. To be more mathematically rigorous (as the above calculation is done for a 2D case), we know that we could have a non-uniform FS with the cross sectional area perpendicular to $B$ varying along the $k_z$ direction. Thus, we would have oscillations of the form

$$\sin \left( \frac{2\pi F (k_\parallel)}{B} \right)$$

and would need to integrate this over $k_z$. However, making use of the fact that at most values of $k_z$ this sine function is rapidly varying, we can make the saddle-point approximation and would therefore only expect an oscillatory component of the magnetization to arise from so-called “extremal” orbits, those which represent a local or global maxima or minima [58]. This allows allows us to treat the situation using the assumption that the chemical potential remains fixed. Finally, before arriving at the governing equations of de Haas-van Alphen oscillations, we also note that in addition to multiple maxima and minima, real materials can have multiple FS sheets, thus we now refer to the observed frequencies by $F_n$, and $A_n$ represents extremal orbits only.

**Lifshitz-Kosevich Formula without Damping**

Building upon the previous section, we can present the key elements of using the de Haas-van Alphen effect as an actual measurement tool. Eq. 1.82 represents the fundamental equation for dHvA measurements, though I first present it without the inclusion of non-ideal factors which act to decrease the overall amplitude of the oscillations. These are presented in Sec. 1.3.2.

$$\tilde{M}_{LK} = -\left( \frac{e}{\hbar} \right)^{3/2} \sum_F \frac{\beta F B^{1/2} V}{2^{1/2} \pi^{5/2} (A')^{1/2}} \sum_{p=1}^{\infty} \frac{1}{p^{3/2}} \sin \left[ 2\pi p \left( \frac{F}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right],$$

(1.82)

For,

$$\beta = \frac{e\hbar}{m^*}$$

(1.83)
Equation 1.82 is known as the Lifshitz-Kosevich (LK) equation [64] which relates the de Haas-van Alphen frequencies to the oscillations in magnetization at \( T = 0 \). From this one can see that the strength of the oscillation is dependent on the curvature of the FS in the vicinity of the extremal orbit, \( \mathcal{A}'' \), such that the amplitude is decreased for strong FS curvature, but that the oscillation amplitude increases as \( \sqrt{B} \).

1.3.2 \( T > 0 \) and Other Real World Issues

The following subsections present so-called damping factors that act to reduce the overall amplitude of the dHvA oscillations, but through which (specifically in this thesis is the case for the temperature damping factor) one can obtain information often as interesting as the frequency of the oscillations themselves. These complications set some critical restrictions on the conditions which must be met in order to observe the oscillations at all. Generally speaking, the damping factors can be treated as a phase smearing, i.e. the superposition of oscillations of a particular frequency shifted by some phase value. This effectively broadens the Landau levels and allows one to derive the effect of a particular damping factor using a generalized approach [57].

**Temperature Damping Factor, \( R_T \)**

The first, and perhaps most obvious, complication is the effect of non-zero temperature on the oscillations. From the previous section, we can write the spacing between Landau tubes as,

\[
\Delta E_n = \frac{\hbar e B}{m^*}
\]  

which shows that the larger the mass, the closer the Landau tubes are together, and the higher the field, the larger the energy between the tubes. Temperature has the effect of broadening the Fermi-Dirac function, so for oscillations to show up, the Fermi-Dirac function must be narrow with respect to the spacing between the Landau levels. We can then define a maximum temperature for the oscillations by dividing eq. 1.84 by Boltzmann’s constant, \( k_B \). The temperature damping factor, \( R_T \), is defined as,

\[
R_T = \frac{X}{\sinh X}
\]
where,

\[ X = \frac{2\pi^2 k_B T}{\beta B} = \frac{2\pi^2 k_B T m^*}{e\hbar B} \]  

(1.86)

For increasing T, this factor falls quickly to zero and kills the oscillations. The temperature damping of the oscillations is actually a very powerful tool used in chapter 3; fitting \( X/\sinh X \) to the temperature dependent oscillation amplitude allows for measurement of the quasiparticle effective mass, \( m^* \).

**Dingle Factor, \( R_D \)**

Another factor which contributes to the reduction of the dHvA oscillation amplitude comes from the finite quasiparticle lifetime, \( \tau \), due to impurities. This reduction is known as the Dingle factor [57, 65], which could be explained as a broadening of the Landau level energy with a Lorentzian distribution such that the probability of the \( n \)th Landau level having an energy between \( \epsilon_n \) and \( \epsilon + d\epsilon \) is,

\[ P(\epsilon) \propto \frac{d\epsilon}{(\epsilon - \epsilon_n)^2 + (\hbar/2\tau)^2}, \]  

(1.87)

which for \( \tau \) independent of \( \epsilon \) is equivalent to a spread of the Fermi energy, \( \mu \), about its true value [57], \( \epsilon_F \), such that the probability of the Fermi energy lying between \( \mu \) and \( \mu + d\mu \) is,

\[ P(\mu) \propto \frac{d\mu}{(\mu - \epsilon_F)^2 + (\hbar/2\tau)^2} \]  

(1.88)

Since the frequency of the oscillations is dependent on the Fermi energy through the area of the Fermi surface, this effect is equivalent to a phase smearing, dampening the oscillations. This has a similar effect to a rise in temperature associated with the Dingle factor, where the “temperature” is,

\[ x = \frac{\hbar}{2\pi k_T} \]  

(1.89)

which yields a Dingle factor of,

\[ R_D = e^{-2\pi^2 kx/\beta H}, \]  

(1.90)
with $\beta = \frac{e\hbar}{m^*}$, as in eq. 1.86. Phenomenologically, this says that oscillations will only be observable if the level width, $\hbar/2\tau$, is smaller than the spacing between the levels. Bergemann rewrites the Dingle factor in a very convenient fashion such that,

$$ R_D = e^{-(B_D/B)} \text{ where, } B_D = \frac{\hbar C_F}{2e l_o} $$

where $C_F$ is the circumference of the cyclotron orbit, $r_c$ is the radius of the cyclotron orbit in $k$-space and $l_o$ is the quasiparticle mean free path [58]. An additional factor, identical in form to eq. 1.90, arises from other sample inhomogeneity such as crystal orientation or internal sample strains, though the impurity scattering is generally the dominant reduction [57].

Electron Spin Factor, $R_S$

The final reduction factor considered in this thesis is the spin-splitting reduction factor, $R_S$, which results from the change in energy caused by Zeeman splitting in a magnetic field,

$$ \Delta \epsilon = \pm \frac{1}{2} g \mu_B H, $$

where,

$$ \mu_B = \frac{e\hbar}{2m_e}, $$

and $g$ is the electron “g-factor” which normally has a value of $\approx 2$. This results in in two separate Fermi surface sheets, one for each spin species, with the “up” spin, i.e. the spin parallel to the direction of the applied magnetic field, reduced by the energy given in eq. 1.93, and is thus preferentially occupied compared with the spin down branch. In the scenario called spin-splitting I or normal spin-splitting by Bergemann, the up spin sheet grows in size, while the down spin sheet shrinks, resulting in two sheets which are identical in overall shape, but different in size [58]. The resulting phase difference between the two sheets is,

$$ \phi = \frac{2\pi \Delta \epsilon}{\beta B} $$
This comes from now two levels for each oscillation passing through the Fermi surface, separated by the fraction of $2\pi$ corresponding to $\Delta\epsilon/\beta B$ \cite{57, 66}. The reduction in oscillation amplitude from the spin-splitting is,

$$R_S = \cos \left( \frac{p\pi \Delta \epsilon}{\beta B} \right) = \cos \left( \frac{1}{2} p\pi g \frac{m^*}{m_e} \right)$$  \hspace{1cm} (1.96)$$

A very nice way of thinking of this is presented by Bergemann, in which (to first order) we describe the situation using a field dependent Fermi wave vector, $k_{00}^{\uparrow\downarrow} = k_{00} \pm \chi_{00} B$, where $\chi_{00}$ is a term proportional to the spin susceptibility \cite{58}. This yields $R_S$ for a cylindrical Fermi surface, given as,

$$R_S = \cos \frac{2\pi k_{00} \chi_{00}}{e \cos \theta_0}$$ \hspace{1cm} (1.97)$$

where $\theta_0$ is the angle between the long axis of the cylinder and the applied field. This result holds for all quasi-2D materials. There exists a situation in which the spin-splitting of the Fermi surface causes not only a contraction or expansion of the spin surfaces to occur, but also in which the spin-splitting distorts the shape of the resulting sheets. Bergemann calls this anomalous spin-splitting in which a more general Fermi wave vector is written, $k_{\mu\nu}^{\uparrow\downarrow} = k_{\mu\nu} \pm \chi_{\mu\nu} B$ \cite{58}. This anomalous spin-splitting was not used explicitly in this thesis, though spin-splitting is essential to the interpretation of the dHvA data for YbRh$_2$Si$_2$ presented in chapter 3. In this material, extreme splitting in the large applied field causes a topological change in the Fermi surface, which drastically alters the observed dHvA frequencies. In that case, however, the spin splitting is assumed to be very large, and non-linear, so that the spin-split branches of the Fermi surface show up as separate frequencies, rather than one frequency with a modified amplitude.

We are now able to write the final form of the Lifshitz-Kosevich (LK) equation for the oscillatory magnetization,

$$\tilde{M} = - \sum_F \left( \frac{e}{\hbar} \right)^{3/2} \frac{2 F k T V}{\sqrt{2\pi B A^d}} \sum_{p=1}^{\infty} \frac{\exp \left( -2p\pi^2 pkx/\beta B \right) \cos \left[ \frac{1}{2} p\pi g \left( \frac{m^*}{m} \right) \right]}{p^{3/2} \sinh \left( 2p\pi^2 pkT/\beta B \right)} \times \sin \left[ 2p\pi \left( \frac{F}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right]$$ \hspace{1cm} (1.98)$$
which, keeping the reduction factors as symbols and packaging the constant up in its own symbol, yields,

\[
\bar{M} = - \sum_{F} \sum_{p=1}^{\infty} R_T R_D R_S C_0 \sqrt{B} \sin \left[ 2\pi p \left( \frac{F}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right] A_p(T,B) \sin (2\pi p \frac{F}{B} + \phi_p) \tag{1.99}
\]

where,

\[
C_0 = \left( \frac{e^2 V}{2 \pi^2 p^{3/2} m^*} \right) \frac{F}{\sqrt{F''}}.
\tag{1.100}
\]

\(F''\) is the second derivative of the frequency in the direction of the applied field, evaluated at the extremal area of the Fermi surface. Given the inverse relationship of the oscillation amplitude to this second derivative, it can be seen that those surfaces which have little curvature at the extremum will produce stronger oscillations that those which have large curvature [60].

1.3.3 Experimental Observation

The background information about the de Haas-van Alphen effect in the previous section forms the basis upon which we come to an understanding of our data, but does not describe how the actual measurement of the oscillations is performed in practice. Many devices and techniques exist but arguably the most powerful technique is known as the field modulation method. This is the sole method used throughout this thesis. Other methods, including static methods, and torque measurements exist, but are beyond the scope of this thesis. The reader is once again referred to Shoenberg’s book on the subject for a comprehensive overview of each technique, as well as their particular strengths and weaknesses [57]. Certain considerations apply generally to all methods including the need for high fields, low temperatures, and very pure samples. Additionally, typical signal strengths tend to be weak, and so highly sensitive techniques are required for observation. Lastly, strongly anisotropic magnetization can cause samples to torque, while rigidly fixing samples in place causes stresses on the samples, destroying the oscillations. This was particularly important in our measurement of YbRh\(_2\)Si\(_2\). These numerous concerns aside, the dHvA effect is an extremely powerful tool for 3D mapping of the Fermi surface of a material subjected to an applied field (chapters 3 and 4), measurement of quasi-particle masses (chapter 3), and could possibly be used for low temperature thermometry (chapter 4). While
the results of the section are well known and provided in numerous other sources, including
that of Shoenberg, Bergemann, Julian and Rourke [57–60], I provide the derivations again as
they help to elucidate the key results that allow for measurement of dHvA oscillations using
the field modulation method.

The basic premise of the field modulation dHvA method, developed by Shoenberg and Stiles
[67], is the periodic variation of the magnetization by application of a comparatively small time
varying magnetic field atop the quasi-static (read: very slowly varying) large main magnetic
field, i.e.

\[ B = B_0 + b_0 \cos (\omega t) \]  

(1.101)

where \( B_0 \) is on the order of 1-20 T and \( b_0 \) is on the order of 0.1 T. In order to measure the
variation in magnetization of the sample, a pair of balanced, counter-wound pickup coils are
wrapped so as to have the sample fit in one side as closely as possible. The so-called filling
factor of the coil is extremely important as the pickup of the coil is directly related to the ratio
of the sample volume to coil volume [68]. Ideally, any background pickup would be exactly
cancelled by the pair of coils, though they are rarely perfectly balanced. The voltage induced
in the coil is given as,

\[ v = c \left( \frac{dM}{dt} \right) = c \left( \frac{dM}{dB} \right) \left( \frac{dB}{dt} \right) \]  

(1.102)

and from \( B \) defined in eq. 1.101,

\[ \frac{dB}{dt} = -b_0 \omega \sin (\omega t) \]  

(1.103)

Following Shoenberg, we write the voltage induced in the pickup coil using a Taylor expansion
for \( b_0 \) small compared with \( B_0 \) [57],

\[ v = c \left( \frac{dM}{dB} \right) \left( \frac{dB}{dt} \right) \]

\[ = -c b_0 \omega \sin (\omega t) \left\{ \frac{dM}{dB} + \frac{d^2M}{dB^2} b_0 \cos (\omega t) \right\} \]

\[ + \cdots + \frac{d^kM}{dB^k} \frac{b_0^{k-1}}{(k-1)!} \left[ \cos (\omega t) \right]^{k-1} + \cdots \]  

(1.104)

\[ \bigg|_{B=B_0} \]
Taking the expression for the magnetization given in eq. 1.99, and simplifying further by assuming we are only looking at the fundamental for a single frequency, i.e. we eliminate the summations and take \( p = 1 \),

\[
\tilde{M} = -\frac{R_T R_D R_S C_0 \sqrt{B}}{c} \sin \left[ 2\pi \left( \frac{F}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right] \\
= -C \sqrt{B} \sin \left( \frac{2\pi F}{B} + \phi \right)
\]  

(1.105)

The total magnetization of the sample is given as the sum of that from the “static” main field, \( B_0 \) and time varying part, \( b_0 \cos (\omega t) \), thus,

\[
\tilde{M}(t) = M_0 \cos (\omega t) - C \sqrt{B_0 + b_0 \cos (\omega t)} \sin \left[ \frac{2\pi F}{B_0 + b_0 \cos (\omega t)} + \phi \right]
\]  

(1.106)

where the \( M_0 \) term represents the time varying portion of the static spin-susceptibility. Now assuming that \( b_0 \ll B_0 \) we can expand eq. 1.106 and use the trigonometric identity that \( \sin(u-v) = \sin u \cos v - \cos u \sin v \) and obtain [60],

\[
\tilde{M}(t) \approx M_0 \cos (\omega t) - C \left( \sqrt{B_0 + b_0 \cos (\omega t)} \right) \times \left[ \sin \left( \frac{2\pi F}{B_0} + \phi \right) \cos \left( \frac{2\pi F}{B_0} b_0 \cos (\omega t) \right) \\
- \cos \left( \frac{2\pi F}{B_0} + \phi \right) \sin \left( \frac{2\pi F}{B_0} b_0 \cos (\omega t) \right) \right]
\]  

(1.107)

Now making the substitution that,

\[
\lambda = \frac{2\pi F b_0}{B_0^2} = \frac{2\pi b_0}{\Delta H}
\]  

(1.108)

we get,

\[
\tilde{M}(t) \approx M_0 \cos (\omega t) - C \left( \sqrt{B_0 + b_0 \cos (\omega t)} \right) \left[ \sin \left( \frac{2\pi F}{B} + \phi \right) \cos (\lambda \cos (\omega t)) \\
- \cos \left( \frac{2\pi F}{B_0} + \phi \right) \sin (\lambda \cos (\omega t)) \right]
\]  

(1.109)
Using now one final substitution, that \( \sin (\lambda \cos (\omega t)) \) and \( \cos (\lambda \cos (\omega t)) \) can be written as an infinite sum of functions \( \cos (\nu \omega t) \) with coefficients of Bessel functions of the first kind, \( J_\nu (\lambda) \), the result is,

\[
\tilde{M}(t) \approx M_0 \cos (\omega t) + C \sqrt{B_0} \sum_{\nu=1}^{\infty} 2J_\nu \sin \left( \frac{2\pi F}{B_0} + \phi - \frac{\nu\pi}{2} \right) \cos (\nu \omega t)
\] (1.110)

Finally, we take the time derivative of eq. 1.110 to determine the pickup voltage in the coil,

\[
v = c \frac{dM}{dt} = -c\omega \left( M_0 \sin (\omega t) + 2C \sqrt{B_0} \sum_{\nu=1}^{\infty} \nu J_\nu (\lambda) \sin \left( \frac{2\pi F}{B} + \phi - \frac{\nu\pi}{2} \right) \sin (\nu \omega t) \right)
\] (1.111)

A number of very important features arise from this result. Firstly, by measuring on a harmonic, \( \nu \geq 2 \), using a lock-in amplifier we eliminate pick-up in the fundamental which immediately eliminates the first term in eq. 1.111, and acts to remove noise from the measurement resulting from unbalanced pick-up coils or vibrations of the sample and the contribution from the normal magnetic susceptibility, which is often very large \([59, 60]\). The summation is also eliminated yielding,

\[
v_\nu \approx -2\omega c C \sqrt{B_0} \nu J_\nu (\lambda) \sin \left( \frac{2\pi F}{B_0} + \phi - \frac{\nu\pi}{2} \right)
\] \( \equiv \tilde{M}_\nu \) (1.112)

And so by measuring on the harmonic, we are directly measuring the oscillatory magnetization of the sample. This is the critical result of the very long winded derivation. As noted by Patrick Rourke, pre-amplifiers and other electronic device can distort the resulting signal, however, the distortions tend to occur at odd harmonics, and as such, the measurements are normally carried out on the even harmonic numbers, though the usefulness of harmonics higher than \( \nu = 2 \) is limited as an increase in \( b_0 \) is required to maximize \( J_\nu (\lambda) \), but this causes eddy current heating in the sample, which acts to raise the temperature \([60]\). Since low temperatures are required to mitigate the \( R_T \) damping factor, selection of \( \lambda \), as in eq. 1.108 is critical. Tuning of the Bessel zero can drastically alter the amplitude of the pickup of a particular frequency. This is a blessing and a curse. It’s essential that one select an appropriate value for \( \lambda \), but one may need to alter \( \lambda \) in order to observe a particular frequency that could very well lie on a Bessel zero. In the same vein, one can eliminate frequencies that are of limited interest. Tuning
of $\lambda$ was carried out for both materials studied, and determination of the Bessel function and comparison of the resulting amplitude augmentation (or reduction) of a particular frequency allowed us to determine whether a frequency observed in YbRh$_2$Si$_2$ was a harmonic of a lower frequency or a distinct frequency.

**Applications of Oscillation Phase vs. Temperature**

In the majority of the analyses of dHvA data, the important quantities are the frequencies of the oscillations obtained from Fourier transform of the signal data, which correspond to extremal orbits of the Fermi surface, and the temperature dependence of the amplitudes of each of the observed frequencies. However, another potentially useful quantity in the LK equation is the phase of the oscillations. If we write down the expression for the oscillatory magnetization given in the underbrace of eq. 1.99 we can explore the importance of the phase more fully, i.e.

$$\tilde{M}_p = A_p(T, B) \sin \left( 2\pi p \frac{F}{B} + \phi_p \right),$$  \hspace{1cm} (1.113)

where $A_p$ is the coefficient of the sin term, as described in eq. 1.99, and

$$\phi_p = \frac{1}{4} \pm \frac{1}{4} - \gamma_p \pm \frac{1}{8},$$ \hspace{1cm} (1.114)

The first $\pm$ depends on the sign of the spin-splitting reduction factor and $\gamma$ is taken to be 1/2. The sign of the second $\pm$ can indicate whether the orbit is a maximum (+) or minimum (-) [57]. We extend the idea of determination of the phase even further in chapter 4. In PrOs$_4$Sb$_{12}$ the phase is used to measure slight changes in Fermi surface area with field. Adopting functions of the form,

$$\tilde{M}_f = A_f(T) \sin \left( 2\pi \frac{F_f(T_0)}{B} + \phi_f(T) \right),$$ \hspace{1cm} (1.115)

where only the $p = 1$ fundamental frequency is considered and the $f$ subscript is used to denote a fit to the magnetization 3 oscillations wide centered at a particular field value, $B_0$. The value of phase at different temperatures is obtained by this fit and a difference in phase with
temperature with respect to the lowest temperature value, $T_o$ is determined, i.e.,

$$\Delta \phi_f(T) = \phi_f(T) - \phi_f(T_o)$$  \hspace{1cm} (1.116)

In chapter 4 I show that,

$$\Delta \phi_f (T, B_o) = \frac{\hbar}{eB_o} \Delta A (T, B_o) ,$$  \hspace{1cm} (1.117)

i.e. a small-temperature dependent change in the extremal area of the FS, $\Delta A$, can be determined from measuring the change in phase of the oscillations [69, 70].

**Magnetic Breakdown**

Another important effect than can occur in dHvA studies of materials is magnetic breakdown, which in simplest terms allows electrons or holes to quantum mechanically tunnel between different orbits through a small energy gap. I will give a simple overview of the situation, and the reader is referred to chapter 7 of Shoenberg’s book for a 30 page discussion [57]. Magnetic breakdown can produce observed dHvA frequencies inconsistent with theoretically predicted extremal orbits. This very effect was extremely important in our initial (though incorrect) understanding of the results for YbRh$_2$Si$_2$ (chapter 3), as we thought it possible that certain observed frequencies could be obtained by mixing orbits on different FS sheets. The original magnetic breakdown idea sprung from the observation of orbits in magnesium larger than the BZ itself by Priestley [71] and was explained in the subsequent work of Cohen and Falicov [72], with refinement of the condition required for breakdown to occur by Blount [73]. The criterion for breakdown to occur is

$$\hbar \omega_c \gtrsim \frac{\epsilon_g^2}{\epsilon_F} ,$$  \hspace{1cm} (1.118)

where $\epsilon_g$ and $\epsilon_F$ are the energy gap between orbits and Fermi energy respectively. One explanation of this effect comes from the diffraction argument of Stark and Falicov [74]. If one imagines electrons with wave vector, $k_F$, the presence of the magnetic field causes curvature of the electron path such that the electrons travel a distance in the solid, $d = R \Delta \theta$ where $\Delta \theta$ is...
the change in the angle of incidence of the electron caused by the field and $R$ is the radius of curvature of the electron trajectory. An example breakdown orbit is shown in fig. 1.3. Given an extinction path length, $\xi$, or length over which Bragg scattering can occur, a percentage of the electrons continue on their path without being scattered and can continue on to a trajectory in a different zone, where the percentage is

$$P = \exp(-d/\xi) = \exp(-R\Delta\theta/\xi) \quad (1.119)$$

This follows from the argument that the separation between the branches, $\Delta k$ is approximately,

$$\frac{\Delta k}{k_F} \sim \frac{\epsilon_g}{\epsilon_F} \quad (1.120)$$

In the nearly free electron picture, gaps come from Bragg diffraction. If the quasiparticle follows a curved path, due to the application of the magnetic field, diffraction can be inhibited, so quasiparticles can be turned from one Fermi surface sheet to another. Specifically, the Bragg condition gives that $\sin \theta \propto 1/k_F$, so the angular range over which Bragg reflection can occur is related to an uncertainly in $k$, such that

$$\Delta \theta \sim \frac{\Delta k}{k_F} \quad (1.121)$$

Likewise, the extinction length is related to $k$ by,

$$\xi \sim \frac{1}{\Delta k} \quad (1.122)$$

The radius of curvature for a free electron at the Fermi surface is,

$$R = \frac{v_F}{\omega_c} = \frac{\hbar k_F}{eB} \quad (1.123)$$

and the Fermi energy is given by the standard formula,

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \quad (1.124)$$
According to Shoenberg, and based on the work of Falicov and Stark, the probability of breakdown occurring is then,

$$P = \exp^{-B_0/B}$$

(1.125)

where the breakdown field, $B_0$, is

$$B_0 \sim \frac{m}{\epsilon} = \frac{B e^2}{\hbar \omega_c \epsilon_F},$$

(1.126)

which is an equivalent condition to eq. 1.118 [57, 74]. Note that it is also possible for electrons to cross-over to hole orbits and vice versa, which was a requirement in our preliminary understanding of YbRh$_2$Si$_2$ [75].

**True Frequency**

One final consideration, applicable to all of the measurements made in this thesis, pertains to the actual frequency obtained by Fourier transform of the measured waveform. While ideally the Onsager relation (eq. 1.74) yields the relationship between the measured dHvA frequency and the area of the extremal orbit, this simple picture is not necessarily the case for those Fermi surfaces which have a field dependent shape. Instead, the observed frequency, $F_{\text{obs}}$, is actually the “back projection” of the “true” frequency, $F_T$. $F_{\text{obs}}$ is the $B = 0$ intercept of the tangent to $F_T$ [69]. Thus, if determination of the true area of the extremal orbit is required, one must use the relation that,

$$F_{\text{obs}} = \left(1 - B \frac{\partial}{\partial B}\right) F_T$$

(1.127)

It is, however, not possible directly know the exact value of $F_T$ from this equation, as a number of possible solutions which could yield the observed dHvA frequencies exist.
Figure 1.3: Example breakdown orbit. Two separate orbits, A and L exist. Failure of the quasiparticle to undergo Bragg scattering at the point indicated by the red dot causes the particle to traverse most of orbit A, followed by all of orbit L, and finally completes the rest of A, causing an oscillation with the frequency of A + L. Many such orbits exists in various combinations. Adapted from Shoenberg [57].
Chapter 2

Instrumentation and Analysis

Software

The primary experimental technique employed in this thesis for the study of heavy fermion metals is the field modulation de Haas-van Alphen (dHvA) method, the theory of which is described in detail in the introduction chapter in section 1.3. As one might infer from the previous discussion of the theory of the dHvA effect, the extraction of the frequencies corresponding to extremal orbits of the Fermi surface is quite straightforward, consisting mainly of a background subtraction of the data followed by a Fourier transform. However, in order to get to the point of analyzing the software one must be able to successfully measure the dHvA oscillations, a task which is anything but trivial. It is essential, therefore, to closely examine both the electronics and equipment involved in the measurement and to understand what manipulation of the data is being done to achieve the end result. This chapter gives an in depth look at the equipment used in our lab at the University of Toronto and the custom Python software written to analyze the resulting data.
2.1 Equipment

2.1.1 Dilution Refrigerator

The focal point of our laboratory setup is the Oxford Instruments Kelvinox MX400 $^3\text{He}/^4\text{He}$ dilution refrigerator which has a cooling power of 400 $\mu$W at a temperature of 100 mK and a theoretical base temperature of 7 mK. In practice, we have, as of the time of this writing, been unable to achieve a sample temperature lower than about 25 mK likely due to the quality of our heat sinking wires and the lack of a full radiation shield, though both of these issues are currently being addressed. This temperature is sufficiently low for measuring dHvA oscillations in most materials, though as was discussed in the introductory theory, it results in a decrease in the amplitude of the observed peaks for high mass quasiparticles, as described by the temperature dependent factor, $R_T$, in the Lifshitz-Kosevich equation (eq. 1.82). The normal operating temperature is between about 40 mK and 600 mK, though in microcirculation mode we are able to go up to about 10 K safely. The Kelvinox insert sits within a cryostat, which acts as a large thermos with a liquid helium bath in the centre and outer shield at liquid nitrogen temperature in order to keep the system cold and to minimize heat leaks to the dilution refrigerator. In the base of the cryostat sits a 16/18 T superconducting magnet made up of Nb/Ti outer windings and Nb$_3$Sn inner windings, embedded in a copper matrix. Additionally, for the field modulation dHvA technique we require a secondary field produced by a modulation coil with a maximum field of a few hundred Gauss. As the measurements are extremely sensitive to all forms of noise, the cryostat is set on top of a piece of plywood, under which sit rubber shock absorbing feet, all of which is set set atop a large concrete block which is about 5 feet below ground. This helps to reduce noise caused by vibrations. Additionally, the cryostat and dilution unit are grounded electrically to eliminate another form of noise. When in use, the dilution unit is connected to a manually controlled gas handling system with the still, lambda fridge, and 1 K pot lines set in another, ground level, concrete block. This is again done to reduce noise caused by vibrations of the system. A series of vacuum pumps are required for fridge operation, including a sealed $^3\text{He}$ pump, which ensures the helium mixture remains intact in the event of failure, and can be pumped into the “dumps” storage container at the end of a run. The fridge itself is equipped with a variety of different thermometers at various locations within the fridge.
Using these, the temperature can be measured at both the 1 K pot and mixing chamber quite accurately. The mixing chamber includes thermometers that operate at different temperatures ranges, allowing us to monitor the fridge temperature during cool down and warm up. Above about 4 K a calibrated cernox thermometer is used, whereas below this temperature a calibrated RuO “m70” thermometer is used. Having an accurate method of determining temperature is essential in dHvA measurements, both for ensuring proper fridge operation and for completing the highly temperature dependent measurements. The m70 thermometer isn’t calibrated for use below about 30 mK and so the desire for accurate low millikelvin thermometry spawned the SQUID noise thermometry project, discussed in appendix B.

2.1.2 dHvA Equipment

The heart of field modulation dHvA measurements is the counter-wound pickup coil. The coils are wound by hand using a coil winding machine. The coil dimensions are chosen specifically to match the sample to be measured and a coil former on which the coil is wrapped is made to order, so to speak. For example, for the YbRh$_2$Si$_2$ measurements, a coil former made of 100 µm aluminum foil folded over on itself (making it about 200 µm thick) was cut to a width of about 2 mm. This foil was coated in a thin layer of vacuum grease, and finally a piece of Mylar is wrapped around the aluminum and epoxied to itself. It is essential that no epoxy comes into contact with the aluminum during this process or else when the coil is completed one will not be able to remove it, and the whole process will have been for nought. Once the epoxy has dried, small rectangles of card stock are cut to form the support of the coil. Three such pieces are cut and slid into place and fixed using 5 minute epoxy. In this step, one must take care to not get any epoxy leaking through the hole in the cardboard into the centre where the wire will be wrapped or during the wrapping procedure you won’t be able to get the wire tightly wrapped around the Mylar. Once this is done, the actual coil winding begins. The wire used for this procedure is 10 µm self-bonding Cu wire. The number of turns for each section of the coil depends on the dimensions required, but the number of turns I used is generally around 1000 per half of the coil in approximately 10 layers of 100. Once one section of the coil is completed, the wire is bonded to itself using a drop of ethanol, and the wire is cut from the spool and another coil is wrapped to form the second section. The wire itself is wrapped
in the same direction as before, as this is the only direction that the lathe-like spindle of the coil winder turns in. Once the second section is completed, a top and bottom piece of card stock are added across all three upright sections of the card stock for protection and to affix an 80 µm twisted triplet that will eventually be connected to the tag board in the fridge. These wires are significantly more sturdy than the 10 µm wire and thus are suitable for soldering, manipulating, etc. The end of the twisted triplet is spread apart, and the three wires tinned. The triplet is then fixed to the card stock at the point where the wires once again become twisted using 5 minute epoxy. After many unsuccessful attempts at making coils, I decided to add two more pieces of card stock to the sides, thus enclosing it on all sides and protecting it from any accidental breakage caused by touching or rubbing the coil against something, as becomes an issue when sliding it into the graphite bobbin described later. A small gap is left between the side card stock pieces and the top to allow for the 4 ends of the 10µm copper wire to come out of. Now, in the ideal case, both sides of the coil are identically balanced and wound opposite to each other so as to cancel out any background that is common to both. In practice, the coils are not identical and have been wrapped in the same direction. In order to address the direction of winding, we connect the “ends” of both coils together forming the centre of the coil and ensuring that the direction of winding of either side is opposite. While it was previously suggested to me that small pieces of 40 µm wire be soldered between the 80 µm twisted triplet and 10 µm coil wire, I found it impossibly difficult to solder all of the joints properly and get good electrical connection. Thus, in my coils, the 10 µm wires are connected directly to the 80 µm wire, with protection being provided by the surrounding card stock. The two “end” wires are wrapped around a single wire of the twisted triplet and are soldered in place. There is no need to remove insulation from the 10 µm wire, as the heat and a small blob of solder will be sufficient to remove it. Once this is complete, the two remaining wires of the coil are connected separately to the two remaining wires of the twisted triplet. Generally, each section of the coil will have a resistance on the order of a few kΩ. The coil is then carefully slid off of the former and any excess Mylar is trimmed using a very sharp knife. A diagram of the coil can be seen in fig. 2.1.

After completion of the coil, the sample can be inserted. Before doing this, it’s essential (as we’ll see from some of the issues I had during my measurements) to know that the sample is
Figure 2.1: Simplified schematic diagram of the counter-wound coil used in the field modulation de Haas-van Alphen technique. Below is a cartoon representation of the final form of the coil, including protective housing.
in the orientation desired. Once oriented, a 50 µm silver wire is soldered (or affixed in another way if soldering isn’t possible) in order to attach the sample to the larger annealed silver wires connected to the mixing chamber for heat sinking. A small “gallows” is made out of thin pieces of wood and is epoxied to the side of the coil directly beside the opening. The sample is then placed into the hole in one side of the coil and the silver wire is epoxied to the gallows. Layer after layer of epoxy is applied to the silver wire until it is rigid and fully supports the sample.

Because our primary concern in performing dHvA measurements is the determination of the shape of the Fermi surface, it is essential that we rotate the sample in order to determine the angular dependence of the frequencies. It would be very inconvenient, and extremely slow, to warm up the fridge, reorient the sample, and reconnect it in order do this. Thus we have a rotation mechanism, capable of rotating the sample through an angle of almost 90 degrees. The rotation mechanism consists of a graphite tail with three sample holders and a push/pull arm controlled by the rotation of a screw that extends up the length of the fridge and out to room temperature. The position of the rotation mechanism tail is governed by the length of the quartz tube it is connected to, placing the samples directly in the bore of the magnet. The samples (in their coils) are placed into graphite bobbins and are fixed in place using epoxy and small pieces of fishing line to allow them to be suspended within the bobbin. The bobbins are fixed into the rotation mechanism at their centres using polycarbonate screws with holes drilled through the middle, allowing the twisted triplet (connected to the coil) and the silver heat sinking wire (connected to the sample) to be passed out of the bobbin and sample holder, while still rotating freely. The graphite of the bobbin against the graphite of the rotation mechanism tail is good for self lubrication, reducing friction and allowing free rotation of the bobbin at low temperature. The push/pull rod is fixed with a small polycarbonate rod to the top corner of the bobbin, which causes the bobbin to rotate about the polycarbonate screw as the rod moves up and down. In the original design of the rotation mechanism as described in Patrick Rourke’s thesis, a drive rod from the top of the fridge was connected to the screw which would drive the push/pull arm up and down via a belt made of Kevlar fishing line [60]. This, however, was shown to cause some slipping at low temperatures. Early on in my PhD I redesigned this section of the rotation mechanism, replacing the two rods connected by a Kevlar belt with two bellows connected together using polycarbonate joiners, shown in fig. 2.3. This allowed for a
rigid connection and eliminated the problems with slipping. This rotation setup also allows one
to run automated sweeps by attaching a motor to the drive rod at the top of the fridge. Once
a field sweep is completed, the motor can rotate the rod by a fixed amount corresponding to a
particular angle of rotation of the bobbin, and a new sweep can be started.

Figure 2.2: Graphite rotation mechanism used for measurement of YbRh$_2$Si$_2$ and PrOs$_4$Sb$_{12}$. Polycarbonate pull rod in center of figure.

Returning to the actual electronics involved, the silver wire attached to the sample and
coming up from the rotation mechanism, out of the polycarbonate screw, is soldered to a large
annealed silver wire running down the length of the quartz tube and fixed at the top to the
sample stage at the underside of the mixing chamber. This allows for good thermal connection
and thus we are able to state the sample temperature as that measured at the mixing chamber.
The twisted triplet is fixed down to the quartz tube using GE varnish, and runs up to a tag
board at the mixing chamber for electrical connection to room temperature. At this point, the
full coil (not just one half, but rather the sum of the counter-wound coils) is connected across a
low temperature transformer built by Alix McCollam. The low temperature transformer is used
to match the impedance of the coil to the optimal value needed to minimize the preamplifier
noise based on the noise contours of the particular pre-amp. Additionally, the low temperature
transformer acts to amplify the small dHvA signal above the noise level of the pre-amp, allowing
for the largest signal-to-noise ratio (SnR), while a capacitor at room temperature creates a
resonant circuit which allows the transformer to operate at a lower frequency but restricts the
useful frequencies to a narrow band [76]. In addition to the total coil output being connected
into the low temperature transformer, both sides of the coil are accessible directly, allowing
a resistor to be connected in parallel to one half of the coil for balancing unmatched coils.
From the low temperature transformer, the secondary is connected via LEMO cable to a small
capacitor, and finally to a 1000x pre-amplifier before the data is finally collected. Additionally,
Figure 2.3: Redesigned drive mechanism for *in-situ* rotation of samples. This design uses bellows to translate the desired rotation from the top of the dilution fridge, which prevents slipping.
if we desire to measure the signal on the second harmonic instead of the primary in order to improve the measurement by the lock-in amplifier, a notch or twin-t filter is added in series, after the pre-amp in order to reduce the primary frequency. This exact setup is repeated for any other samples being measured.

There is one other addition to the bobbin with the sample to enable us to directly measure the angle of rotation. While we know the orientation of the bobbin before cooling, and the change in angle corresponding to a rotation of the drive shaft at the top, upon cooling there can be a considerable shift in the angle. To eliminate this uncertainty, a single loop of wire is wrapped around the outside edge of the bobbin. From this loop, also connected to the tag board at the mixing chamber, we can measure the direct field pickup and by fitting this to a cosine function we are able to determine the current angle of the bobbin.

While this rotation mechanism was the sole mechanism used in the measurement of PrOs$_4$Sb$_{12}$ (chapter 4), and the primary mechanism used for the YbRh$_2$Si$_2$ measurements, a secondary rotation mechanism made of polycarbonate was constructed allowing for two samples to be measured simultaneously, about a perpendicular axis, without having to remove them from the graphite bobbins in which they were originally fixed. Instead of the bellows drive system, the platform of the polycarbonate rotation mechanism was held under tension by a spring located within the quartz tail. Fishing line fixed at the bottom of the platform was tightened by rotation from the top of the fridge (as with the graphite mechanism), and applied a torque to the end of the polycarbonate platform. Because of the spring, the platform would rotate back when the fishing line was released. This enabled rotation of the platform in steps of about 3 degrees and was used for the most recent YbRh$_2$Si$_2$ measurements. A 3D model of the rotation mechanism is shown in fig. 2.4a, and a picture of the completed part in fig. 2.4b.

2.1.3 Data Collection

I will refer the reader to the thesis of Patrick Rourke for an in depth description of all of the functions and subsystems of the Data Acquisition and Virtual Instrumentation Experiment System DAVIES for the sake of avoiding a repetitive discussion on this topic. Also found in Patrick’s thesis is a complete list of all the devices and their functions involved in DAVIES [60]. I will only mention hardware that I’ve changed since Patrick’s departure or devices essential
(a) Polycarbonate rotation mechanism, which made use of fishing line and counter tension by spring. This setup allowed for rotation of two samples, still in their graphite rotation mechanisms to be rotated simultaneously about a perpendicular axis.

(b) Image of the polycarbonate rotation mechanism used in select measurements of YbRh$_2$Si$_2$. Sample mounted in graphite bobbin.
to understanding the operation of the system. That being said, I will give a general overview of the program and how it was used in my measurements. In addition, I will try to comment on any modifications or issues that have arisen since I’ve been at the helm, so to speak. For the extremely keen reader or perhaps a future graduate student, I will also refer you to the full DAVIES operation manual found in the lab.

Overview

DAVIES is a sophisticated data collection system consisting of a number of pieces of hardware and a set of control programs written in the LabVIEW programming language, which while not the most lightweight or straightforward programming language to use, interfaces very nicely with the hardware purchased from National Instruments and, in retrospect, has proved fairly easy to work with in the unavoidable event of a computer upgrade. The brunt of the data collection is physically completed using a National Instruments PXI-1042 (PCI eXtensions for Instrumentation) chassis, which simply acts as a breakout box for a variety of PCI cards, such as an analog output card, multimeter card, multiplexer, analog input card, etc. This avoids attempting to put a multitude of cards on a motherboard that certainly cannot handle the sheer quantity of devices required. The output of the PXI box is then connected into the data collection computer named Max via a PC-to-PXI card. A variety of the cards in the PXI box have additional hardware components, such as the National Instruments BNC-2210 connection block connected to the National instruments PXI-6143 8-channel analog DAQ card. This breakout box allows for access to all of the available channels on the card and provides the user with the physical BNC (or other type) connector to connect the input or output cables to. All of the data collected by the PXI box is stored on Max and is accessible by the control computer known as Dew through what LabVIEW calls the DataSocket server. In simple terms, the DataSocket server allows a computer to provide variables present in a LabVIEW program on one computer to another LabVIEW program running on a separate computer or to a program running on the host computer in a fairly simple and straightforward manner. The variables are served up via the network, so as long as the computers are able to talk to each other, and very importantly, able to talk to each other fast enough, variables can be read and written from one computer to another or by running Virtual Instruments (VIs) on the same
computer. In our system, Dew is used to control the DAVIES Main Front Panel (MFP) by the Virtual Networking Connection (VNC) protocol. The MFP provides the user with all of the controls of the system including but not limited to: current temperature measured by a selected thermometer, current magnetic field value, temperature control, field control, starting and stopping of data collection, setup of automated field and/or temperature sweeps, etc. The collected data is served up via the data socket server to a program running on Dew called Real Time Analysis, which provides graphical output of any of the collected variables. In order for the computers to check that the other is functioning properly, and to allow software on one computer to open or control software on another computer, the requirement is that DAVIES MFP must be running on Max and Dew Nerve Centre (DNC) be running on Dew. Also, both computers have shared error handling, so in the event of an issue with one computer, the other computer is able to modify its behaviour or even stop operation in order to compensate. As described by Patrick Rourke, one of the key design features of DAVIES is the ability to clear issues that aren’t show stoppers without causing the other running VIs to crash \[60\]. There was, however, an issue known affectionately as the “Route 66” error which was previously unsolved. In the following section I will describe the issue and how I have almost entirely eliminated it. The section after that will briefly describe the procedure used for computer upgrades.

**DAVIES Data Collection Backend**

Besides the control interface, and sweep automation that DAVIES provides, the real heart of the system is its data collection routine with the central program being **LockinSub.vi**. The **LockinSub.vi** provides 4 virtual lock-in amplifiers based on the National Instruments Lock-In Start-up Kit and modified by Patrick Rourke. For a typical experiment, up to 8 analog voltages are read into the analog input card in the PXI box at a common rate of 50 000 samples/sec. Exactly analogous to a real lock-in amplifier, one of these 8 channels must contain a reference signal, which can either be generated by the **PFgen.vi** built into DAVIES or from an external source (often the signal generated by our hardware lock-in amplifier, a Stanford Instruments SR830). Unlike a hardware lock-in, the virtual lock-ins are capable of sampling the data at up to 6 user-specified harmonics of the reference signal for a single measurement input signal, effectively allowing the 4 virtual lock-ins to act as 24 separate devices. The virtual
lock-in amplifiers also allow for the user to specify a number of parameters including, time constant, roll-off, and filter type. Thus, the virtual lock-ins are significantly more configurable than the hardware version. The data from the lock-ins, in addition to the measured field and temperature data, is provided to the DataSocket server every $\sim 100 - 250$ ms and are periodically read by the `SampleAndSave.vi` and saved to a data file on Max. The sampled data is displayed on Dew using the previously mentioned `RealTimeAnalysis.vi` which opens automatically upon beginning data collection and is capable of displaying two plots, with each having a user selectable X and Y value. Additionally, one can do a very quick and basic FFT of the first plot in order to get a general sense of whether or not dHvA peaks are present in the signal as it comes in.

**Route 66 Error**

The “Route 66” or simply error 66 was an issue encountered sporadically by Patrick Rourke while running DAVIES and repeated attempts to completely remedy the issue or even understand the underlying cause, were for the most part unsuccessful. The issue occurred within the DataSocket subsystem and multiple calls to the engineering team at National Instruments were unsuccessful in elucidating the root cause. As Patrick noted, the error 66 error was preceded by a slow down of the temperature control VI (`TControl.vi`), with a loop of the VI going from $\sim 100$ms to 50 or 60s before causing the error. It was also noticed, that rebooting the control software on Dew (`DewNerveCentre.vi`) prevented the route 66 error from occurring. Hence, the (`Route66.vi`) program was created to check the time between subsequent loops of `TControl.vi` and reboot `DewNerveCentre.vi` as necessary. While this almost completely prevented a complete crash of DAVIES, the Route 66 error continued to occur on occasion. Over time the slow downs of the system and the occurrence of the Route 66 error started to become more and more frequent, preventing us from consistently taking data. I used the down time between measurements to try to remedy the situation. Because the issue seemed to originate with the slow down of `TControl.vi` with the issue propagating to `DewNerveCentre.vi`, I postulated that the issue was one of the communication between Max and Dew. The router in use was an old D-Link DI-704P 10BaseT/100BaseTX model, I decided that we might benefit from a router with a faster on-board processor and gigabit ethernet ports. According to the
Dell Optiplex G620 (Max) and Dell Optiplex G280 (Dew) both computers had built-in gigabit ethernet and so there was no harm and only the possibility of a communication speed boost in replacing the router. The router itself was upgraded with third party firmware to allow for features previously unavailable and to allow for more customization of the ones already present. After this, a small improvement in the Route 66 issue was realized, but not enough to be able to state the issue was resolved. The final communication speed improvement came from the thought that the router was too slow in communicating to the computers at which IP address the other was located. The LabVIEW VIs referred to the other computers by hostname, but left the resolution of this name from a word to an actual IP up to the router. I believe that prior to this point, as well, the computers were being assigned their IP addresses statically by the router upon connection to the network. To eliminate any work done by the router, I set the computers to have static IPs on the computers themselves with Max being located at 192.168.0.119 and Dew being located at 192.168.0.133. Lastly, I edited the hosts file on each of the machines, located generically for the Microsoft Windows operating system in %SystemRoot%\system32\drivers\etc\hosts. It should be noted that at this point, both Max and Dew were running the latest version of Windows XP. The files were edited and the lines,

127.0.0.1 Max
192.168.0.133 Dew

were added on Max and the lines,

127.0.1. Dew
192.168.0.119

were added on Dew. Since having made these minor modifications, to the best of my knowledge we haven’t encountered a randomly occurring Route 66 error. That being said, there does still seem to be an issue with DAVIES in that it tends to slow down over time, possibly indicating a slow memory leak. It is, therefore, important to restart the software at the beginning of each new fridge run, and possibly after collecting data for an extended period of time. Occasionally, simply restarting DAVIES and LabVIEW in general does not remedy the slow down and thus the computers must both be restarted. The order of this doesn’t matter, however as a general
rule, I tend to restart Max first, as it’s controlled over VNC from Dew. After this I restart Dew and finally open \texttt{DewNerveCentre.vi} on Dew before starting DAVIES on Max. A schematic of the entire setup can be seen in fig. 2.5

\section*{2.1.4 Data Analysis}

\textbf{Python Data Analysis Software}

For the first few years of my research, the standard method of extracting the dHvA frequencies from the raw data was using \texttt{netcdfHvAanalyzer.vi} created by Patrick Rourke for analysis of his data. The program is written in LabVIEW and provided a very nice graphical interface for inspecting the data, subtracting any background, removing so-called data spikes (to be discussed later), and for windowing of the data before taking the Fast Fourier Transform (FFT). The program was convenient in that you could check off the order of the background polynomial to be fit, select the range of the data to be analyzed, change the windowing function and take the FFT and the graphical display would show you which step was being completed and the result. After obtaining the FFT spectrum one could then determine the dHvA peaks and plug them into a phase optimization routine to determine the optimal phase angle of between the X and Y outputs of the virtual lock-in amplifier in order to maximize the amplitude of a given peak. The raw waveform and FFT spectrum were saved to data files for future use. That being said, I found it quite slow to have to run each dataset multiple times and write the dHvA peaks and their amplitudes into a text file by hand. I decided it would be prudent to write my own analysis software. For this purpose I chose to use Python as the programming language and more specifically the Enthought Python Distribution due to its inclusion of the necessary libraries for reading our data files which are stored in the NETCDF4 format. NETCDF4 is based on the HDF5, a Hierarchical Data Format, originally based on the Common Data Format (CDF) developed by NASA. It provides a machine independent data format for large datasets in a multidimensional array accessible in a file system tree-like manner allowing for POSIX type addressing of the variables. While this file format is excellent for storing all of the variables present in the measurement, it also requires a not so straightforward method in order to extract the necessary data to simply plot the waveform. The data is not stored in a standard text file
Figure 2.5: Schematic diagram of the experimental setup, including sample, low and room temperature electronics, and data collection devices
and thus one can’t simply open the data in a program like MatLab or even Microsoft Excel to plot the various columns. This is where the Python NETCDF package comes in. It allows one to open the data set, import the variables by name into arrays and finally plot the data. My analysis software accomplishes this task, and like Patrick’s software, is also capable of storing the raw data into a text file.

The basic flow of the software is as follows, though it should be noted that in terms of modifying the routine, one must edit the main program file called *dhva_main.py* and thus it is certainly less straightforward than the previously mentioned graphical utility. First, the program determines the operating system in use in order to determine the proper file path addressing format. Once completed, the user enters the path and filename of the data to be analyzed. You then have the option of converting the dataset into a .dat file, a procedure that is handled by the *convert_CDF.py* subroutine. You can then select which samples (at present corresponding to virtual lock-ins 1-3, though the implementation of the 4th lock-in is trivial) labelled A, B, and C are to be analyzed for this set, depending on how many samples were present during the measurement. For each enabled sample, one can then select the harmonic number to be analyzed, the field range, whether or not the data is to have spikes removed, which mother wavelet to use (more on this momentarily), how many levels of wavelet filtering to use, whether or not the data should be windowed, which type of windowing function to use (hanning, blackman, etc.), and finally whether or not you want the resulting dHvA frequency and peak amplitude to be recorded. Generally, I first run through the data with the save to file option turned off in order to get an idea of what the data looks like, and then on a second pass choose the correct peaks and save them to a file. The resulting data files are labelled sampleA.dat, sampleB.dat, etc. Because during the analysis one typically goes through dozens of data files, each corresponding to a different field angle with respect to the sample orientation, the program checks for an existing data file and appends the new frequency information to the end of this file. The order is generally not important, as the Python program used to relate data file name to actual angle based on the small single pickup loop attached to the bobbins (a program written by my supervisor, Stephen Julian) adds in the angular information based on the filename.

Once the data and options have been selected, the user is presented with a 4 pane plot
Chapter 2. Instrumentation and Analysis Software

showing the raw data (both X and Y from the lock-in), the background subtracted data, the despiked and windowed data, and finally the FFT spectrum. The user can then select a dHvA peak by clicking to the left, the centroid, and finally the right of the peak with their left mouse button. A Gaussian function is then fit to the peak, and the amplitude and central frequency are stored in an array until the user is finished selecting subsequent peaks. This triple click procedure can be completed as many times as necessary to select all the present peaks, and erroneous clicks can be removed using the right mouse button. The procedure is finished when the user presses the middle click button on their mouse. The peak frequency, and errors are then output to the Python console and saved to a file if this option was previously selected. It should be noted that while this all sounds very simple, there are some small bugs related to the clicking procedure that need to be ironed out, but reflect my lack of knowledge of the ginput Python library responsible for selecting x,y coordinates on a plot by mouse click. Specifically, for the moment a user is unable to delete an entire selected peak once the third click has been made. This is not an enormous issue, as one could simply reselect the peak on the next pass, but would be required to manually edit the resulting data file, an issue which disrupts the flow and ultimately the speed of the analysis procedure. Secondly, it is common to want to zoom the plot in around a peak, in order to get it to fill the entire graphical pane. The zoom function is built into the Python plotting interface, however, when one clicks and drags the zoom box around the peak in question, ginput recognizes this as a single mouse click. Again, this is not a major issue unless the user is unfamiliar with the software. The best practice is to zoom around the peak first, right click a few times to delete any coordinates registered by ginput, and then proceed with the three clicks. Zooming out does not present this issue.

It is important to discuss the improvements made over Patrick’s analysis program, as there was absolutely nothing wrong with the procedure as completed previously, and in fact, my original data collected in 2009 was first analyzed with his software, and then redone a second time using my software. I believe, that once one becomes accustomed to my software, the speed improvement is measurable. While both my software (though not a necessity) and the LabVIEW program often require multiple passes to achieve the desired result, I find a savings of at least one minute on each dataset due in part to the speed of the “click-click-click” procedure, and as well because of the program automatically saving the data to a file instead of having to
manually type it. Lastly, the ability to analyze all of the samples in one pass, allows us realize a large speed increase, as in the LabVIEW analysis program, this would have required multiple passes of the same dataset and would require the user to manually changes the variables being analyzed. The largest non-speed improvement comes in the form of the spike removal routine in which I implemented a very modern approach to removing outlier data points. When taking data, often on the first few sweeps of a new run, we noticed a large jump in the magnetic field, which was termed a “flux jump”. This would result in a jump in the measured waveform that we wanted to remove as we know that it doesn’t correspond to an effect present in the sample. Patrick had implemented an interpolation based method of spike removal, which worked perfectly fine, but required a bit of processing time. Instead, I have employed a mathematical technique known as a wavelet transform in order to remove the spikes.

If one first considers a Fourier transform, the basic idea behind it is to analyse a waveform into sines and cosines and based on the relative amplitudes of these sines and cosines, determine the relative importance of each of the frequencies in the given signal. This, however, has one issue, you lose time resolution (imagining of course, that the x-axis is in time, though this is not the case in our measurements). In the Fourier transform the sines and cosines span the entire selected range of data, which is not an effective way of analyzing an isolated event, like a spike in the data. This issue is tackled using the wavelet transform. Instead of using sines and cosines, one uses a so-called mother wavelet function as the basis of the transform, with the selection of the mother wavelet based on the data to be analyzed. For our data I’ve been using the Coiflet2 mother wavelet based on the suggestion of this wavelet for spike removal by Veneri et al [77]. The mother wavelet is convolved with the waveform data on a short time scale, and moved along through the entire range of data, preserving time resolution. This procedure can be done for a number of “levels” of decomposition, compressing the mother wavelet function and passing it through the data again. The result is a number of datasets corresponding to the number of levels of the transformation. If one uses a sufficient number of levels, and thus a highly compressed wavelet, one can strip this high level transform of the data, removing features short in time, while preserving the rest of the signal. This is what has been done for removal of the spikes, as they occur very quickly on the scale of the dHvA oscillations. I decompose the signal into 2 or 3 levels, remove the resulting waveform corresponding to the
highest compression of the mother wavelet and finally recombine the remaining decompositions and recover the original signal with the spikes removed. The mother wavelet, \( \phi \), with scaling and shifting parameters, \( a \) and \( b \), is written as,

\[
\phi_{a,b}(t) = \frac{1}{\sqrt{|a|}} \phi \left( \frac{t - b}{a} \right) \quad a, b \in \mathbb{R} 
\]  

(2.1)

The integral wavelet transform is then defined as,

\[
[W_\phi f](a,b) = \frac{1}{\sqrt{|a|}} \int_{-\infty}^{\infty} \phi \left( \frac{t - b}{a} \right) f(t) dt, \quad (2.2)
\]

where \( f(t) \) is our time varying waveform. The wavelet coefficients are written as,

\[
c_{jk} = [W_\phi f] (2^{-j}, k2^{-2}) \quad (2.3)
\]

which in our case means that,

\[
a = 2^{-j}, b = k2^{-j} \quad j, k \in \mathbb{R}, \quad (2.4)
\]

with \( \mathbb{R} \) representing the so-called aleph number or the cardinality of the set of functions constructed by dyadic translations of \( \phi \) [77]. While this is fairly complicated mathematics, the challenges of implementing this technique are alleviated by the use of the PyWavelets module in Python, which allows you to simply specify a mother wavelet and the number of desired levels of decomposition, sparing me from having to obtain a PhD in mathematics.

The windowing and background subtraction algorithms were implemented in a similar fashion to those in netcdf/HvAnalyzer.vi. The windowing is done in the standard fashion by selecting a window width (user selectable) and multiplying the waveform by the window function. The smoothing of the data is done as a part of the analysis_sub.py routine in a function called smooth.py which implements flat, hanning, hamming, blackman, and barlett windows and is based on the SignalSmooth code of the SciPy.org code cookbook. The hanning window with windowing function,

\[
w(n) = 0.5 \left( 1 - \cos \left( \frac{2\pi n}{N-1} \right) \right) \quad (2.5)
\]
provides very low aliasing, allowing for differentiation of nearby peaks, at the cost of slightly decreased resolution (broadening) of the peak after the Fourier transform. It is one of the commonly used window functions for signal processing involving a transform to the frequency domain.

After writing the analysis software, it was important to determine whether or not we had good agreement with the tried and tested LabVIEW analysis code. The original YbRh$_2$Si$_2$ data from 2009 was at that time analyzed with the LabVIEW software, while the data from 2012 was analyzed with my Python code. Since we repeated one of the rotations from the 2009 runs (more on this in the YbRh$_2$Si$_2$ chapter), I was able to compare the results of my analyzer with those of Patrick’s. As can be seen in fig. 2.6, we have good agreement.

Figure 2.6: Comparison of my analysis software, written in Python, with the LabView based software of Patrick Rourke. My Python software was used for all data from 2012 on, and this analysis was done as a consistency check to ensure agreement with data previously analyzed using Patrick’s software.
Chapter 3

YbRh$_2$Si$_2$

I will start with an introduction to YbRh$_2$Si$_2$, followed by information on the experiments I completed and finally a discussion of the results. The experimental results are also described in two journal articles, one which is published [78], and one which is currently in the final stages of completion.

3.1 Introduction

YbRh$_2$Si$_2$ is a prototypical heavy fermion material, and there has been keen interest in its properties since the discovery of non-Fermi-liquid nFL behaviour by Trovarelli et al. in 2000 [79]. Prior to this discovery, much research had been conducted into the behaviour of 4$f^{1}$-Ce$^{3+}$ compounds, including the discovery of the first heavy fermion superconductor, CeCu$_2$Si$_2$ by Steglich et al. in 1979 [21, 38]. 4$f^{13}$-Yb$^{3+}$ represents the hole analogue of the Ce based compounds, with one hole instead of one electron in the 4f-shell. Prior to Trovarelli, research into the Yb compounds Yb$_2$Ni$_2$Al [80], YbCuAl [81], and YbCu$_2$Si$_2$ had shown magnetic ordering at high pressures, but these high pressures prevented study of the behaviour in the quantum critical regime using the relevant thermodynamic measurements [79]. YbRh$_2$Si$_2$ with ThCr$_2$Si$_2$ (I4/mmm, a=b=4.010 Å, c=9.841 Å) crystal structure (similar to many families of superconductors including the high-$T_c$ superconductors like YBCO, fig. 3.1), shows a very large coefficient of specific heat and heavy quasiparticle effective masses below the Kondo temperature, $T_K \approx 25$ K, due to hybridization of the f-electron moments with the conduction electrons.
Lowering the temperature further, YbRh$_2$Si$_2$ enters a zero field weak antiferromagnetically ordered state at $T_N \sim 70$ mK, as seen in measurements of the staggered moment and entropy gain [38, 82]. This transition is suppressed to a quantum critical point at the very low in-plane field of 0.06 T ($B \perp c$) or 0.6 T ($B \parallel c$). YbRh$_2$Si$_2$ represented the first stoichiometrically pure HF material with readily accessible QCP [79]. Beyond this critical field, a highly enhanced paramagnetic state is entered [82]. The onset of nFL behaviour at zero field begins below 10 K as evidenced by the near linear $T$-dependence of the low-temperature resistivity ($\rho(T) - \rho_0 \propto T$) and the logarithmic divergence of the $T$-linear coefficient of specific heat, $\gamma$ [38]. There was particular interest in this material as AFM to PM critical points are often associated with nFL behaviour, and additionally with unconventional forms of superconductivity [25]. YbRh$_2$Si$_2$ played a central role in understanding these quantum phase transitions because the AFM to heavy paramagnetic Fermi liquid critical point coincides with the $T \rightarrow 0$ K limit of the $T^*$ line, a line which indicates a distinct change in Hall coefficient and upper limit of the $T^2$ behavior of resistivity [38, 83, 84]. It has been argued that this sudden change across the $T^*$ has indicates a change in the volume of the Fermi surface from a so-called “small” surface at low field, which does not include the 4f Yb quasi-hole in the Fermi volume, to a “large” surface at higher fields, which does include this quasi-hole. A number of different mechanisms for this crossover have been proposed, including a delocalization transition within the Kondo breakdown scenario [37], Bragg scattering of the heavy quasiparticles off of spin-density wave fluctuations [37], a fluctuating valence state [85, 86], or a Lifshitz transition caused by the large Zeeman splitting as a result of the applied field [87]. More interesting still, is the proposition put forth by Si et al., that YbRh$_2$Si$_2$ exemplifies a new form of criticality, known as “local” criticality, in which local fluctuations of the order parameter coexist at the critical point with those at long wavelengths [88, 89]. More recently, however, ARPES measurements seem to indicate that the Fermi surface is “large” even at zero field, casting doubt on the hypothesis of a drastic Fermi volume change at $T^*$ [90]. These topics will not be discussed in much detail as this region of the phase diagram was not explicitly studied for this thesis. As was mentioned before, dHvA measurements require high fields for observation and thus the electronic landscape above 10 T was explored. In CeRu$_2$Si$_2$, above the critical Kondo energy scale of about 20 K (corresponding to a field of about 7.8 T) it was proposed that the f-electrons would become completely localized and the
heavy fermion state would be killed [91]. For YbRh\textsubscript{2}Si\textsubscript{2} this critical scale was determined to be about 10 T, determined by a kink in the magnetization [91, 92]. While there is certainly evidence of some cross-over in the vicinity of 10 T, e.g. the Sommerfeld coefficient of specific heat, \( \gamma \) decreases from a zero-field value of about 1.7 J/molK\textsuperscript{2} to a value of about 100 mJ/molK\textsuperscript{2} at high field, it appears that the suppression of the HF state is incomplete, leaving at high field quasiparticle masses on the order 20\( m_\text{e} \) (as determined by my dHvA measurements discussed below and published elsewhere [78]). The basic phase diagram, adapted from the thesis of Patrick Rourke, can be seen alongside the small and large Fermi surface scenarios in fig. 3.2.

Numerous dHvA rotation studies, as well as mass studies during the earliest measurements, were completed for this thesis. The data represents the three best data sets collected from 2009-2014 and covers the entire rotation of the sample. This is discussed in section 3.2. Additionally, band structure calculations were completed for both the small and large Fermi surface scenarios and Patrick Rourke’s SKEAF algorithm was used in order to determine the frequencies of the orbits [93]. This is discussed in section 3.3.

### 3.2 Experiment

The single crystal samples used for all measurements of YbRh\textsubscript{2}Si\textsubscript{2} in this thesis came from Gerard Lapertot at CEA Grenoble, and were part of his LAP-420 batch. These were members of the same batch used by Patrick Rourke in his thesis, and in fact, our “A” samples are the same [60]. Additionally, the “B” sample used in the 2009 measurement was the same as Patrick’s “C” sample. However, for the subsequent measurements, a new sample from batch LAP-420 was chosen, as the original was broken while trying to mount it in a different orientation. The samples were grown using indium flux and are of high quality. The residual resistivity ratio, \( \text{RRR} = \rho(300\, K)/\rho(0\, K) \) was measured by the group of Knebel et al. in Grenoble to be about 300 with the residual resistivity, \( \rho(0\, K) = \rho_0 < 1\, \mu\Omega\text{cm} \) [94]. The “A” sample measured roughly 4.5 mm x 2.2 mm x 0.3 mm, while the new “B” sample measured about 2.0 mm x 2.0 mm x 0.2 mm, both of which were smaller than ideal for these measurements. The samples were originally oriented in 2009 using Laue diffraction with image produced on medical X-ray film, but were oriented incorrectly (described in section 3.4.1). The samples were reoriented using
Figure 3.1: Crystal structure of YbRh$_2$Si$_2$ pink atoms are Yb, silver is Rh, and teal is Si. The crystal is tetragonal with space group #139 (I4/mmm).
Figure 3.2: Phase diagram of YbRh$_2$Si$_2$ modified from Rourke [60]. Calculated small and large Fermi surface are included to aid in visualization of change of the electronic structure across the $T^*$ line.
Laue diffraction with our newly obtained CCD camera in 2014 (fig. 3.3), and this orientation was confirmed by 4-circle X-ray performed by Dr. Kemp Plump (fig. 3.4).

Figure 3.3: X-ray diffraction pattern for the “A” sample of \(\text{YbRh}_2\text{Si}_2\) captured by CCD for a 20 minute long exposure using a tungsten filament and tube voltage and current of 20 kV and 35 mA respectively.

Figure 3.4: Final orientation of the “A” sample of \(\text{YbRh}_2\text{Si}_2\) determined by four circle X-ray.

Rotation studies using the setup described in chapter 2, utilizing the standard field modulation technique described in section 1.3.3, were completed. The counter-wound pickup coils in which the samples were placed consisted of approximately 1000 turns of 10 \(\mu\text{m}\) wire in each direction and were customized to the size of the sample to ensure maximal filling factor. The
Chapter 3. YbRh$_2$Si$_2$

coil used for sample “A” is shown in fig. 3.5 and sample “B” mounted in its coil and bobbin can be seen in fig. 3.6.

Figure 3.5: Coil for sample A used for the standard field modulation dHvA technique. The coil consists of two counter-wound sections of approximately 1000 turns of 10 $\mu$m copper wire each.

All field sweeps for the rotation studies of YbRh$_2$Si$_2$ were done at the base temperature of our Oxford Instruments Kelvinox 400MX $^3$He/$^4$He dilution refrigerator without the use of the booster pump, i.e. approximately 40 mK. All reported sweeps were done from 16 to 13 T, though longer sweeps were occasionally conducted to determine the lowest field value at which oscillations could be observed. The modulation field used was set to a frequency of 6.527 Hz, 3V peak-to-peak, such that the 2f pickup would lie within the region of optimal response of the transformer and electronics. The 2009 data consisted of one sample rotating in-plane, and one sample rotating from (110) towards (001). The 2012 data had both samples rotating out of plane, one from (100) towards (001) and the other rotating from (110) towards (001). The 2013 data had both samples rotating in-plane, one beginning on the (100) axis and the
Figure 3.6: New sample B of YbRh$_2$Si$_2$ mounted in a graphite bobbin for *in-situ* dHvA rotation studies.
other beginning on the (110) axis, and utilized the rotation mechanism in fig. 2.4a. While the measurement was successful, due to noisy results the 2013 data is not shown. Lastly, the 2014 dataset consisted of just the “A” sample rotating in-plane using the original graphite rotation mechanism shown in fig. 2.2, which was used for the 2009 runs as well. The 2014 in-plane rotation was completed in order to clear up any outstanding orientation issues. All rotations were done in steps of 2-3° to an angle of 45° away from the original alignment axis for the in-plane measurements and through an angle of about 60° for the out of plane rotations. Mass studies were done on the in-plane axes of high symmetry for the 2009 measurement by observing the amplitude of the oscillations of a particular frequency at various temperatures between 40 and 600 mK, followed by fitting the temperature coefficient of the Lifshitz-Kosevich equation (eqs. 1.85, 1.86) to the amplitude vs. temperature data. An example fit to a few of the frequencies obtained from the 2012 data can be seen in fig. 3.7.
(a) $F = 6.15 \, kT$, $m^* = 8.72 \pm 0.40 \, m_e$.

(b) $F = 6.57 \, kT$, $m^* = 11.47 \pm 0.11 \, m_e$. 
(c) $F = 13.9 \, \text{kT}$, $m^* = 17.88 \pm 0.05 \, m_e$. Fit was to only 3 data points and thus was not published.

Figure 3.7: Example fits of amplitude vs. temperature in order to determine effective masses. This data was not published and is given as an example.

### 3.3 Calculations

The results of dHvA quantum oscillation measurements are generally not presented on their own, rather, it is common practice to compare the observed frequencies to theoretical ones obtained using some form of band structure calculation. For my purposes, it was sufficient to use the commercially available Wien2k software package [45, 53]. This is a Fully-Augmented Linear Plane Wave (FLAPW) method utilizing the Local Density Approximation and on-site Hubbard interaction (LDA + U) with fully relativistic spin-orbit coupling. The basics of this method are described in section 1.1.3. After computing the Fermi surface, the theoretical orbits were extracted using the SKEAF algorithm [93]. The calculations were performed with $a=b=4.010\,\text{Å}$ and $c=9.841\,\text{Å}$ for the tetragonal space group $\#139 \, I4/mmm$, on the Yb-based
Chapter 3. YbRh$_2$Si$_2$

compound, representing the “large” Fermi surface scenario mentioned in refs.[95, 96]. Relative atomic positions of Yb (0,0,0), Rh (0, $\frac{1}{4}$, $\frac{1}{4}$), and Si (0,0,$z_{si}$) were used. Based on the refined lattice parameter of Friedemann et al., a silicon position, $z_{si} = 0.379c$, was used in our most recent calculations [96]. This $z$-parameter yields excellent agreement with our observations, better than that of our previous calculations using $z_{si} = 0.375c$ [78, 97]. The Purdew-Burke-Erzerhoff 96 generalized gradient approximation (GGA) to the exchange correlation potential was used for a 20000 k-point mesh in the Brillouin zone with $R_{k_{\text{max}}}$ = 8.0, $E_{\text{min}}$ and $E_{\text{max}}$ of -10.1 Ry, and 5.0 Ry respectively [51]. The separation energy between core and valence states was set at -7.1 Ry. Spin-orbit coupling was turned on for the Yb sites. All of the parameters, other than the silicon position, were consistent with the previously reported studies from our group [97]. The Fermi energy was rigidly shifted from the value determined by calculation in small steps between -18 mRy and 18 mRy and was determined to most closely resemble the low frequency observations for a shift of +12 mRy, discussed further in section 3.4. This was done to simulate the effect of spin-splitting on the various Fermi surface sheets. The “small” Fermi surface scenario was calculated using the identical parameters, replacing only the Yb atoms with Lu ones. The resulting small and large surfaces are shown in fig. 3.8, and the effect of rigidly shifting the Fermi energy on the large Fermi surface can be seen in fig. 3.9.

While for my purposes, the Wien2k calculations provided a straightforward and qualitatively good method of determining the Fermi surface, there are noted issues in computing the FS of Yb based compounds [50]. Thus, more sophisticated electronic structure calculations have been devised. One such method carried out was the renormalized band structure method of Zwicknagl, and Naren et al.[91, 98]. They found that, starting from the “large” Fermi surface shown in fig. 3.10, the effect of large spin-splitting between 0 and about 12 T is to split the D-sheet into a minority-spin surface that looks like the J-sheet and a majority-spin surface that looks like the small version of the D-sheet, while the J-sheet splits into a small minority-spin pocket and a somewhat larger version of the J-sheet. We note that, if the minority J-sheet pocket were to completely disappear, then this would closely correspond to the scenario presented in Rourke et al.[97], and based upon the model of Kusminskiy et al. [99], in which there is a surface (in this case “J”) that at high field has two spin components that originally arise on different sheets of the Fermi surface, plus one single-spin Fermi surface, and one spin-direction
Figure 3.8: Comparison of the “small” (LuRh$_2$Si$_2$) Fermi surface vs the “large” (YbRh$_2$Si$_2$) Fermi surface. Yellow represents an electron surface while blue represents a hole like surface.
Figure 3.9: Large Fermi surfaces of YbRh$_2$Si$_2$ for rigid Fermi energy shifts between -18 mRy and +18 mRy from $\epsilon_F$. Calculated using Wien2k LAPW software for relative Si position $z=0.379c$. Band 39 is the donut D-sheet, band 40 is the jungle Gym J-sheet, and band 41 is the pillbox P-sheet.
Fermi surface that has vanished. A significant issue that will arise later is whether or not there is a hole in the center of the D-sheet (the name originally comes from “doughnut” due to the hole in the +18 mRy shifted Fermi surface of fig. 3.9). The hole actually exists in the +12 mRy calculation as well, as there is a very narrow vertical section in the center of the D-sheet, though it's not as clearly observed. The renormalized band structure calculations do not show such a hole, but there is clear evidence for it in my quantum oscillation study.

![Figure 3.10: Spin-polarization of the Fermi surface of YbRh$_2$Si$_2$. The effect of spin-splitting at high field. The D-sheet splits into one spin-polarized surface that is similar to the unpolarized “small”, D-sheet and a second spin-polarized surface that looks like the J-sheet; the J-sheet splits into a larger version of itself, and a small pocket. Note that the majority spin J-sheet and the minority spin D-sheet are very similar. Figure reproduced from Naren et al. [91] and is licensed under a Creative Commons Attribution (CC-BY) 3.0 license.]

### 3.4 Results

The summarized results of this section are provided in two journal articles, one published in Physica Status Solidi [78], and one paper that is nearly complete. I expand upon those papers here in the hopes of both providing more comprehensive results, and as well in order to better clarify the orientation issue that arose in the original set of measurements. Though the original data was published with the (100) and (110) axes reversed, the results themselves, and especially the observation of a previously unseen orbit at 14 kT attributed to the J-sheet of the Fermi surface, represent a significant result, one which has aided in the understanding of the electronic
structure of this material.

### 3.4.1 Orientation Issue

I begin by discussing the orientation issue that plagued this measurement for a significant amount of time. The reason for leading with this is that it allows me to present the results of the original measurement, in their original form without providing the reader with any incorrect information and shows the reader how the issue was eventually resolved. I setup the original measurement in 2009, and the purpose was to continue the measurements of Patrick Rourke made for his PhD thesis [60]. In order to do this, I setup my “A” sample to rotate in the plane (repeating Patrick’s measurement), and it was desired that I set my “B” sample (Patrick’s “C”) sample to rotate from (100) towards (001), the rotation that had not yet been completed. I mounted samples in their coils, and made use of the alignment Patrick had made for his thesis, which on p.163 states “that the long axes of both samples are aligned along the (110) direction”. I attempted to confirm this using Laue diffraction, which proved to be extremely difficult. Not only were the samples very tiny, but I was trying to perform the diffraction on the small piece of sample that extended out of the bore of the coil and was capturing the diffraction on blue medical X-ray film, which provided poor contrast for the diffraction spots even with lengthy exposure times. I erroneously confirmed that the long axis of the sample was (110). This mistake was corrected in the 2014 data.

### 3.4.2 Measurements

For the 2009 measurement quantum oscillations were observed for both samples with a significant result obtained for the “A” sample, which rotated in the (100)-(110) plane. The “A” sample both confirmed the results of Rourke [95], and added significant new information. A new dHvA frequency around 14 kT with an angular range of about 10° from (100) was observed. The raw oscillatory magnetization trace can be seen in the upper panel of fig. 3.11, while the bottom panel shows the resulting Fourier spectrum after simple background subtraction and filtering. The data above 12 kT was multiplied by a factor of 10 in order to make the 14 kT peak more visible.

The resulting full rotation study is shown in fig. 3.12. In order to determine whether or not
Figure 3.11: Original observation of the new high frequency peak in the dHvA spectrum in the vicinity of 14 kT. Reprinted figure with permission from [78].
the new peak, around 14 kT, was an actual new orbit and not simply a harmonic of the lower, 7 kT frequency. Mass studies were carried out on the axes of high symmetry. The masses are provided in table 3.1. As was previously mentioned, the axes in fig. 3.12 were reversed compared to the true sample orientation, however the axes at which the masses were determined were also flipped, which resulted in them being correct.

<table>
<thead>
<tr>
<th>$F$ (kT)</th>
<th>$m^*/m_e$</th>
<th>$F$ (kT)</th>
<th>$m^*/m_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.64</td>
<td>12.5 ± 0.5</td>
<td>3.22</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>3.48</td>
<td>6.1 ± 0.4</td>
<td>5.65</td>
<td>8.9 ± 0.1</td>
</tr>
<tr>
<td>5.37</td>
<td>9.2 ± 0.2</td>
<td>6.15</td>
<td>8.44 ± 0.1</td>
</tr>
<tr>
<td>7.01</td>
<td>12.3 ± 0.3</td>
<td>6.54</td>
<td>13.2 ± 0.2</td>
</tr>
<tr>
<td>14.0</td>
<td>21 ± 2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Frequencies and their corresponding masses on the (110) and (100)-axes. The axes are flipped here with respect to the orientation in fig. 3.12, but are the correct orientation. Reprinted table with permission from [78].

The results of the mass study were inconclusive, as the mass of the 14 kT orbit was nearly twice that of the 7 kT orbit. However, the angular dependence of the two was drastically different as the sample was rotated away from the axis. The 14 kT orbit increased in frequency, while the 7 kT orbit decreased, and the ratio of the two frequencies varied over the angular range. Likewise, the 7 kT orbit, which itself could have been a harmonic of the frequency observed at 3.5 kT, was determined to be a distinct orbit, due to the much larger angular range over which it was observed.

Figure 3.12 shows three distinct groups of frequencies. One group around 2.5-3.5 kT, another between 5 and 7 kT, and the high frequency orbit around 14 kT. The two lowest frequency groups had been previously observed [94, 95], and we noted the similarities in these groups, with roughly a factor of two between a number of the frequencies, and some frequencies disappearing in one group and appearing in the other. This was interpreted as both groups of frequencies originating on the D-sheet of the Fermi surface, with the lower group arising from orbits that pass through the hole in the donut, while those in the higher frequency group encircle the entire surface. This would explain the near factor of two difference; the orbits are nearly the same, however, the lower set only orbits part of the surface. The orbits that pass through
Figure 3.12: Original angle rotation study with incorrect orientation. While publication indicated angle from (100), the orientation had been mistaken and should read (110). The data is compared against the “large” and “small” Fermi surface calculation of Rourke [95]. Reprinted figure with permission from [78].
the hole in the donut are so-called “central” orbits, whereas the orbits that do not go through the hole must be non-central. Comparing the observed frequencies to those corresponding to the large and small Fermi surface calculations of Rourke et al. [95], we see that the lowest two frequencies are better explained by the small surface scenario, which exhibits a hole in the donut, as both exist in this calculation. Only the higher frequency group exists in the large surface scenario. The idea that the topology of the Fermi surface was closer to the small surface was reinforced by the presence of the 14 kT orbit. The calculated large surface did not predict any high frequency orbits in the vicinity of the (100) axis, while the small Fermi surface did have an orbit at about 12.5 kT over a very narrow angular range. That being said, there were a number of predicted orbits from the J-sheet of the small surface at lower frequencies that were not observed. Generally, it is not a good idea to infer anything from a lack of observed dHvA frequencies, due to the complicated nature of dHvA measurements, however, the large surface scenario produced a J-sheet which had qualitatively better angular correspondence to the measured values, though at the significantly lower frequency of about 9.5 kT, and also did not predict other orbits above 8 kT. Thus the determination of whether or not the experimental Fermi surface was better explained by a small or large surface scenario was indeterminate, but it was conclusive that no predicted D-sheet orbit could explain such a high frequency, and thus the 14 kT orbit must originate on the J-sheet. In the original paper from our group on YbRh$_2$Si$_2$ it
was also suggested that perhaps what was being observed at high field was a Lifshitz transition which resulted in the disappearance of one of the spin branches of the Fermi surface resulting in the suppression of the heavy fermion state [95]. It was hoped that these measurements would spur some of the groups doing theoretical calculations on heavy fermion materials to employ their advanced techniques on YbRh$_2$Si$_2$. We conducted another rotation study on YbRh$_2$Si$_2$ in 2012, this time focusing on the out-of-plane rotations. One sample rotated from (100) towards (001) and the other sample rotated from (110) towards (001), both through an angle of about 60°.

The aforementioned advanced calculations, specifically the renormalized band structure calculation of Zwicknagl [100], which were completed in 2013, provided the spin-polarized Fermi surface of fig. 3.10, and predicted a series of Lifshitz transitions at high field but which did not involve the disappearance of one spin branch. Also, these calculations refined the so-called z-parameter, representing the relative atomic position of the Si atom in the crystal structure of YbRh$_2$Si$_2$, to be $z = 0.379c$ [91, 96]. Previously, as in the calculation of Rourke, $z = 0.375c$ was used [95]. In order to clarify the outstanding issue of the origin of the 14 kT orbit (which at this time was still believed to exist in the vicinity of the (100) axis) a number of theories were postulated. It appeared that no single calculated orbit existed at such a high frequency. Our original proposal was a scenario whereby very strong spin splitting of the surface could produce the necessary change in FS topology to accommodate our observations, causing the large FS to resemble the small FS at sufficiently high fields [78, 95]. This suggestion seemed to contradict the more advanced band structure calculations of Naren, et al., who included the effects of magnetic field on the FS structure. Their calculation obtained a J-sheet with majority spin branch resembling the large J-sheet scenario and a minority spin branch pocket. The D-sheet majority spin branch resembles the large surface D-sheet and minority spin branch appears to resemble the large J-sheet (see fig. 3.10). However the spin splitting did not cause either spin species to resemble the small Fermi surface over the range of fields at which our experiment was conducted. Another suggestion was the possibility of magnetic breakdown orbits, as the cylindrical rod section of the J-sheet is in close proximity to the hole in the D-sheet, as seen in Fig. 3.14. In breakdown orbits, the quasiparticles are able to quantum mechanically tunnel from one orbit of the FS to another (see section 1.3.3), creating multiples and superpositions
of the standard orbits [57]. This could yield a frequency of about 14 kT, but would necessitate multiple loops around the FS sections and would require the orbit to begin on a hole surface followed by a crossover to an electron surface, which is possible [75]. We were, however, slightly suspicious of this explanation, as there were a variety of possible combinations of orbits that were not observed.

![Diagram](image)

Figure 3.14: 2-dimensional cut through the D- and J-sheets of the Fermi surface, with the cut plane perpendicular to the (100) direction. The blue surface belongs to the D-sheet and yellow surface to the J-sheet. Adjacent Fermi surfaces have been plotted in the extended zone scheme to allow visualization of orbits that may cross Brillouin zone boundaries. Breakdown orbits could include those that circle one half of the blue surface before tunneling through the gap and encircling the yellow central cylinder in the opposite direction.

Given the complexity of this explanation coupled with discussions with our collaborators, we decided it was necessary to re-orient the larger of the two samples and to repeat the measurement. This time we made use of 4-circle X-ray, as was mentioned earlier. From this it was determined that the in-plane axes had been flipped and the high frequency orbit was actually found in the vicinity of the (110) axis. We subsequently repeated the in-plane rotation study with the “A” sample to compare against the original measurement. Additionally, I carried out new calculations using $z = 0.379c$, as was previously mentioned, resulting in the small and large
Fermi surfaces in fig. 3.8.

The results of all of the rotation studies, including the 2009 measurements (in the corrected orientation), are presented in the top panel of Fig. 3.15. The discrete points made up of circles and squares are the angular dependence of the observed frequencies from all dHvA measurements while the lines made up of “+” symbols in pink and cyan are predicted frequencies obtained from WIEN2k calculations using the SKEAF extremal area finder \cite{53, 93}. The additional dHvA data was provided by our collaborator, Georg Knebel. Beneath the angular rotation data, the orbits at a few selected angles are shown in order to illustrate the electron/hole orbits that give rise to the predicted frequencies.

Examining the rotation plot shown in the center panel of fig. 3.15, the most prominent frequencies are seen between 5.5 and 6.5 kT. There is extremely good agreement between the angle dependence of those frequencies and the triplet of D2 orbits (adopting an orbit naming convention similar to that of Friedemann et al. \cite{96}), which encircle the pillow section of the D-sheet but narrowly miss the doughnut hole.

To obtain this agreement between experiment and theory, I rigidly shifted $E_F$ by $+12$ mRy in order to simulate the effect of Zeeman splitting on the FS structure. Additionally, the calculated frequencies arising on the D-sheet have been shifted up by 0.5 kT and those on the J-sheet have been shifted by 0.15 kT as the qualitative angular dependence of the frequencies from $E_F + 12$ mRy best fit the data, but the predicted values of the frequencies were slightly lower than observed. Comparing the calculation of Friedemann, et al. on LuRh$_2$Si$_2$ (the small FS scenario), our triplet of D2 orbits is in better agreement throughout the plane with our calculated large FS.

Between 2 and 4 kT, we observe frequencies that can be attributed to the J5 and D3 orbits (see Fig. 3.15). The frequencies around 3 kT beginning at about 7$^\circ$ from the (100) axis and extending to 15$^\circ$ from (110) belong to the D3 orbit, which passes through the hole in the donut D-sheet. As per the suggestion of Friedemann et al. \cite{96}, it does appear that the frequencies at about 5 kT in the plane are a second harmonic of those attributed to D3. These are marked with “X” in Fig. 3.15. This is further discussed in the “Analysis of Harmonics” (section 3.4.3 below).

Beginning at the (100) axis and extending over 15$^\circ$ towards (110), we observe frequencies
Figure 3.15: (a) Compiled dHvA rotation study including all datasets from 2009 to present. Our dHvA data is compared against that from our collaborator, Georg Knebel, in Grenoble and my more recent theoretical calculations completed using Wien2k with relative Si position $z=0.379c$. X’s indicate data points removed as they correspond to harmonics of lower frequencies. (b) Corresponding Fermi surface orbits at selected angles computed using XCrysDen, SKEAF, and a patch to XCrysDen for plotting orbits modified by me and provided by Pascal Reiß.
that agree extremely well with those predicted for the J5 orbit, which encircles the waist section
of the J-sheet. Near the (110) axis, another set of frequencies with an upward curvature over
an angular range of 10° towards (100) also match the qualitative angular dependence of the J5
orbit, though in both the Toronto and Grenoble data, the observed frequency is about 1 kT
lower than predicted.

Near 3.5 kT over 10° from (110) we observe a set of frequencies with a downward curvature
that cannot be ascribed to any predicted orbit. This frequency is approximately half of that
observed at at 7 kT, leading Friedemann et al. to suggest that the 7 kT frequency is a harmonic,
as opposed to a separate fundamental orbit, but we argue that this is, in fact, not the case.
The 7 kT orbit does not appear to be a harmonic due to the variation in frequencies through
the in-plane rotation, as is discussed below in section 3.4.3.

We do not observe an orbit corresponding to the small cylindrical J7 orbit predicted over
a wide range of angles both in- and out-of-plane, nor do we see any oscillations that would
correspond to the minority J-sheet pocket predicted by Naren et al. [91].

An outstanding issue from my 2009 paper was the origin of the frequencies found at 14 kT
that exist over a range of 15° in-plane. Using the correct orientation, these oscillations arise from
the large, nearly circular orbit labelled J3, as seen in the bottom panel of fig. 3.15, which has
a slightly higher predicted frequency, but exhibits a quantitatively similar angular dependence.
We do not observe a splitting of this high frequency orbit, as a small splitting of the theoretical
J3 orbit can be seen close to the (110) axis.

Despite the agreement between my results and the LDA calculations, there remain unan-
swered questions. The hypothesis of Rourke et al. [95], Pfau et al.[101] and Friedemann et
al.[96], is that there is a large splitting of the Fermi surface in this field range. It is curious that
we are able to explain almost all of the observed frequencies using D- and J- Fermi surfaces
for only one spin direction (in this instance, it would be the one corresponding to the majority
spin species). Why do we not observe the other spin direction? One possibility is that there are
no closed orbits on the “missing” Fermi surfaces. Another possibility is that the unexplained
frequencies at 7-8 kT from about 15° to 5° from (110) in the Grenoble dHvA data and the
frequencies around 12kT from 5-10° to (100) may arise from the missing spin sheet of the Fermi
surface.
According to the picture of Naren, and Zwicknagl et al. [91, 98], discussed in section 3.3, at high field there is a single-spin D-sheet, in accord with our original suggestion [97]; however the J-sheet should be spin-split, but with the two spin components originating at low field on the D- and J-sheets. If these two sheets were sufficiently degenerate, then they might appear as only a single quantum oscillation. It might be interesting in future studies, if these oscillations could be observed over a large enough field range, to look for signatures of spin-splitting, such as spin-zeroes [102]. Finally, they predict a small, quasi-spherical minority spin sheet of the J-sheet, which we do not observe. It seems likely to us that this surface has shrunk to zero, as suggested in the original picture of Rourke et al. [95]. In this way it may be possible to account for the observations.

While the previous discussion has focused primarily on the in-plane measurements, the results of the out-of-plane dHvA studies are presented in left and right panels of fig. 3.15. Looking at the out-of-plane data, there is general agreement between the Toronto and Grenoble dHvA measurements, but detailed agreement, especially in the (100) to (001) plane is surprisingly poor. This may come from changes in the sample orientation due to torque on the sample that arises from the anisotropic magnetization, with the a-b plane being the easy plane of magnetization. In quantum oscillation measurements the sample cannot be glued down on a substrate, because thermal strain upon cooling will destroy the oscillations. Thus the samples are held delicately by one corner. Rotation in the a-c or b-c plane could thus cause the sample to twist so that the crystal axes no longer align with the rotation mechanism. Further evidence of sample misalignment is that there appears to be a slight discontinuity for the frequencies between 5.5 and 6.5kT at both the (100) and (110) axes going from the in-plane to out-of-plane studies.

For the dHvA data, the highest of the triplet of D2 frequencies extends, experimentally, towards the c-axis over about 40° from (110) and 60° from (100), with good agreement with good agreement between the Toronto and Grenoble dHvA measurements and with calculated frequencies in the (110) plane. We also observe frequencies from the (100) axis through about 20° towards (001) which are attributable to the D3 orbit, though the observed frequencies are slightly lower than predicted. Rotating from the (110) axis towards (001), we do not observe any oscillations that can be positively attributed to the predicted D3 orbit. In both (110) to (001) and (100) to (001) rotations we observe oscillations that can be ascribed to the J5 orbit.
Chapter 3. YbRh$_2$Si$_2$

This orbit is also observed in the Grenoble dHvA rotations in both planes, though our data appears at a slightly lower frequency, due possibly to the torque-induced sample misalignment discussed above. While there is very good agreement with the theoretical J5 orbit for the data in the (100) plane, the observed frequencies are about 1 kT lower than predicted in the (110) rotation, though the angular dependence does appear to validate the belief that these come from the J5 orbit. Near 1.5 kT, we observe frequencies from (110) towards (001) that do not appear to be in agreement with any of the calculated orbits. These extend 35 degrees from (110) and do not fit the frequency or angle dependent shape of either of the predicted J-sheet orbits. Finally, near (110) and 14 kT, we observe the high frequency orbit previously observed for only the in-plane rotation showing agreement with the predicted J3 orbit.

3.4.3 Analysis of Harmonics

With reference to my 2009 published data, as suggested by Friedemann et al.[96], the orbit at $\sim$5 kT between 7 and 25$^\circ$ from (100) can be assigned to be a second harmonic of the orbit at $\sim$2.5 kT. The frequencies around 5 kT are, to three decimal places, twice those around 2.5 kT, with both frequencies appearing together at nearly all angular steps and with the amplitude of the 5 kT peak greatly reduced compared to that of the 2.5 kT peak. These harmonics have been indicated using an “X” in the upper panel of fig. 3.15. This, however, is not true of the frequencies at 3-3.5 (D3) and 6-7kT (D2) which Friedemann also suggested might be harmonics. Observing quantum oscillations using the field modulation technique, and measuring the oscillations on the second harmonic of the signal can artificially favour harmonic pickup over that of the fundamental, as was described in section 1.3.3. In order to account for this, we have scaled the FFT peak amplitudes by the Bessel function coefficient of a particular orbital frequency [57].

As is seen in fig. 3.16, the amplitude of the 2.5 kT peak is strongly enhanced after accounting for the Bessel coefficient, and it remains significantly larger than the 5 kT peak as expected for a second harmonic. This is not the case for the 3 and 6 kT peaks. The second panel of fig. 3.16 shows that the 6 kT oscillation is preferentially selected by the Bessel coefficient, but remains significantly larger than the 3 kT peak even after scaling. Additionally, the 6-7 kT peaks exist over a much wider angular range than the peaks below 4 kT, indicating that they are neither a
second nor higher order harmonic of a lower fundamental frequency. The in-plane frequencies around 5 kT starting 5° from (110) have been left in, as it’s not clear that they are second harmonics since they are not exactly twice those at 2.5 kT.

Figure 3.16: Scaling of observed dHvA frequencies at one angle to Bessel function of the first kind with chosen central field value in the middle of the sweep. This is plotted to show the precision to which we are able to resolve frequencies and thus determine if the frequencies represent harmonics of another. The peaks are also scaled in amplitude to eliminate the effects of selectively picking up certain frequencies. In the top panel it can be seen that the frequency of 5 kT peak is twice the 2.5 kT to 3 decimal places. This is not the case in the lower panel, where the 6.1 kT peak is not twice the 3.08 kT peak and even after scaling, the higher frequency peaks remain larger in amplitude, which is not to be expected if the higher frequency is a second harmonic of the lower frequency.
Chapter 3. YbRh$_2$Si$_2$

3.5 Conclusions

de Haas-van Alphen rotation studies have been completed on samples of YbRh$_2$Si$_2$, which have been compared against predicted frequencies from more basic band structure calculations, which I completed using Wien2k and Patrick Rourke’s SKEAF algorithm [93]. We see that by rigidly shifting the bands, in order to simulate the effects of Zeeman splitting at high field, we obtain very good agreement between experiment and theory. This has resulted in the confirmation of the first observed orbit attributable to the J-sheet of the Fermi surface and has corrected an orientation issue present in our initial publication of these results. Additionally, I have qualitatively compared the experimental results to those predicted by the advanced band structure calculations of Zwicknagl et al., which take into account the effect of field on Fermi surface topology, and which predict a large Fermi surface-like structure. We are, at present, unable to confirm this scenario as definitive signatures of spin-splitting have not yet been observed, and our data is best explained by the Fermi surface corresponding to only the majority spin branch. Future research into this material could focus on attempting to observe the splitting of the Fermi surface by utilizing wide field sweeps in the quantum oscillation measurements.
Chapter 4

PrOs$_4$Sb$_{12}$

4.1 Introduction

PrOs$_4$Sb$_{12}$ is a heavy fermion material with observed masses on the order of $\sim 50m_e$ as determined by specific heat, and cyclotron effective masses around $7.6m_e$ from dHvA studies, with the discrepancy possibly arising due to different measurement conditions [103, 104]. Additionally, it was the first example of a praseodymium based heavy fermion superconductor, with $T_c = 1.85$ K [103]. The nature of this exotic form of superconductivity has been extensively studied and is believed to represent a so-called multiband superconductor with one band exhibiting an s-wave type isotropic gap symmetry and the other band having a nodal gap symmetry [105]. This is evidenced by specific heat [106–108], thermal transport [109], London penetration depth [110], Andreev spectroscopy [111], and nuclear quadrupole resonance (NQR) [112] measurements. As well, a double superconducting transition has been shown to occur in high quality samples at $T_{c1} \sim 1.89$ K and $T_{c2} \sim 1.72$ K, though the nature of this double transition is hotly contested [113]. Another interesting area of the phase diagram occurs between about 4 and 12 T. Here, PrOs$_4$Sb$_{12}$ transitions into a type of hidden ordered state known as antiferroquadrupolar (AFQ) order, where the electron density around the praseodymium sites has a non-zero electric quadrupole moment that alternates on adjacent sites, as described in section 1.2. The interaction of the crystal electric fields (CEF$s$), present due to the arrangement of Sb ions around the Pr site, may be responsible for the supposed heavy fermion behaviour in this material, as well as a number of other praseodymium HF compounds such as PrInAg$_2$.
and PrFe$_4$P$_{12}$ [114, 115], and the related superconductor PrRu$_4$Sb$_{12}$ [116]. The isostructural compound LaOs$_4$Sb$_{12}$ is, in fact, a standard BCS type superconductor which lacks f-electrons, highlighting the importance of the interplay of f-electrons and CEFs [117]. The phase diagram of this material can be seen in fig. 4.1. This AFQ phase is considered a form of hidden order as the standard techniques used to probe phases couple only weakly [69]. Utilizing dHvA quantum oscillation measurements as a probe of this form of hidden order is the central topic of this chapter of my thesis.

The zero field energy levels of the Pr ions are strongly influenced by their crystalline environment, thus an understanding of this structure is essential to understanding the observed properties of the material. PrOs$_4$Sb$_{12}$ is a cubic skutterudite material with $a = 9.30311$ Å [104]. The Pr$^{3+}$ ion has a 4f$^2$ electronic arrangement, and as with YbRh$_2$Si$_2$ it is important to understand whether we are looking at a 4f localized or 4f itinerant situation in order to be able to make a useful theoretical model of the experimental results [103, 118]. By Hund’s rules we place the first 4f electron in the $\ell = 3$ orbital with $m_S = 1/2$ and the second electron in $\ell = 2$, $m_S = 1/2$. This yields a total angular momentum value for a less than half-filled shell, $J = L - S = 5 - 1 = 4$. In free space, this would yield $2J + 1 = 9$ degenerate energy levels. The degeneracy of this is lifted by the CEF which yields a ground state singlet, $\Gamma_1$ and low lying triplet, $\Gamma_4^{(2)}$. There was some debate on whether or not the ground state was best represented by a $\Gamma_3$ non-Kramers doublet state, though it is now widely agreed that the experimental magnetization, as well as entropy measurements are better represented using a $\Gamma_1$ ground state [69, 103, 118]. All other energy levels are much higher and are not considered [119]. A schematic picture of the CEF splitting of the ground state energy levels in applied field can be seen in fig. 4.2, the importance of the relative occupations of the different $\Gamma$-levels is explored in the discussion section of this chapter (4.4). A more complete, though by no means exhaustive, discussion of the energy states of this system is found in Appendix A and is based on the work of refs. [118–120].

The resistivity of the material shows a $T^2$-dependence for $7.5 \, \text{K} \lesssim T \lesssim 45 \, \text{K}$ with $A$ coefficient of 0.009 $\mu\Omega\text{cm/K}^2$, yielding a Kadowaki-Woods ratio two orders of magnitude smaller than that expected for a heavy fermion material ($A_{KW} \sim 1 \, \mu\Omega\text{cm/K}^2$ for $\gamma \sim 500 \, \text{mJ/molK}^2$ [35]). At low temperature, for field $3 \, \text{T} \leq H \leq 8 \, \text{T}$, the resistivity is well described by a
Figure 4.1: The phase diagram of PrOs$_4$Sb$_{12}$ showing the double superconducting transition at $T_{c1} \sim 1.89$ K and $T_{c2} \sim 1.72$ K. The AFQ phase exists between fields of $\sim 4 - 12$ T and with a maximum transition temperature of $\sim 1$ K. The pink lines within the AFQ phase are believed to represent changes in the ordered structure [118]. Adapted from [69].
Figure 4.2: Diagram of the splitting of the relevant crystal electric fields in PrOs$_4$Sb$_{12}$ with magnetic field. As field increases, there is a level crossing of $\Gamma_1$ and $\Gamma_4^{(2),+}$ around 8.5 T, where $\Gamma_4^{(2),+}$ becomes energetically favorable. Diagram based on ref. [118], and is adapted from [69].

The resistivity can also be described by a $T^2$ dependence over the more limited temperature range of 0.1 $\leq T \leq$ 0.8 K with $A = 1.6 - 3.4 \mu\Omega\text{cm/K}^2$, in agreement with the Kadowaki-Woods ratio [103, 106].

Furthermore, dHvA quantum oscillation measurements were previously carried out by Sugawara et al. for fields between 17 and 3 T and yielded effective cyclotron masses of 4.5, 2.5, and 7.6 times the bare electron mass. Using this to compute the Sommerfeld coefficient, Sugawara estimated $\gamma \sim 150$ mJ/molK$^2$, at least a factor of two lower than that predicted by Bauer based on the measured jump in the specific heat at the superconducting transition, $\Delta C/T_c$ [103, 104]. The Fermi surface and angular dependence of the frequencies is shown in fig. 4.5.
Figure 4.3: Crystal structure of PrOs$_4$Sb$_{12}$ grey atoms are Pr, red is Os, and blue is Sb. The Pr atoms are surrounded by a cage of 12 Sb atoms. The crystal is a cubic structure with space group #204 (Im-3).
Figure 4.4: Crystal structure of PrOs$_4$Sb$_{12}$ grey atoms are Pr, red is Os, and blue is Sb. The Pr atoms are surrounded by a cage of 12 Sb atoms. The crystal is a cubic structure with space group #204 (Im-3).
(a) Fermi surface of PrOs$_4$Sb$_{12}$ as calculated by Sugawara et al. using the FLAPW LDA + U method of Harima [104, 121, 122]. Experimentally observed orbits are labelled $\alpha$, $\beta$, and $\gamma$. Reprinted figure with permission from [104]. Copyright (2002) by the American Physical Society.

(b) Angle dependence of the dHvA frequencies as calculated and measured by Sugawara et al. Reprinted figure with permission from [104]. Copyright (2002) by the American Physical Society.

Figure 4.5: Experimental and theoretical Fermi surface and dHvA frequencies for PrOs$_4$Sb$_{12}$
measurements can yield many different properties of the material being studied, this includes, but is not limited to, the most frequently utilized technique whereby the frequencies of the oscillation are related to the extremal orbits of the FS. Another commonly exploited property of dHvA measurements is the change in amplitude of oscillations vs. temperature which yields the effective masses of the quasiparticles. For PrOs$_4$Sb$_{12}$ we make use of an often overlooked quantity, the phase of the oscillations, which can be measured at different temperatures and field ranges in order to quantify a change in the FS size, which for this material is related to the relative occupation of the crystal field energy levels of Pr. The dHvA effect arises from oscillations in the DOS of states at the Fermi level, periodic in inverse applied magnetic field and can be expressed as in eq. 1.99, where we have dropped the summation of different frequencies and obtain,

$$\tilde{M} = \sum_{p=1}^{\infty} A_p (T, B) \sin \left( 2\pi p \frac{F}{B} + \phi \right)$$

(4.1)

This equation (and subsequent discussion) follows the form of the paper of McCollam et al. [69]. I will restrict this discussion to the phase, which is relevant for the following analysis of PrOs$_4$Sb$_{12}$. The reader is referred to sections 1.3.2 for discussion of the coefficients of the LK equation. Normally, the phase, $\phi$, is taken to be a constant over the magnetic field sweep range. In the case of PrOs$_4$Sb$_{12}$ it was shown by McCollam that over the length of the sweep (fig. 4.6a), the Fourier transform of the raw data showed a cluster of peaks for the $\beta$ oscillation, instead of one single frequency, as is shown in fig. 4.6b. This was interpreted as a drastic change in the area of the Fermi surface with field. In order to examine this, McCollam et al. fit a function, nearly identical in form to eq. 4.1, over a narrow field range, corresponding to just three oscillations, where,

$$A_f \sin \left( 2\pi p \frac{F_f}{B} + \phi_f \right).$$

(4.2)

The subscript $f$ is used to denote the fitted value of the particular variables. An example of the data, after filtering to select the $\beta$ frequency and fitting can be seen in figure 4.6d. The phase change between the two temperatures is clearly visible.

By fitting eq. 4.2 for 3 oscillations steps throughout the entire field sweep, McCollam et al.
Figure 4.6: a) An example dHvA trace for PrOs$_4$Sb$_{12}$ over a field sweep from 18 to 4 T. b) Fourier transform of a) after plotting a) in $1/B$. c) Oscillation amplitude temperature dependence for the section of the data from 7 to 4 T and for temperatures of 30-1000 mK. d) Fit of the data using equation 4.2, for a narrow field range. There is a phase shift between 800 and 200 mK. Reprinted figure with permission from [69]. Copyright (2013) by the American Physical Society.
were able to observe the onset of the AFQ phase as a jump in the dHvA frequency (and thus a change in the Fermi surface area) [69]. The analysis of the fit data was complicated by the fact that the extremal area of the Fermi surface was dependent on the temperature, and as well is affected in a way that is impossible to quantify by the back projection of the observed frequency and the relation to the “true” frequency, as was described in the introduction and summarized in eq. 1.127. Thus, the observed frequency $F_f$ is more accurately described as $F_f(T, B)$. If, following McCollam et al., we write the frequency from the Onsager relation (eq. 1.79), and rewrite the argument of the sin term in eq. 4.2 for the area of the FS and expand about a sweep centered on field, $B_o$ we get,

$$
\frac{\hbar}{eB}A(B, T) + \phi_o \\
\simeq \frac{\hbar}{eB}A(B_o, T) + (B - B_o) \frac{\partial B A(B, T)|_{B_o}}{B_o} + \phi_o \\
= \frac{\hbar}{eB}A(B_o, T) - B_o \frac{\partial B A(B, T)|_{B_o}}{B_o} + \frac{\hbar}{e} \frac{\partial A(B, T)}{\partial B}|_{B_o} + \phi_o \\
\equiv 2\pi \frac{F_f(B_o, T)}{B} + \phi_f'(B_o, T)
$$

\hspace{1cm} (4.3)

where $\partial_B \equiv \partial/\partial B$. The resulting frequency centered at $B_o$ is

$$
F_f(B_o) \equiv \left(1 - B \frac{\partial}{\partial B}\right) \frac{\hbar A}{2\pi e}
$$

\hspace{1cm} (4.4)

and is the same result as eq. 1.127. From this, it is likely that the jump in the observed frequency at the onset of the AFQ phase is, in fact, related to a sudden change in the slope of the area of the FS vs. field, and not directly from a jump in the area. Now, we need to attempt to understand the temperature dependence of this result. As is seen in eq. 4.4, the frequency is a complicated function of both the area and the derivative of the area of the FS with respect to field. If the fit value, $F_f$, is fixed at the lowest temperature sweep, $T_o$, and we now fit higher temperature data for only $A_f(T)$ and $\phi_f(T)$, we are able to obtain extremely useful information, without some of the difficulty present in the above. Now, we use the function,

$$
A_f(T) \sin \left[2\pi \frac{F_{f,o}}{B} + \phi_f(T)\right].
$$

\hspace{1cm} (4.5)
where $F_{f,o} = F_f(B_o, T_o)$. We now, once again, write the argument of the sine function and include the back projection of the true frequency,

$$
\hbar \frac{A(B, T)}{eB} + \phi_o = \hbar \frac{A(B, T_o)}{eB} + \Delta A(B, T) + \phi_o \\
\simeq \hbar \frac{A(B, T_o)}{eB} + \hbar \frac{\Delta A(B_o, T)}{eB_o} + \phi_o \\
\simeq 2\pi F_f(B_o, T_o) + \hbar \frac{\Delta A(B_o, T)}{eB_o} + \phi'(B_o, T_o) .
$$

(4.6)

Thus, the change in frequency over a few periods of the oscillation can be accounted for by a phase shift, where,

$$
\Delta \phi_f (B_o, T) = \hbar \frac{\Delta A(B_o, T)}{eB_o} 
$$

(4.7)

and

$$
\Delta \phi_f (B_o, T) \equiv \phi_f (B_o, T) - \phi_f (B_o, T_o) .
$$

(4.8)

And so by fitting eq. 4.5 for the $T > T_o$ data, and by comparing the resultant change in phase, we are now able to determine the change in extremal area caused by a change in temperature. It should, however, be noted that we don’t know precisely the actual value of the extremal area, $A$, as the base temperature value is still dependent on the back projection of the frequency, we do however know very accurately how much the area has changed with temperature.

### 4.2 Experiment

de Haas-van Alphen quantum oscillation measurements were performed on one single crystal sample of PrOs$_4$Sb$_{12}$. The sample, which was grown using a Sb-self-flux growth method, weighs 40 mg and has dimensions of 1.7×1.6×2.12 mm$^3$, and was the same one used in the measurement of Alix McCollam [69]. In fact, the sample remained mounted in its counter wound pickup coil after Alix’s measurement, and thus was mounted identically. RRR for the sample was between 70-80. The standard field modulation dHvA technique, as was used for YbRh$_2$Si$_2$ in section 3.2 and is described in 1.3.3, was employed to study the oscillations for a single orientation, with the field parallel to (110). Field sweeps were completed over two ranges, 10 to 7 T and 6 to 3 T, with a sweep rate of $\sim 0.03$ T/min and a modulation frequency of 6.527 Hz (the
Figure 4.7: Calculation of the Bessel function for modulation fields of 100 and 180 Gauss for field sweep of 6 to 3 T. 100 Gauss was selected for this low field sweep as the Bessel function has its zero low in the field range and remains large over the fields of interest for the particular dHvA frequency.

The same as was used for YbRh$_2$Si$_2$). The amplitude of the modulation field was different for the two ranges, in order to eliminate the observed frequency falling near the zero of the Bessel function (described in section 1.3.3, equation 1.110 of this thesis). For 10 to 7 T the modulation field was set to $3V_{pp}$ from pfgen, the signal generator found in DAVIES (section 2.1.2), which corresponded to a field value of about 180 Gauss. For the 6 to 3 T sweep, the field was set to approximately 100 Gauss. A plot of the corresponding low field Bessel functions can be seen in fig. 4.7. The field sweeps were completed at numerous fixed temperature points between $\sim 23.6$ and 2800 mK, with those runs below about 50 mK being performed using the additional fridge booster pump, and those above about 800 mK being completed by operating the fridge in the so-called “micro-circulation” mode. Data collection was done using the setup shown in fig. 2.5.

An example of the raw data trace for one of the 10 to 7 T field sweeps is shown in the top panel of fig. 4.8 with corresponding peak in the FFT spectrum shown in the bottom panel.
Figure 4.8: Example raw data trace for PrOs$_4$Sb$_{12}$ taken from run 2015_03_15_01_PrOs4Sb12_001 with temperature fixed at 24.0 mK. Simple background subtraction and windowing for the FFT has been completed using the same python routine as was used to analyze YbRh$_2$Si$_2$. Multiple $\beta$ peaks, as in ref. [69], are not observed due to the short length of the sweep.
4.47 4.48 4.49 4.50 4.51 4.52
Field $[T]$ 23.6 mK 600 mK

Figure 4.9: Comparison of 3 periods of the oscillation data for 23.6 mK (blue) and 600 mK (green), filtered to select the $\beta$ frequency. The large phase shift between runs is clearly visible. The plot has been made to closely resemble that of McCollam et al. [69].
4.3 Calculations

The calculation used to compare the experimental phase of the dHvA oscillations is based on the mean field treatment of the system by Kusunose et al. with our inclusion of the effects of the hyperfine interaction, which is shown to be extremely important at low-temperature [123]. This calculation also built upon the similar treatment of McCollam et al. [69]. The code used in this calculation was modified from code provided to me by my supervisor, Stephen Julian.

The mean field Hamiltonian of Kusunose et al., keeping with their notation, is given as,

\[ \hat{H}_{MF} = \sum_i \hat{H}_i - \xi \]  

(4.9)

for,

\[ \hat{H}_i = - \sum_\alpha \phi_i^\alpha \hat{X}_i^\alpha + \hat{H}_{CEF}^i, \]  

(4.10)

and where \( \xi \) represents the intersite dipolar and quadrupolar interaction with interaction strength \( D_{ij}^{\alpha\beta} \) such that,

\[ \xi = \frac{1}{2} \sum_{ij} \sum_{\alpha\beta} D_{ij}^{\alpha\beta} X_i^\alpha X_j^\beta. \]  

(4.11)
The quadrupolar operators for the lowest lying quartet of states are written as,

\[
\hat{X}_i^{(4g)x} = \frac{1}{\sqrt{c_1^2 + c_2^2}} \begin{pmatrix}
0 & -c_1 i & 0 & c_1 i \\
c_1 i & 0 & -c_2 i & 0 \\
0 & c_2 i & 0 & c_2 i \\
-c_1 i & 0 & -c_2 i & 0
\end{pmatrix},
\]

\[
\hat{X}_i^{(4g)y} = \frac{1}{\sqrt{c_1^2 + c_2^2}} \begin{pmatrix}
0 & c_1 & 0 & c_1 \\
0 & 0 & c_2 & 0 \\
c_1 & 0 & c_2 & 0 \\
0 & c_1 & 0 & c_2
\end{pmatrix},
\]

\[
\hat{X}_i^{(4g)z} = \frac{\sqrt{2}}{\sqrt{c_1^2 + c_2^2}} \begin{pmatrix}
0 & 0 & c_1 i & 0 \\
0 & 0 & 0 & -c_2 i \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{pmatrix},
\]

(4.12)

where \( c_1 = 4\sqrt{35}\sqrt{1-d^2} \) (\( d \) is defined in appendix A) and \( c_2 = \sqrt{3} (13 - 20d^2) \). The dipolar operators are given as,

\[
\hat{X}_i^{(4u)x} = \frac{1}{\sqrt{c_3^2 + c_4^2}} \begin{pmatrix}
0 & -c_3 & 0 & c_3 \\
-c_3 & 0 & c_4 & 0 \\
0 & c_4 & 0 & c_4 \\
c_3 & 0 & c_4 & 0
\end{pmatrix},
\]

\[
\hat{X}_i^{(4u)y} = \frac{1}{\sqrt{c_3^2 + c_4^2}} \begin{pmatrix}
0 & -c_3 i & 0 & -c_3 i \\
c_3 i & 0 & -c_4 i & 0 \\
0 & c_4 i & 0 & -c_4 i \\
c_3 i & 0 & c_4 i & 0
\end{pmatrix},
\]

(4.13)

\[
\hat{X}_i^{(4u)z} = \frac{\sqrt{2}}{\sqrt{c_3^2 + c_4^2}} \begin{pmatrix}
0 & 0 & c_3 & 0 \\
0 & c_4 & 0 & 0 \\
c_3 & 0 & 0 & 0 \\
0 & 0 & 0 & -c_4
\end{pmatrix}
\]
Unlike the calculation of McCollam et al., the full form of the quadrupolar order is included in the calculation, and the AFQ phase is not included by hand [69]. The molecular field at each site, $\phi^\alpha_i = h^\alpha_i - \sum_{j\beta} D^{\alpha\beta}_{ij} X^\beta_j$, for which only nearest neighbor interactions are included and we get $\phi^\alpha_{A,B} = h^\alpha_{A,B} - z \sum_{\beta} D^{\alpha\beta} X^\beta_{B,A}$, where $z$ is the coordination number [123]. The $X$ terms without the hat are Boltzmann averaged values of the operators provided above, such that,

$$X^\alpha_i = \langle \hat{X}^\alpha_i \rangle = \sum_m e^{-\beta \epsilon^{(i)}_m} Z_i \hat{X}^\alpha_i$$  \hspace{1cm} (4.14)$$

where $\hat{H}_i |m\rangle_i = \epsilon^{(i)}_m |m\rangle_i$, $\beta = 1/T$, and $Z_i = \sum_m e^{-\beta \epsilon^{(i)}_m}$. The sub- and superscript $i$ is used to indicate the particular site at which we are working.

We also include the effects of the crystal-field in the presence of a magnetic field, where,

$$\hat{H}_{CF} = \begin{pmatrix} 0 & 0 & -\delta h & 0 \\ 0 & \Delta - h & 0 & 0 \\ -\delta h & 0 & \Delta & 0 \\ 0 & 0 & 0 & \Delta + h \end{pmatrix}$$  \hspace{1cm} (4.15)$$

In eq. 4.15, $\Delta$ is the spacing between the ground state singlet and $\Gamma_4$ triplet ($\Delta = 8$ K in the calculation) with no field. $h$ is the Zeeman term for the spin-up and spin-down (+,-) branches of the triplet, given as, $h = g\mu_B \alpha H$. $\delta$ mixes the $\Gamma_1$ and $\Gamma_4^{(2),0}$ levels, where $\delta = \beta/\alpha$ for $\alpha = 5/2 - 2d^2$ and $\beta = 2\sqrt{5/3}d$ [69]. $d$ reflects the mixing of the $\Gamma_4^{(0)}$ and $\Gamma_5^{(0)}$ crystal fields states from the $O_h$ symmetry group upon lowering of the symmetry to the $T_h$ group, relevant for PrOs$_4$Sb$_{12}$ (see Appendix A). This mixing parameter, $d$, is expected to be small in PrOs$_4$Sb$_{12}$ [119, 123].

Like the calculation done by McCollam et al. we include an additional contribution to the mean field Hamiltonian in the form of the hyperfine dipole interaction, where,

$$\hat{H}_{HF} = A I \cdot J = AI_z J_z + \frac{A}{2} (I_+ J_- + I_- J_+)$$  \hspace{1cm} (4.16)$$
Thus the full form of the Hamiltonian used in the calculation looks like,

\[ \hat{H} = \hat{H}_{MF} + \hat{H}_{CF} + \hat{H}_{HF} \]  

(4.17)

The Hamiltonian is solved self consistently, calculating the Hamiltonian for one site, diagonalizing it to obtain the eigenvectors, eigenvalues, and Boltzmann averaged operators, and then utilizing this mean field result on the second site. This is done in a loop until the solution converges. The full Hamiltonian is a 24x24 matrix consisting of 6 hyperfine split states (given the Pr nuclear moment I takes values of -5/2,...,5/2) for each of the 4 \( \Gamma \) states. The eigenvector looks like,

\[
\begin{bmatrix}
|\Gamma_1\rangle, I_z = -5/2 \\
|\Gamma_1\rangle, I_z = -3/2 \\
|\Gamma_1\rangle, I_z = -1/2 \\
|\Gamma_1\rangle, I_z = 1/2 \\
|\Gamma_1\rangle, I_z = 3/2 \\
|\Gamma_1\rangle, I_z = 5/2 \\
|\Gamma_4^{(2),+}\rangle, I_z = -5/2 \\
\vdots \\
|\Gamma_4^{(2),+}\rangle, I_z = 5/2 \\
|\Gamma_4^{(2),0}\rangle, I_z = -5/2 \\
\vdots \\
|\Gamma_4^{(2),0}\rangle, I_z = 5/2 \\
|\Gamma_4^{(2),-}\rangle, I_z = -5/2 \\
\vdots \\
|\Gamma_4^{(2),-}\rangle, I_z = 5/2 \\
\end{bmatrix}
\]  

(4.18)

Using the Boltzmann weighting factor again, as was used in eq. 4.14, one can then obtain the contribution to the total occupation of each of the hyperfine states for each of the original \( \Gamma \) basis states, or one could determine the total percentage occupation of \( \Gamma_1 \) by computing,

\[
\%\Gamma_1 = \frac{e^{-\beta \epsilon_1}}{Z} \langle \Gamma_1 | \psi \rangle
\]  

(4.19)
The basis state of the system, as described in eq. 4.18, was used and the eigenvectors of the system were computed by iteration over two adjacent sites, A and B, until convergence of the z-direction magnetization was obtained, utilizing a Boltzmann weighted average for temperature points between 0.001 and 2.6 K and fields less than 15.2 T in 0.5 T increments.

In addition to allowing the calculation of the theoretical AFQ phase boundary, mentioned in greater detail below, this also enabled us to be able to calculate the percentage occupation of each of the crystal field levels for a given temperature over a full field sweep. An example of this is shown for $T = 1$ mK in fig. 4.10.

Figure 4.10: Determination of the percentage occupation of the crystal field levels, $\Gamma_1$ and $\Gamma_4^{(2),j}$, for PrOs$_4$Sb$_{12}$ at $T = 1$ mK for field applied in the (110) direction as determined by our mean field calculation. Crossover of the levels occurs around 7 T, which seems to coincide with the anomaly in the phase diagram around 7 T, see fig. 4.17.
4.4 Results

The analysis of the resulting dHvA traces for PrOs$_4$Sb$_{12}$ were analyzed in a different fashion to that used for YbRh$_2$Si$_2$. In this case, and as described in section 4.1, the primary quantity of interest was the phase of the oscillations compared against that of a base temperature, and not the value of the frequency peaks obtained by FFT. The only processing of the data consisted of the application of a Gaussian low pass filter to the FFT spectrum of the 2nd harmonic voltage trace from the virtual lock-in amplifier, centered about the $\beta$-frequency, $\sim 1012$ T. The raw data trace for a few selected temperatures through the high field sweep can be seen in fig. 4.11. The resulting filtered data after inverse Fourier transform can be seen in figs. 4.12 and 4.13.

The data was fit to a function of the form shown in eq. 4.2 with $p = 1$, as was done by McCollam [69], an example of the observed phase shift between temperatures can be seen in fig. 4.9. The function was centered on field values in steps of 0.01-0.05 T and was fit for a window 3 oscillations wide. For extraction of the phase information, the frequency of the lowest temperature run was determined for a given central field value and was fixed. This left only the amplitude and phase as free parameters in the fits of the higher temperature runs. The difference in phase from the base temperature run was determined, allowing us to plot the phase difference, $\Delta \phi$ vs. temperature at a given field value, seen in fig. 4.14b. This was compared against theoretical $\langle \Gamma_1 \rangle$ vs. $T$ plots computed by the calculations of section 4.3, which can be seen for two different quadrupolar coupling strengths, $D = 0.175$ (fig. 4.14a) and $D = 0.300$ (fig. 4.14c). Examining the plots in fig. 4.14, we see some qualitative agreement with the theoretical plots of $\langle \Gamma_1 \rangle$ vs. $T$, though the calculated values of the onset temperature of the AFQ phase tend to be considerably higher than those determined experimentally, leading us to believe that our basic mean field type calculations do not quite capture the real physics of the system. It appears that the $D = 0.175$ calculation yields a temperature dependence that more accurately represents the experimental data, though it was determined that the $D = 0.300$ calculation does a better job of predicting $H_{c1}$ and $H_{c2}$. Interpreting the phase difference to yield information about the size of the $\beta$-sheet of the Fermi surface and with the FS area larger for higher occupation of the $\Gamma_1$ vs. the $\Gamma_1^2$ energy state, we see that below the lower phase boundary, $H_{c1}$, the size of the Fermi surface remains quite constant vs. temperature until
Figure 4.11: Raw data traces for sweeps of 10–7 T for all PrOs$_4$Sb$_{12}$ runs. Traces go from lower to higher temperature.
Figure 4.12: dHvA traces for 10-7 T sweeps after low pass filtering to select out the $\beta$ frequency (see fig. 4.5a). Compared with fig. 4.11, one can see the oscillations turn “on” and “off”.
Figure 4.13: dHvA traces after low pass filtering to select out the $\beta$ frequency (see fig. 4.5a). Oscillations are considerably smaller than those in fig. 4.12, but are still clearly visible.
Figure 4.14: Comparison of the change in phase of the dHvA oscillations with respect to base temperature, $\Delta \phi$, for theoretical calculations with differing quadrupolar interaction strengths and experimental observation at select fields.

(a) Theoretical $D = 0.175$, $H_{c1} = 4.85$ T, $H_{c2} = 9.05$ T  
(b) Experimental, $H_{c1} = 4.56$ T, $H_{c2} = 11.50$ T  
(c) Theoretical, $D = 0.300$, $H_{c1} = 3.45$ T, $H_{c2} = 9.45$ T
about 0.5 K in the experimental plot, where it begins to drop off. This can be understood as thermal occupation of the $\Gamma_2^4$ state at the cost of the occupation of the $\Gamma_1$ state, which causes the Fermi surface to shrink [69]. This is the behaviour predicted in both calculations as well, though the temperatures at which this begins to occur differ from the experimental results. Looking at the energy level diagram of fig. 4.2, we can see that at low field there is a large separation of $\Gamma_1$ and $\Gamma_2^{2,+}$, which shrinks with increasing field though they remain well separated until eventually crossing over around 8 T. Experiments were not carried out above the upper phase boundary, $\sim 11.5$ T, but calculations were, with both showing the reverse behaviour seen at low field. Since by this point in field, $\Gamma_1$ and $\Gamma_2^{2,+}$ have long since crossed over, $\Gamma_1$ now becomes thermally occupied with increasing temperature and the Fermi surface area increases. As McCollam notes, the phase behaviour within the AFQ phase is not as well understood. The AFQ phase itself represents a superposition of the $\Gamma_1$ singlet and triplet of $\Gamma_2^4$, $\sum_j a_{i,j}(B,T) |\Gamma_j^4\rangle + b_i(B,T) |\Gamma_1\rangle$, for sublattice index $i = 1, 2,$ and $j = +, 0, -. As the temperature is increased within the AFQ phase, the order parameter decreases, which is seen through a change in the coefficients $a_{i,j}$. For fields just above $H_{c1}$, this is reflected in an increase in occupation of the $\Gamma_1$ state with increasing temperature from $T = 0$, causing an increase in the size of the Fermi surface, which reaches a maximum around $T_c$ [69]. This is seen clearly in fig. 4.14b for the 1.05 and 1.23 $H_{c1}$ datasets. Zooming into the low temperature region (below 1 K) of the experimental phase vs. temperature plot, shown in fig. 4.15a, we see that for all values of the field within the AFQ phase, this increase in the phase with increasing temperature is seen up to about 400 mK. This is not observed in the data for field values less than $H_{c1}$, in which there is little or no change in phase at low temperature, thus this increase in phase at low temperature is taken to be a hallmark of the AFQ state. The experimental observation of increasing phase with temperature is confirmed for the calculations shown in figs. 4.14a and 4.14c, where a change in phase is predicted within the AFQ phase boundary, but not outside of the AFQ phase in which the phase should remain flat. At fields above the crossover point in the energy level diagram, the opposite behavior to that for fields below the AFQ phase would be expected, thus there should be a minimum in the phase with increasing temperature. With the exception of the plot for $B = 0.83H_{c2}$ and $D = 0.300$, this is not observed. The experimental data shows monotonic increase in the phase
with temperature, but becomes extremely noisy at higher temperatures and doesn’t appear to resemble the calculations. A comparison of the experimentally determined phase shift and that determined from $\langle \Gamma_1 \rangle$ is shown in fig. 4.15b. Each of the theoretical curves have been scaled independently in the Y-axis in order to best fit the experimental data. Additionally, the highest field value, $0.83H_{c2}$, has had all temperature values scaled by a factor of 2 and shows excellent agreement with the experimental data up to about 1.6 K. It is believed that further theoretical work on the relationship between the percentage occupation of the crystal field levels and the phase of the dHvA oscillations may be able to give a physical understanding of this result.

### 4.5 The $H_{c1}$ Quantum Critical Point

The calculations described in section 4.3 allowed for the determination of the quadrupole moment on adjacent lattice sites. By comparing these moments using $Q_A - Q_B$, for lattice sites $A, B$, a plot of the predicted boundary of the AFQ phase was constructed for $D = 0.300$ with the hyperfine interaction both “on” and “off”. The value of $D = 0.300$ was used for this calculation as it yielded an upper and lower field boundary closer to the experimentally determined values. $D = 0.175$, which was used in the phase vs. temperature plot, yielded a much narrower AFQ phase and was not included here. An example plot of $Q_A - Q_B$ can be seen in fig. 4.16. The inflection points of this plot were used to construct the phase plots shown in fig. 4.17. Compared against the lower D calculations, increasing the nearest neighbor coupling constant has the effect of increasing the robustness of the AFQ phase, causing the lower boundary to shift lower, and upper boundary to increase in field. This, however, also increases $T_c$, shifting it to higher temperatures than are determined experimentally. The two plots in fig. 4.17 compare the phase boundaries with the hyperfine interaction turned off (a) and on (b). They are very similar throughout the diagram, with the major exception being the low field phase boundary for which the “hyperfine on” condition predicts a tail at very low temperatures.

We attempted to observe this experimentally. The low field phase boundary was extracted from the data using two different methods. The first, which was touched upon briefly above, assumed a fit function $A \frac{Be^{-C/x^3/2}}{1 + Be^{-C/x^3/2}} + D$, to the phase vs. temperature data below the $H_{c1}$ phase boundary. The range of the fit was selected to be the higher temperature section and
(a) View of the low temperature range of the phase vs. temperature plot shown in fig. 4.14.

(b) Direct comparison of $D = 0.175$ calculation of $\langle \Gamma_1 \rangle$ and experimental data, previously seen in figs. 4.14a and 4.14b for select field values. Values of field selected for $D = 0.175$ were selected as close to the quoted values as possible due to calculation steps size. Calculation shown with open symbols and dashed line. The temperature scale of the highest theoretical field plot has been scaled by a factor of 2, and each theoretical plot has been scaled independently to relate the percentage occupation of $\langle \Gamma_1 \rangle$ to the change in dHvA phase.

Figure 4.15: Expanded look at phase shift vs. T plot and comparison to theoretically calculated value, previously shown in fig. 4.14.
Figure 4.16: Determination of the AFQ phase boundary in PrOs$_4$Sb$_{12}$ by taking the difference of the quadrupole moment on adjacent sites obtained using the mean field calculation described in section 4.3. Inflection points were used to determine the location of the phase boundary.
Figure 4.17: Determination of the AFQ phase transition from a large change in the difference of the quadrupole moment on adjacent sites as determined by our self-consistent calculation based on the method of Kusunose [123]. a) Hyperfine interaction terms in the Hamiltonian are turned off, yielding a flat transition at low temperature. b) Hyperfine terms in the Hamiltonian are included, yielding curvature in the lower field phase boundary. Insets in both show an expanded view of the low field boundary.
corner of the plot, and this procedure was repeated for field cuts from 4-5.9 T in steps of 0.01 T.

The origin of this fit function comes by analogy to the phase transition of dimerized antiferromagnets, such as TlCuCl$_3$. In this material, a phase transition to a canted (XY) antiferromagnet occurs when the energy level of an exited triplon state overlaps with the ground state singlet energy, by application of magnetic field [124–126]. The splitting of the triplon energies with field is resembles the splitting of the $\Gamma_4^{(2)}$ states in PrOs$_4$Sb$_{12}$. Assuming then, that the triplet energy levels in PrOs$_4$Sb$_{12}$ disperse as a cosine, in a similar fashion to those triplon states in TlCuCl$_3$ where [127],

$$\epsilon(k) = J_0 + J_1 [\cos(k_x a) + \cos(k_y a)] - g\mu_B HS^z,$$  \hspace{1cm} (4.20)

and there is a minimum energy gap between the $\Gamma_1$ and $\Gamma_4$ levels, $\Delta$ at some wave vector, $q_0$. A diagram of this is shown in fig. 4.18. We are then able to calculate the probability of occupation of $\Gamma_4$ with temperature using the Boltzmann weighting function, so,

$$\langle \Gamma_4 \rangle \sim \frac{V}{(2\pi)^3} \int \frac{d\mathbf{q}}{\text{B.Z.}} e^{-\beta \epsilon(\mathbf{q})}$$  \hspace{1cm} (4.21)

Approximating the cosine of the energy of $\Gamma_4$ at its minimum value to be represented by a quadratic in $q'$, we can write the energy of the triplet as,

$$\epsilon(\mathbf{q}) \simeq \Delta + \alpha q'^2,$$  \hspace{1cm} (4.22)

providing the exponential tends to zero when the true value of $\epsilon(\mathbf{q})$ deviates from this approximation. Also, making the substitution, $\mathbf{q}' = \mathbf{q} - \mathbf{q}_0$, the integral becomes,

$$\int_{\text{B.Z.}} e^{-\beta \epsilon(\mathbf{q})} \simeq \int_0^\infty d\mathbf{q} e^{-\beta (\Delta + \alpha q'^2)} \simeq e^{-\beta \Delta} \int_0^\infty q'^2 d\mathbf{q}' e^{-\beta \alpha q'^2}$$  \hspace{1cm} (4.23)
Figure 4.18: Dispersion of the $\Gamma_4$ triplet energy level in PrOs$_4$Sb$_{12}$ with wave vector, $q$ (blue). $\Gamma_1$ level is taken to be the zero of energy in the plot and does not disperse (red). Estimate of cosine function for small values about $q_0$ taken to be proportional to the square of the wave vector (green). Minimum of energy gap between $\Gamma_1$ and $\Gamma_4$ is $\Delta$. 
Making the further substitutions in order to aid in the integration,

\[ C = \frac{\Delta}{k_B} \]

\[ x = \beta \alpha q'^2 \]

\[ \therefore q' = \frac{\sqrt{x}}{\sqrt{\beta \alpha}} \]

\[ q'^2 dq' = \frac{1}{(\beta \alpha)^{3/2}} \sqrt{x} dx \]

And so,

\[ \int_{\text{B.Z.}} dq \ e^{-\beta \epsilon(q)} \simeq \frac{1}{(k_B \alpha)^{3/2}} \frac{T^{3/2} e^{-C/T}}{B} \int_0^\infty \sqrt{x} dx \]

\[ = BT^{3/2} e^{-C/T} \]

Thus,

\[ \langle \Gamma_4 \rangle \simeq \frac{BT^{3/2} e^{-C/T}}{1 + BT^{3/2} e^{-C/T}} \]

(4.26)

to which a scaling factor, \( A \), and constant offset, \( D \) are added to aid in fitting. This yields the fit function, \( A Be^{-C/x_{\beta \alpha}^{3/2}} + D \).

In fig. 4.19a, we see no deviation of the phase from this fit curve at low T. It should also be noted that the fit was done only for \( 25 < T < 800 \) mK, so the section from 800-1000 mK does not fit the experimental data. In fig. 4.19b, we see that the phase deviates significantly from the fit at a temperature value of \( 200 \pm 40 \) mK. The temperature point at which the measured \( \Delta \phi \) departed from the fitted function was taken to be \( T_c \).

A second method was used in order to determine the lower field phase boundary involving the dHvA frequency vs. field for specific temperature cuts. The dHvA frequency was plotted against field for a given temperature and the onset of the AFQ phase was determined by finding the intersection of the line going through the low field frequencies and that leading up to the peak frequency. An example is shown in fig. 4.20. This drastic change doesn’t necessarily represent a discontinuous change in the shape of the Fermi surface at this point, but rather could indicate a change in the slope of the “true” frequency, leading to a drastic change in the back projection of this frequency and a large change in the observed frequency \([69]\). It is clear
Figure 4.19: Determination of the AFQ phase boundary for PrOs$_4$Sb$_{12}$ by fitting of a polynomial (red dashed line) determined using a Boltzmann averaged statistical treatment of the occupation of the $\Gamma_{4}^{2+}$ level. It can be seen that the phase does not deviate from the fit when we are outside of the AFQ phase.
Figure 4.20: Determination of the low field AFQ phase boundary for PrOs$_4$Sb$_{12}$ by examining the point at which a drastic change in the dHvA frequency is observed.
that this data was quite a bit noisier than that of McCollam et al. and as well was a more
difficult method of determining the AFQ transition, evidenced by large error bars. The results
of the two methods are compared to the published values determined by the magnetization
measurements of Tayama et al. [118]. This is shown in fig. 4.21. The results of the F vs.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure421.png}
\caption{Phase boundary of PrOs$_4$Sb$_{12}$ determined by phase vs. temperature fits and
frequency vs. field fits from dHvA data collected for fields from about 4.5-5.9 T at temperatures
between 25-700 mK. The results are compared against the phase boundary determined using M
vs. H measurements by Tayama et al. including their interpolated guide to the eye (blue dashed
line) [118]. Also, we have compared the experimental data against the lower phase boundary
determined by our mean field calculations for $D = 0.300$. The mean field calculation (magenta
dashed and dotted line) is shifted in x by 0.95 T to better line up with experimental values.
The scaled mean field calculation (red dotted line) is shifted in x by 0.95 T and has had the
temperature values scaled to 46% of the value determined by the calculation in order to better
agree with the experimental data.

B method of determining the phase boundary tended to be shifted to lower fields than those
determined using the $\Delta \phi$ vs. T method, which deviated slightly from the values determined by
the Tayama et al. measurement at lower fields, but were in good agreement above 5 T.

It is informative to compare qualitatively the experimentally obtained results to those,
previously mentioned, by mean field type calculations with the hyperfine interaction turned “on” and “off”. Fig. 4.17a predicts a lower field phase boundary with no slope from about 400 mK all the way down to 0 K with the hyperfine interaction “off”. This differs greatly from the phase boundary predicted with the hyperfine interaction “on”, which shows a large change below about 100 mK. While we are able to observe a change in the slope of the phase boundary, we do not observe a change as drastic as the one predicted. The measured phase boundary follows neither prediction, although it is possible that at the lowest temperatures of our measurement there was a loss of thermal contact with the sample. Looking at a direct comparison of the lower phase boundary, shown in fig. 4.21, we see that the phase boundary predicted by the mean field calculation for \(D = 0.300\) greatly overestimates the temperature of transition. Scaling the calculated temperatures by a factor of 0.46, we are able to much more closely reproduce the experimental results, and even predict some of the observed kinks in the boundary. The temperature of the phase boundary can be reduced by decreasing the AFQ coupling strength, \(D\), which was done in the \(D = 0.175\) calculations, though this has the effect of increasing the lower phase boundary in field and decreasing the upper phase boundary to a value well below that observed experimentally, around 11.5 T [69].

### 4.5.1 Comparison to LiHoF\(_4\)

The tail in the phase boundary predicted for inclusion of the hyperfine interaction in the Hamiltonian is reminiscent of LiHoF\(_4\). LiHoF\(_4\) is the experimental realization of an Ising type ferromagnet, which is represented by the simplest quantum spin model, thus providing the testbed for exploring the nature of the quantum phase transition, while eliminating the complications in theoretical understanding of the transition present in other materials [128]. This system has been studied by mean field approach, with the basic Ising type Hamiltonian being given by,

\[
H = \sum_{i,j}^{N} J_{ij} \sigma_i^z \sigma_j^z - \Gamma \sum_{i}^{N} \sigma_i^x, \tag{4.27}
\]

where the \(\sigma\)'s are the Pauli spin-matrices, and \(\Gamma\) is an applied transverse magnetic field. This Hamiltonian resembles the mean field Hamiltonian utilized in the calculations for PrOs\(_4\)Sb\(_{12}\) shown in eqs. 4.9 and 4.10, though it lacks much of the complication introduced by the inclusion
of quadrupolar operators, and utilizes the crystal field ground state doublet as the realization of the spin-1/2 eigenstates \[128\]. By exploring the magnetic susceptibility of LiHoF\(_4\) with temperature and field, Bitko et al. mapped the ferromagnetic phase boundary and found it exhibited a small tail tending towards higher fields at low temperatures. They compared this result to calculations incorporating the hyperfine interaction of the Ho\(^{3+}\) \((J = 8, I = \frac{7}{2})\) ion and solved self-consistently for the Hamiltonian,

\[
H = V_c - g_\perp \mu_B H_t \hat{J}_x + A \left( \hat{I} \cdot \hat{J} \right) - 2J_0 \left\langle \hat{J}_z \right\rangle \hat{J}_z,
\]

(4.28)

where \(V_c\) is the zero-field crystal field operator, \(g_\perp\) is the transverse electron g-factor, \(A\) is the strength of the hyperfine interaction, and \(J_0\) is an averaged spin-spin longitudinal coupling constant \[128\]. The hyperfine interaction, through a core polarization effect, mixes the nuclear and electronic eigenstates, and stabilizes the ferromagnetism at low temperatures, increasing the field needed to suppress the magnetism \[128, 129\]. At high temperatures, the effect of the hyperfine interaction is not felt, and the phase boundary follows the mean field value without its inclusion \((A = 0)\), however, at low-T the hyperfine interaction becomes extremely important and creates an effective \((I + J)\) spin, leading to the observed tail \[128\]. The calculation with the hyperfine interaction “turned on”, compared against that without the hyperfine interaction and the experimental results are shown in fig. 4.22. The agreement between the hyperfine modified mean field theory and experiment in this case is excellent. This bears a striking resemblance to the result of the inclusion of the hyperfine interaction in the mean field calculations utilized for PrOs\(_4\)Sb\(_{12}\), seen in fig. 4.17. Whereas the phase boundary in LiHoF\(_4\) was determined by the spontaneous onset of magnetism \[128\], the phase boundary of PrOs\(_4\)Sb\(_{12}\) was determined by the spontaneous onset of AFQ order, evidenced by a distinct change in the quadrupolar moment on adjacent lattice sites. In LiHoF\(_4\), the hyperfine interaction altered the low-T phase boundary of the FM state, shifting the critical field to higher values, making it more resilient to the applied transverse field. In PrOs\(_4\)Sb\(_{12}\), the low-T lower field AFQ phase boundary was shifted to lower fields, leading to the inference that the hyperfine interaction enhances the overall effect of the quadrupolar interaction, but is rendered effectively irrelevant by about 110 mK. While there are discrepancies between experiment and mean field theory in PrOs\(_4\)Sb\(_{12}\) it is certainly an
Figure 4.22: Phase boundary of LiHoF$_4$. The experimental results (black circles) are compared against a mean field type calculation considering only the electronic degrees of freedom (dashed line) and a calculation which includes the effect of the Ho$^{3+}$ hyperfine interaction (solid line). Reprinted figure with permission from [128]. Copyright (1996) by the American Physical Society.

avenue for continued research into this material.

### 4.6 Conclusions

Utilization of the temperature dependence of the phase of the quantum oscillations, $\Delta \phi$ vs. $T$, has yielded a novel method of exploring the AFQ phase of PrOs$_4$Sb$_{12}$, which can be directly compared to mean field type calculations. The phase information sheds light on the change in size of the Fermi surface with field, which is related to the occupancy of the relevant crystal field levels. It was shown that improvements must be made to the calculations for better agreement with the experimental results, as the calculation with a lower value of the quadrupolar coupling constant, $D$, required a rescaling of the predicted field of the phase boundary, and the calculation with larger coupling constant required significant rescaling of the temperature of the phase boundary. Our method of fitting the phase of the oscillations to determine the
phase boundary, based on an approach analogous to that used for triplon excitations in anti-ferromagnets, has proven quite successful, and further progress could be made by determining a quantitative relationship between the occupation of the crystal field levels and the phase of the oscillations. This provides a starting point for further research into this material. As well, additional measurements at the lowest temperature values would help to confirm the current results.
Chapter 5

Summary

In this section I summarize the major results of my thesis and suggest possible avenues for continued research.

5.1 Data Collection

I have modified the hosts files on the Windows data collection computers in an attempt to eliminate some of the effects of stalling caused by poor network communication between the data collection machine, Max, and the data visualization and control computer, Dew. I have also upgraded the computer systems themselves in order to give more processing power and memory to the very hungry LabView software. While this seems to have helped reduce the frequency with which one must restart the computers and PXI box to avoid losing data or having program crashes, the situation is far from perfect. Patrick Rourke attempted valiantly to create an all in one data collection and fridge control solution with DAVIES, but unfortunately, as is the case with basically any software in which features are grafted on after the fact, DAVIES has become bloated and unreliable. As well, the software seems to be decaying over time, with new issues cropping up frequently. I believe that it would be a good idea for a new graduate student, with a sufficient amount of time left in their program, to rewrite this software, ideally from scratch. Because of the hardware, one is likely limited to using LabView as it’s the simplest way to interact with the PXI box.

Secondly, I have posted my dHvA analysis code on GitHub so that other students can use
and modify it as they see fit [130]. It certainly needs to be cleaned up to conform to coding best practices. Also, I intended to create a GUI for it in order to improve usability and efficiency of use, so maybe one day someone will get around to accomplishing this.

5.2 YbRh$_2$Si$_2$

I completed multiple rotation studies on samples of YbRh$_2$Si$_2$ using the standard field modulation de Haas-van Alphen technique. I completed multiple rotations in-plane, (100)-(110), and multiple rotations out of plane, (100)-(001) and (110)-(001). In doing so, I corrected a long standing issue with the sample orientation and observed a new high frequency oscillation, which is the first that can be positively ascribed to the jungle gym J-sheet of the Fermi surface. These measurements were compared against new calculations completed using Wien2k with a refined silicon atomic position, $z = 0.379c$. Good qualitative agreement between theory and experiment has been obtained, but further improvements in both of these areas would help elucidate the high field nature of this material. Specifically, searching for signatures of spin-splitting by conducting studies over a wide field range could aid in understanding the topology of the high field Fermi surface.

5.3 PrOs$_4$Sb$_{12}$

I have conducted dHvA quantum oscillation measurements using the standard field modulation technique on one sample of PrOs$_4$Sb$_{12}$. Field sweeps from 6 to 3 T and 10 to 7 T at temperatures between about 23 and 2800 mK allowed me to study the Antiferroquadrupolar (AFQ) phase of this material, focusing specifically on the nature of the low field AFQ phase boundary. This transition was explored using a novel technique which makes use of the phase of the oscillations vs. temperature, $\Delta \phi$ vs. $T$, and allows for determination of the low temperature crystal field level occupancy. These results were compared against self-consistent mean field calculations which took into account the AFQ interaction and modifications to the Hamiltonian introduced by the hyperfine interaction. These calculations, assuming a ground state singlet and a nearby triplet of crystal field states, allowed for theoretical determination of the relative occupation of the various energy levels as they were modified by increasing field and temperature. The
theoretically determined lower phase boundary, while qualitatively similar to the experimental \( \Delta \phi \) vs. \( T \), only agrees quantitatively if we rescale the mean field theory by using small nearest neighbor quadrupolar coupling and rescale the determined field, or if we use a larger coupling, \( D \), and rescale the temperature. It’s possible that this basic calculation done using a mean field approach with nearest neighbor interactions could be improved by the inclusion of next nearest neighbor interactions. We believe further refinement of the theory to be a worthwhile endeavour since the lower quantum critical point, involving simultaneous nuclear and electronic ordering, is quite unusual and potentially very interesting.
Appendix A

Crystal Field Levels in PrOs$_4$Sb$_{12}$

For the purpose of the calculations in chapter 4, which make use of the crystal field levels for the Pr$^{3+}$ ions coordinated by a cage of 12 Sb atoms, I present here the explicit form of these wavefunctions. As well, I present the Hamiltonian used in the calculations. This is based on the thesis of Kiss [131] and the papers of Tayama, Shiina, and Kusunose [118, 119, 123]. I must openly state, that I am by no means an expert on the point group mathematics used here. I simply present the form of the ground state wavefunctions and the Hamiltonian, which I used, but which were certainly not derived by me.

In crystal field theory, symmetry operations are used to write down the electrostatic environment of an ion at a particular site based on the potentials created by the surrounding ions, which are treated as points [131]. The site symmetry of the Pr ions, with assumed electronic configuration of 4f$^2$, is the $T_h$ tetrahedral point group. The notation used is that of the octahedral, $O_h$, point group, even though the symmetry is now only 4-fold [119]. For the two 4f$^2$ electrons, the first is placed in the $\ell = 3$ orbital with $m_S = 1/2$. The second $f$-electron is placed in the $\ell = 2$ orbital, again with $m_S = 1/2$. Thus calculating the total angular momentum, $J$, we obtain

$$J = L - S = (3 + 2) - \left(\frac{1}{2} + \frac{1}{2}\right) = 4,$$

for a less than half-filled shell. We then use the $J = 4$ basis to describe the resulting wavefunctions. The basis states of the $T_h$ group are represented using the $\Gamma_1$ singlet, $\Gamma_3$ doublet, and $\Gamma_4$
Appendix A. Crystal Field Levels in PrOs$_4$Sb$_{12}$

and $\Gamma_5$ triplets. Where,

$$|\Gamma_1\rangle = \frac{\sqrt{30}}{12} (|+4\rangle + |-4\rangle) + \frac{\sqrt{21}}{6} |0\rangle,$$

$$|\Gamma_3^+\rangle = \sqrt{\frac{7}{24}} (|+4\rangle + |-4\rangle) - \sqrt{\frac{5}{12}} |0\rangle,$$

$$|\Gamma_3^-\rangle = \sqrt{\frac{1}{2}} (|+2\rangle + |-2\rangle),$$

$$|\Gamma_4^{(2)}, \pm\rangle = \mp \sqrt{\frac{7}{8}} |\mp 3\rangle \mp \sqrt{\frac{7}{8}} |\pm 1\rangle,$$

$$|\Gamma_4^{(2)}, 0\rangle = \sqrt{\frac{5}{2}} (|+4\rangle - |-4\rangle),$$

$$|\Gamma_5^{(2)}, \pm\rangle = \pm \sqrt{\frac{7}{8}} |\pm 3\rangle \mp \sqrt{\frac{1}{8}} |\mp 1\rangle,$$

$$|\Gamma_5^{(2)}, 0\rangle = \sqrt{\frac{5}{2}} (|+2\rangle - |-2\rangle),$$

using the notation of refs. [119, 131]. Upon lowering of the symmetry from $O_h \rightarrow T_h$, the $\Gamma_1$ singlet remains unchanged, however we now write the low-lying triplet as a combination of the $\Gamma_4$ and $\Gamma_5$ levels where,

$$|\Gamma_4^{(2)}(m) = \sqrt{1 - d^2} |\Gamma_5^{(0)}, m\rangle + d |\Gamma_4^{(0)}\rangle$$  \hspace{1cm} (A.3)$$

where $m = \pm, 0$ and,

$$d = \text{sgn}(y) \left[ \frac{1}{2} \left( 1 - \frac{3 + 2x}{\sqrt{(3 + 2x)^2 + 1008y^2}} \right) \right]^{1/2}$$  \hspace{1cm} (A.4)$$

with $x = 0.45$ and $y = 0.07$ in my calculations. The $\Gamma_3$ functions are eliminated now as they are at least 100 K above the ground state [119]. Thus we represent PrOs$_4$Sb$_{12}$ in the $\Gamma_1 - \Gamma_4$ scheme described by Kiss [131], and not the $\Gamma_3 - \Gamma_4$ scheme originally suggested by Bauer [103].

It is helpful, at least in my mind (where intuitive feeling for the system we’re talking about is nearly as important as the math), to think of the basis functions in the pseudo-spin
representation of Shiina, which is an analogy to a spin dimer system [119], where,

\[
|00\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \equiv |\Gamma_1\rangle , \\
|1+\rangle = |\uparrow\uparrow\rangle \equiv |\Gamma_4, +\rangle , \\
|10\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \equiv |\Gamma_4, 0\rangle , \\
|1-\rangle = |\downarrow\downarrow\rangle \equiv |\Gamma_4, -\rangle
\]  

(A.5)
Appendix B

SQUIDs

B.1 Introduction

I have included this appendix on superconducting quantum interference devices (SQUIDs) because it represents a significant amount of work, even if the full implementation of the project never came to fruition. What began as my summer undergraduate project in our lab, to create a low temperature SQUID based noise thermometer, became a long running lab infrastructure project that I would work on in between the dHvA experiments. This section stems from a review paper I wrote on the topic for a graduate level course. I begin with a brief review of the physics behind SQUIDs and then discuss the application of SQUIDs to noise thermometry. For an in-depth review of SQUID operation and applications, the reader is referred to the comprehensive books by Clarke and Braginski [132, 133]. As well, the Josephson Nobel lecture gives an interesting look into the history of the development of the field [134].

B.2 Background

In their simplest form, SQUIDs are extremely sensitive devices used to measure magnetic fields. Field changes as low as $10^{-14}$ Gauss have been measured by NASA’s Gravity Probe B [135]. Being able to measure very tiny magnetic fields has an exceedingly large number of practical applications, including the study of heavy fermion materials, the central topic of this thesis [136]. Another application of SQUIDs is in magnetoencephalography (MEG), where SQUIDs
Figure B.1: Basic concept of a Josephson junction. Two superconductors, 1 and 2, connected by a weak insulating link of width, $d$.

are used to detect the magnetic fields produced by electrical brain activity, which may one day lead to a better understanding of disorders such as autism [137]. For use in our laboratory, SQUID based noise thermometry could be used to measure the temperature of our dilution fridge in the low millikelvin temperature range [138, 139]. I will briefly describe the theory of SQUIDs below, though the discussion will focus on DC SQUID operation as this is the type of device we had available in our lab, and they generally have lower noise figures than their RF counterparts [132].

B.2.1 Josephson Junctions

In order to keep the discussion of SQUID operation brief, it is assumed that the reader has a working knowledge of Cooper pairs and the Bardeen-Cooper-Schrieffer (BCS) theory of conventional superconductivity [13, 140]. The Josephson junction, originally proposed by Brian David Josephson in 1962 [141], is the fundamental element of the SQUID and is composed of two sections of superconducting material separated by a thin section of insulating material, as can be seen in fig. B.1.

For his work on this, Josephson was awarded the Nobel prize in physics, along with Esaki and Giaver, in 1973. A basic understanding of Josephson junctions begins from the basic quantum mechanical effect of tunnelling. From quantum theory, we can easily solve the wave equation for the case of electrons tunneling through a potential barrier of width $d$ and height
V(x) = V. From the Schrödinger equation we have the wave function for a free particle in 1D is:

$$\psi(x) = Ae^{-ikx} \quad (B.1)$$

where A is some amplitude and the wave vector $k$ is related to the particle momentum. Inside the barrier we solve the standard time independent wave equation for the case when the electron energy is greater than the barrier energy:

$$-\frac{\hbar^2}{2m_e} \frac{d^2\psi(x)}{dx^2} + V\psi(x) = E\psi(x) \quad (B.2)$$

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m_e(V - E)}{\hbar^2} \psi(x) \quad (B.3)$$

Thus, $\psi(x) = Be^{i\sqrt{2m_e(V - E)}x}$ \quad (B.4)

We require that $\psi(x)$ and its first derivative be continuous across the boundaries of the different regions of space thus, $A = B$, and on the other end of the junction we again have free electrons, $Ce^{-ikx}$, so the barrier has introduced a change in phase, $\phi$ and so $Be^{i\phi(d)} = C$. While this equation describes free electrons, Brian Josephson in 1962 predicted this effect would also occur for Cooper pairs across two superconductors joined by a very thin intermediary [141]. In this case the phase difference across the barrier would be, $\phi = \phi_2 - \phi_1$, where $\phi_1$ and $\phi_2$ represent the macroscopic phases of the order parameters of the superconductors on either side of the junction [142]. An order parameter that can be used in superconductors is the Ginzburg-Landau complex order parameter [143]. From this basis we are now able to derive the fundamental equations of the junction, called the Josephson equations. Following along with the derivation by Feynman [144], we assume a Cooper pair wave function for superconductor 1, $\psi_1$, superconductor 2, $\psi_2$.

For the time dependent Schrödinger equation we have on each side of the barrier,

$$i\hbar \frac{\partial \psi_1}{\partial t} = U_1 \psi_1 + K\psi_2 \quad (B.5)$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = U_2 \psi_2 + K\psi_1 \quad (B.6)$$

Where $K$ is some constant that characterizes the junction. So if $K$ were equal to zero, $U_1$ and $U_2$ would be the ground state energy of the Cooper pairs. Thus $K$ is a term which couples the
two sides of the junction together. Now we imagine applying a potential difference across the junction such that,

\[ U_1 - U_2 = qV. \]  

(B.7)

We now define the zero of energy to be half the applied potential and so we then rewrite the previous equations as:

\[
    i \hbar \frac{\partial \psi_1}{\partial t} = \frac{qV}{2} \psi_1 + K \psi_2 \]  \tag{B.8}

\[
    i \hbar \frac{\partial \psi_2}{\partial t} = -\frac{qV}{2} \psi_2 + K \psi_1 \]  \tag{B.9}

We rewrite the wave equations on either side of the junction for assumed wave functions of the form,

\[ \psi_i = \sqrt{\rho_i} e^{i\phi_i} \]  \tag{B.10}

Where \( \rho_i \) represents the electron density on either side of the junction. Substituting this into the previous equations we arrive at the fundamental Josephson equations:

\[
    \frac{\partial \rho_1}{\partial t} = \frac{2}{\hbar} K \sqrt{\rho_2 \rho_1} \sin \phi \]  \tag{B.11}

\[
    \frac{\partial \rho_2}{\partial t} = -\frac{2}{\hbar} K \sqrt{\rho_2 \rho_1} \sin \phi \]  \tag{B.12}

\[
    \phi_1 = +\frac{K}{\hbar} \sqrt{\frac{\rho_2}{\rho_1}} \cos \phi - \frac{qV}{2\hbar} \]  \tag{B.13}

\[
    \phi_2 = +\frac{K}{\hbar} \sqrt{\frac{\rho_1}{\rho_2}} \cos \phi + \frac{qV}{2\hbar} \]  \tag{B.14}

The time derivatives of the electron densities on either side of the junction yield the rate of change of the electron populations, which is in fact a current. Solving,

\[ J = \frac{2K}{\hbar} \sqrt{\rho_1 \rho_2} \sin \phi_i \]  \tag{B.15}

The factors in front of the sin function are all constants so we rewrite this equation as:

\[ J = J_0 \sin \phi \]  \tag{B.16}
which is the fundamental Josephson equation [143, 144]. Another important parameter is the critical current, \( J_c \). When biasing a Josephson junction, the apparent voltage difference across the junction is zero until the current reaches \( J_c \). At this point there is a near discontinuous jump in the voltage. At currents greater than the critical current the phase difference across the junction evolves according to,

\[
\frac{\partial \phi}{\partial t} = \frac{2eV}{\hbar} = \frac{2\pi V}{\Phi_0}
\]  

(B.17)

where \( \Phi_0 \) is called the flux quantum as explained below. From this we obtain a non-zero voltage difference across the junction [132].

### B.3 DC SQUIDs

From the concept of the Josephson junction we are now able to construct the SQUID. A DC SQUID consists of a ring (or loop of some shape, i.e. square) of superconducting material with two symmetrically placed Josephson junctions. This can be seen in Fig. B.2 [144].
Following Feynman for this configuration, the maximum current across the junction is,

\[ J_{\text{max}} = 2J_0 \left| \cos \left( e\frac{\Phi}{\hbar} \right) \right|, \tag{B.18} \]

where \( \Phi \) is the magnetic flux through the loop [144]. We write this in units of \( \Phi_0 \), the magnetic flux quantum, originally proposed by London to have a value of \( h/e \) [145], which was later shown to have its accepted value of \( h/2e \) by Deaver and Fairbank [146], and Doll and Nääbauer [147], since London was unaware of Cooper pair formation in superconductors [148]. Thus we see that the current in the SQUID is maximized when the flux through the SQUID is an integer multiple of the flux quantum, given as,

\[ \Phi_0 = \frac{\pi h}{e} \approx 2.068 \times 10^{-15} \text{T} \cdot \text{m}^2 \tag{B.19} \]

As was previously mentioned, DC SQUIDs make use of two symmetrically placed Josephson junctions, as was shown in Fig. B.2. The tunnelling of current through the junctions creates a wave function interference effect equivalent to Fraunhofer diffraction of monochromatic light through a slit. This leads to a sinusoidal modulation of the current through the junction [132, 149]. From equation B.18, it was shown that the maximum value of the critical current in the loop was \( 2J_0 \). Thus, the most direct method of measuring a change in flux would be to simply measure the current itself. In practice, however, this is generally not done. Instead, the SQUID is biased with a current just above the critical current of the junction and the voltage is measured. In addition, flux is applied to the SQUID in a multiple of \((2n+1)\Phi_0/4\). This maximizes the flux-to-voltage transfer coefficient written as \( \left| (\partial V/\partial \Phi_a) \right|_{J_B} \), also called \( V_\Phi \), for the bias current \( J_B \). So, because we have set the SQUID to be operating at the point where the \( V_\Phi \) response is a maximum we obtain the maximum change of voltage, \( \delta V = V_\Phi \delta \Phi_a \), where \( \delta \Phi_a \) is a small change in flux. Thus, the voltage is read out directly as a function of magnetic field or magnetic flux. The critical current is a minimum when the voltage read out is a maximum. This information is highlighted in Fig.B.3 [132]. SQUIDS, therefore, can operate as flux to voltage transducers, and by the inclusion of an input coil to the SQUID, an input electrical signal creates a magnetic field that is coupled into the SQUID. This allows very small electrical
signals to be measured as very small changes in flux through the SQUID. It is this type of operation that is utilized for the noise thermometer.

**B.4 Noise Thermometry**

Our intended use of SQUIDs was for low-temperature noise thermometry. In the original implementation [138], a small resistor made of copper foil, was fixed using a low temperature glue, such as GE varnish, to an insulating, non-magnetic material. The noise resistor was connected to the input coil of the SQUID, which could be located either directly on-top of the SQUID or connected externally via a superconducting twisted pairs of wires. The SQUID is operated in flux-locked mode, and thermal current fluctuations caused by Johnson noise in the
resistor induce flux changes in the SQUID loop. In flux-locked mode, the feedback electronics balance this flux, and the readout of the feedback translates to a coupled flux value. The Johnson noise formula yields a noise voltage,

$$v_n = \sqrt{4k_B TR\Delta f}$$  \hspace{1cm} (B.20)

Where $k_B$ is Boltzmann’s constant, $R$ is the resistance, $\Delta f$ is the bandwidth over which the measurement is made, and $T$ is the temperature (the desired quantity). It is obvious then that the sensitivity is highly dependent on precise measurement of the noise resistor value, often completed via a 4-terminal resistance measurement. Using this technique temperatures have been measured from 4.2K to as low as 300$\mu$K with an accuracy of 0.3% [138]. The setup is shown in fig. B.4.

B.4.1 Realization of the Noise Thermometer

Initially, we attempted to create a noise thermometer based on the design of Lusher, et al. [138], but had much difficulty in getting proper operation of the SQUID, likely due to a large amount of RF noise present in our lab. In 2010, I received an exchange grant from the Ontario/Baden-Württemberg Student Exchange Program and decided to learn more about noise thermometry from a world renowned group in Heidelberg, Germany at the Kirchoff Institute for Physics.

Figure B.4: Schematic diagram of the low-temperature DC SQUID current sensing noise thermometer. Adapted from [138].
While there, I learned a considerable amount about SQUID noise thermometry from Andreas Fleischmann and Christian Enss, who have designed and implemented a number of SQUID noise thermometers, which work well in the low mK range [139, 151, 152]. The device was intended to utilize high purity copper wire as a noise resistor, sitting at the sample stage of our dilution fridge, which would be coupled into the input coil of our SQUID, sitting near the 1 K pot where the magnetic field is considerably lower. The housing for the noise resistor can be seen in fig. B.5. Unfortunately, this project was never completed due to the high RF noise environment of our lab, which prevented the SQUID from operating properly. Attempts were made to eliminate high frequency noise, including the construction of microwave frequency powder filters based on ref. [153], but they were unsuccessful.

Figure B.5: Comparison of the 3D mock-up and final realization of the sensor component of the SQUID based noise thermometer.
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