Electronic Properties of Nanoscale Structures/Devices Atomically Engineered on Metal Surfaces

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Electronic Properties of Nanoscale Structures/Devices Atomically Engineered on Metal Surfaces

By

Brendan Rhyno

A Thesis
Submitted to the Faculty of Graduate Studies
through the Department of Physics
in Partial Fulfillment of the Requirements for
the Degree of Master of Science
at the University of Windsor

Windsor, Ontario, Canada

2016

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Electronic Properties of Nanoscale Structures/Devices
Atomically Engineered on Metal Surfaces

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Declaration of Originality

I hereby certify that I am the sole author of this thesis and that no part of this thesis has been published or submitted for publication.

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Abstract

Currently, there is interest in using a bottom-up approach to fabricate nanostructures i.e. structures whose dimensions are on the order of $10^{-9}$ metres. Discovering devices which exploit/thrive on quantum mechanical effects is vital if the down-sizing of electronics is to continue. The aim of this Thesis is to theoretically design and characterize nanoscale structures/devices built atom-by-atom in a bottom-up approach on a metal surface. By varying the properties of our “building blocks” (i.e. atoms), we demonstrate that one can engineer devices which purposefully exploit novel physics. More specifically, we demonstrate how the strongly correlated state induced by magnetic atoms in a metal can be used for control and transmission of signals between distinct points. Furthermore, we demonstrate a mechanism to drive superconductivity in a single atom; we utilize this mechanism to create superconducting nanostructures with precisely designed properties.
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To my best friend and partner in life, my wife Shelby Rhyno: thank you for always being by my side and supporting me (even when I am a goof). I cannot wait to start the next chapter of our lives together!

This list would not be complete if I did not thank my parents for their constant support and for encouraging me to study science.

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Chapter 1

Introduction

1.1 Present-Day Electronics; Top-Down vs. Bottom-Up

Semiconductor devices lie at the heart of present-day electronics. The central element used to process information is the transistor. Invented in 1947 by Bardeen, Brattain, and Shockley, the transistor has revolutionized technology, earning its creators the Nobel Prize in Physics “for their researches on semiconductors and their discovery of the transistor effect” in 1956.[1] Fig. 1.1 shows a schematic of the metal-oxide-semiconductor field-effect transistor. The bulk of the device consists of a doped silicon crystal – while Si is an intrinsic semiconductor, doping (with impurity atoms) changes its electrical properties;[2] hence, making it possible to control the current through the device via electric fields. It is important to appreciate how information is transferred between locations in a transistor – information is physically carried from one point to another by the flow of currents between the source and drain electrodes.

For many years, engineers have successfully found ways to shrink transistor devices and hence, increased the capacity for complex computation. In fact, Gordon Moore (co-founder of Intel) noticed that approximately every 1 to 2 years the number of transistors which could be fitted onto a single integrated circuit doubled.[3] This observation has held true for the past few decades and is now deemed “Moore’s Law”; as a result of this downsizing, current transistors are nanostructures with dimensions on the order of 10’s of nanometres.[4]
Moore’s law epitomizes the technological revolution we currently enjoy, but it is also a warning of things to come – as current devices/technology shrink down further, quantum effects must be taken into account. For transistors, *quantum tunneling* poses the most severe problem. Tunneling is a purely quantum phenomenon exhibited by particles when faced with an energy barrier – classically, a particle cannot overcome an energy barrier unless provided with sufficient additional energy; however, quantum mechanics gives a finite probability that the particle will be found on the opposite side of the barrier (Fig. 1.2). Fundamentally, transistors work on the assumption that we control the flow of current through them; hence, with the present design, tunneling gives an uncontrollable contribution to the current.
Further problems arise when one considers the pathways in which information travels between devices: the interconnect wires. Modern chips require a dense array of interconnect wires to relay information (i.e. currents) from one transistor to another. Interconnect wires built from conducting materials such as copper and aluminum suffer from scaling, because their resistivity increases as their dimensions decrease into the nanoscale. This coupled with the increased current density each wire must support when downsized leads to concerns over the Joule heating of the wires.

Therefore, further advancements in electronics and, more generally, information processing will require the development of new technologies that embrace quantum effects. To realize these technologies, new systems/approaches are needed. Integrated circuits are currently fabricated using top-down methods – semiconducting crystal wafers are put through a series of material deposit and photolithographic steps to produce a finished circuit which contains (billions of) devices connected via metallic pathways. However, nanometre-scale devices enable an opposite means of fabrication, namely bottom-up – a desired structure is built-up piece by piece using smaller “building blocks” of matter. Inherently, a top-down process is subtractive whereas a bottom-up process is additive.

With this in mind, the goal of this Thesis is to consider a class of nanostructures built bottom-up. Specifically, we design and characterize the properties of structures/devices built atom-by-atom on metal surfaces. By controlling matter on the smallest of scales, these systems allow us to investigate novel physics with the prospect of potential device applications.

### 1.2 Atomic-Scale Engineering

The tool employed both to probe and build these structures is the scanning tunneling microscope (STM). Designed in 1981 by Binnig and Rohrer at IBM, the STM utilizes the phenomenon of quantum tunneling to image matter on the nanoscale. The significance of this device was immediately appreciated and its inventors were awarded the Nobel prize in 1986.
Pictured in Fig. 1.3 is a schematic of the device: the STM consists of an atomically sharp tip brought near a surface (their separation on the order of Å’s); as a result, electrons tunnel between the tip and surface generating a tunneling current. A small bias voltage (less than 0.3 V) is applied between the tip and surface to precisely control this current. Piezoelectric materials (materials which expand or contract in the presence of an electric field) are then used to control the motion of the tip in space.

The two most common measurements made with an STM are the so-called spectroscopic and topographic measurements. In a spectroscopic measurement, the tunneling current (or differential conductance $dI/dV$) is measured as the bias voltage between the tip and surface is swept (while holding the tip’s spatial position fixed). In a topographic measurement, the tip’s height is measured as its position in the plane of the surface is swept (while holding the bias voltage and tunneling current fixed). A constant current is achieved by providing a feedback loop to the piezoelectric servo aligned in the axis of the tip. Furthermore, experiments have been carried out where topographic and differential conductance maps of the surface are generated simultaneously.

The differential conductance measured in STM experiments is proportional to the local density of states (LDOS) for electrons on the surface:

$$A(r; \omega) = \sum_n |\phi_n(r)|^2 \delta(\omega - \epsilon_n)$$  \hspace{1cm} (1.1)
where \( \{ \phi_n(\mathbf{r}) \} \) are the wave functions (eigenvalues) for the surface electrons.[12, 19] [The tunneling current is then proportional to an integral of the LDOS over energy.] Therefore, the physical quantity of primary interest is the LDOS. One finds that the LDOS can be computed efficiently via
\[
A(\mathbf{r}; \omega) = -(1/\pi) \text{Im}[G(\mathbf{r}, \mathbf{r}; \omega)]
\]
where
\[
G(\mathbf{r}, \mathbf{r}'; \omega)
\]
is the (retarded) Green’s function for the surface electrons.[12, 19]

In 1990, Eigler and Schweizer demonstrated that an STM could also be used to perform atomic-scale engineering; specifically, to position individual impurity atoms (or adatoms) embedded in a host material.[20] They achieved this by bringing an STM tip towards an impurity and applying a sufficiently high voltage such that the atom’s bond with the substrate was overcome. The impurity was then relocated to a region of interest.[20, 21] This atomic-scale control is exciting because it allows one to build structures not found in nature.[17, 18, 22]

1.3 The System

To proceed, it is essential to discuss the substrate on which these structures are engineered; namely, the surface of noble metals. It is also essential to discuss the bulk material below as this plays a subtle but essential role in determining the system’s electronic properties.

1.3.1 The Surface

These structures are typically fabricated on the surface of a noble metal (such as copper, silver, and gold).[17, 22] In their crystalline form, these elements form a face-centered cubic (fcc) lattice (Fig.1.4).[23] The (111) plane of this lattice is of particular interest, as the surface states resulting from this cut are orthogonal to the material’s bulk states – the wave function of a surface state decays exponentially fast into the bulk and vacuum.[12] This is important/useful, as the electrons on the surface essentially move within the plane of the surface – the surface states are isolated from the bulk states.

More precisely, electrons on the (111) surface constitute a two-dimensional electron gas (2DEG).[12, 17, 19] This means one can effectively treat these electrons as a collection of noninteracting (quasi)particles with dispersion
\[
\varepsilon_\mathbf{p} = (1/2m)\mathbf{p}^2 - E_F
\]
where \( \mathbf{p} \) is the particle’s
momentum, $m$ is its effective mass, and $E_F$ is the Fermi energy of the surface state. [Note: As written, $\varepsilon_p$ measures the energy with respect to the Fermi energy.] Being able to treat the surface as a 2DEG is advantageous, because having an isotropic dispersion (i.e. the same in all directions of momentum space) enables one to carry out calculations without considering the orientation of the lattice.[12] In this Thesis, we focus on the Cu(111) surface as it is most relevant to experiment.[17, 22] Electrons in the 2DEG of the Cu(111) surface have an effective mass of $m = 0.38m_e$ ($m_e$ is the bare electron mass) with a Fermi energy of $E_F = 450\, \text{meV}$. [17, 18]

### 1.3.2 Impurity Atoms

Introducing impurity atoms has stunning consequences – STM experiments reveal that wave patterns form around the sites of the impurities (Fig.1.5).[22] These waves are a result of electrons in the 2DEG scattering off of the impurity atoms. In treating these scattering centers theoretically, it is useful to know that the Fermi wavelength for a Cu(111) surface is $\lambda_F = 2.95\, \text{nm}$[12, 19] – the wavelength of the electrons in the 2DEG is far larger than the size of the impurity atoms themselves. Since we will be interested in the system’s low-energy (or infrared) properties, one can disregard higher orbital channels and treat the impurities simply as $s$-wave scatterers;[12, 19] namely, we treat the impurity atoms as delta function scatterers.

Of particular interest in this Thesis will be closed configurations of adatoms. When treated quantum mechanically, closed configurations lead to discrete states where the wave function
describes a standing wave (e.g. a “particle in a box”).[24, 25] In the 1990s researchers began to exploit this by using STMs to form (nearly) closed geometries with impurity atoms on a metal surface – the structures were deemed quantum corrals (QCs).[12] The electron scattering results, as revealed by STM measurements, are stunning for their intrinsic beauty but also because they provide a window from which to view the system’s wave function itself (recall Eq. 1.1).

As an example, consider the LDOS of an elliptical QC shown in Fig. 1.6. The unique wave pattern which forms from the superposition of the surface electrons’ wave functions is clearly visible in the image. Furthermore, this elliptical structure is of particular interest to us as it will be the platform for the structures/devices we will consider in subsequent Chapters.

1.3.3 The Bulk

It is not enough to consider only the electrons on the surface. It turns out that impurity atoms couple surface electrons in the 2DEG to the bulk material below. At the site of the
atom, surface electrons are absorbed into the bulk and bulk electrons tunnel to the surface – i.e. at impurity locations, surface states and bulk states are no longer orthogonal.\textsuperscript{[12]} It is through this coupling that the bulk makes its presence “felt” on the surface. Therefore, the effect of placing an impurity atom on the surface at position $r_0$ is described by the potential

$$\hat{V} = U \sum_s \psi_s^\dagger(r_0) \psi_s(r_0) + C \sum_s \left[ \psi_s^\dagger(r_0) \chi_s(r_0) + \chi_s^\dagger(r_0) \psi_s(r_0) \right]$$  \hspace{0.5cm} (1.2)

where $U$ is the strength of scattering on the surface (in the s-wave channel), $C$ is the strength of the coupling between the surface and the bulk, and $\psi_s(r)$ ($\chi_s(r)$) are electron field operators for the surface (bulk) at position $r$ with spin-$s$. \textsuperscript{[Appendix B gives a description of second quantization (as needed for this Thesis).]}

It has been shown that one achieves good quantitative agreement with experiment when impurities are treated using the \textit{black-dot approximation}.\textsuperscript{[12]} Namely, the coupling between the surface and bulk (due to the presence of the impurity atom) is so strong that other scattering processes can be ignored: $U \rightarrow 0$. Historically, the absorption of electrons into the bulk has been seen as a hindrance;\textsuperscript{[12]} however, it is precisely this effect that we exploit later when we investigate bulk materials with properties different from the surface layer.

### 1.4 Thesis Contributions and Outline

The rest of this Thesis is organized as follows:

In Chapter 2, we discuss the formalism to calculate/characterize the electronic properties of these systems; namely, we develop the scattering formalism.

In Chapter 3, we present a novel means of controlling and transmitting signals utilizing magnetic atoms. We begin by reviewing the key physics exhibited by magnetic atoms embedded in metals; namely, the Kondo effect. We then review the seminal experiments which demonstrated how this effect can be used to transmit a signal between distinct points in a QC. We review/develop the appropriate formalism to describe the physics. To conclude, we describe our work showing how this transmitted signal can be controlled using the two-impurity Kondo effect.
Chapter 1. Introduction

In Chapter 4, we present a novel means of fabricating superconducting nanostructures on the smallest scale; namely, atom-by-atom. We begin by reviewing the central properties of superconductors. We then discuss a novel mechanism to make individual atoms exhibit superconducting properties and extend the scattering formalism to allow for these atoms. Lastly, we describe our work demonstrating atomic-scale engineering of superconducting nanostructures and, in particular, precise control over the electronic properties of these structures.

Chapter 5 contains a summary and prospects for future work.

Finally, a collection of Appendices that contain details of the calculations is included.

1.5 Notes

All the calculations in this Thesis are carried out in units where $\hbar = 1$.

For normalization purposes, we put our systems in a large box of volume $V = L^d$, where $d$ is the system’s dimension] and employ periodic boundary conditions; in this case, the momentum is quantized as $p = 2\pi n/L$ where $n \in \mathbb{Z}^d$. 

Chapter 2

Scattering Formalism

The intention of this Thesis is to discuss the engineering of nanoscale systems/devices using adatoms on metal surfaces. In this Chapter, we develop a formalism to understand and, more practically, compute the (electronic) properties of these systems; namely, here we outline the scattering formalism.

2.1 Green’s Functions and the Dyson Equation

Consider a system of fermions with second quantized Hamiltonian \( \hat{H} = \sum_n E_n c_n^\dagger c_n \), where \( c_n \) annihilates a fermion of energy \( E_n \) (Appendix B). Define the Green’s function as

\[
G(r, r'; t) := -i \Theta(t) \langle \{ \psi(r; t), \psi^\dagger(r') \} \rangle
\]

(2.1)

where \( \psi(r; t) \) is the system’s field operator at position \( r \) and time \( t \), \( \langle \cdots \rangle \) denotes a thermal average, \( \{ \cdots \} \) is the anticommutator, and \( \Theta(t) \) is the Heaviside step function. The physical quantity of interest is the local density of states (LDOS) \( A(r; \omega) \), as this is what is measured in STM experiments;\[12\] explicitly,

\[
A(r; \omega) = -\frac{1}{\pi} \text{Im}[G(r, r; \omega)]
\]

(2.2)
where \( G(\mathbf{r}, \mathbf{r}'; \omega) \) \( = \int dt \ e^{i \omega t} G(\mathbf{r}, \mathbf{r}'; t) \) is the Fourier transform of Eq. 2.1. Expanding the field operators in terms of the \( \{ c_n \} \) gives

\[
G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}')}{\omega - E_n + i\delta},
\]

where \( \{ \phi_n(\mathbf{r}) \} \) are the single-body wave functions of the Hamiltonian and \( \delta(= 0^+) \) is a convergence factor. Notice that one must know the energy eigenvalues and eigenfunctions to compute the Green’s function with Eq. 2.3.

Starting with Eq. 2.1 is not always the most convenient way to proceed. Alternatively, one can make use of the resolvent operator:

\[
\hat{G} = (\omega - \hat{H} + i\delta)^{-1}
\]

where \( \hat{H} \) is the Hamiltonian, and \( \omega \) is a real scalar. [As before, \( \delta = 0^+ \).] In particular, by using the corresponding single-body operator for the second quantized Hamiltonian (also denoted by \( \hat{H} \)) and projecting \( \hat{G} \) onto position representation one obtains

\[
G(\mathbf{r}, \mathbf{r}'; \omega) = \langle \mathbf{r} | (\omega - \hat{H} + i\delta)^{-1} | \mathbf{r}' \rangle .
\]

One can show that this is an equivalent form of the Green’s function by expanding in the eigenkets of the single-body Hamiltonian, \( \{|n\} \), and letting the operator act on the energy kets. Doing this yields Eq. 2.3 where \( \phi_n(\mathbf{r}) = \langle \mathbf{r} | n \rangle \).

Our primary focus is systems containing impurity atoms; the Hamiltonian of such a system can be written as

\[
\hat{H} = \hat{H}_0 + \hat{V}
\]

where \( \hat{H}_0 \) is the Hamiltonian of the bare system (i.e. the Hamiltonian without impurities) and \( \hat{V} \) is a scattering potential arising from the impurity atoms. By making the definition \( \hat{G}_0 := (\omega - \hat{H}_0 + i\delta)^{-1} \) and using that \( (\hat{A}\hat{B})^{-1} = \hat{B}^{-1}\hat{A}^{-1} \) one obtains the Dyson equation:

\[
\hat{G} = \hat{G}_0 + \hat{G}_0\hat{V}\hat{G}.
\]
To obtain the Green’s function from the Dyson equation, consider the corresponding single-body operators for the system and project onto position representation:

\[
G(r, r'; \omega) = G_0(r, r'; \omega) + \int dr_1 dr_2 G_0(r, r_1; \omega) \langle r_1 | \hat{V} | r_2 \rangle G(r_2, r'; \omega)
\]

(2.8)

where the bare Green’s function has been defined as \(G_0(r, r'; \omega) := \langle r | \hat{G}_0 | r' \rangle\). We see that the Dyson equation enables one to determine the system’s (full) Green’s function from the bare Green’s function.

### 2.1.1 A Single Scatterer

We now apply this formalism to some example systems which are relevant to the rest of the Thesis. First, consider a two-dimensional electron gas (2DEG) with a single scattering center (an impurity atom) located at position \(r_0\). The Hamiltonian used to describe the system is \(\hat{H} = \hat{H}_0 + \hat{V}\), where \(\hat{H}_0\) is the Hamiltonian of the 2DEG and \(\hat{V}\) is the scattering potential due to the impurity. To simplify things, we take the scattering potential to be an s-wave scatterer i.e. a delta function.\(^{[12]}\) Approximating the impurity as a point scatterer is justified because the wavelength of electrons on the surfaces of interest (noble metals such as copper and gold) are far larger than the size of the impurity itself.\(^{[12]}\)

Our goal is to obtain the system’s Green’s function. To that end, consider the Hamiltonian’s corresponding single-body operator: \(\hat{H} = \hat{H}_0 + \hat{V}\) where \(\hat{H}_0[= (1/2m)\hat{p}^2 - E_F]\) is the Hamiltonian of a free-particle and \(\hat{V}[= V_0 \delta(\hat{r} - \hat{r}_0)]\) is the potential due to the impurity with \(V_0\) characterizing the scattering phase shift (see Appendix E). \[\text{Note: We are measuring energies with respect to the Fermi energy } E_F.\]

By inserting the scattering potential into Eq. 2.8 one obtains

\[
G(r, r'; \omega) = G_0(r, r'; \omega) + G_0(r, r_0; \omega)V_0 G(r_0, r'; \omega)
\]

(2.9)

where \(G_0(r, r'; \omega)\) is the free-particle Green’s function. To solve Eq. 2.9, first let \(r = r_0\). From here one can find an expression for \(G(r_0, r'; \omega)\) which can then be placed back into
Eq. 2.9 to obtain

\[ G(r, r'; \omega) = G_0(r, r'; \omega) + G_0(r, r_0; \omega) T(\omega) G_0(r_0, r'; \omega) \]  

(2.10)

where the \( T\)-matrix has been defined as

\[ T(\omega) := \frac{V_0}{1 - G_0(r_0, r_0; \omega) V_0} \]  

(2.11)

### 2.1.2 Multiple Scatterers

Next, consider a collection of (s-wave) impurity atoms in a 2DEG. Similar to the case of a single scatterer, the Hamiltonian of this system is described by \( \hat{H} = \hat{H}_0 + \hat{V} \) where \( \hat{H}_0 \) is the Hamiltonian of the 2DEG and \( \hat{V} \) is the scattering potential arising from the presence of the multiple impurities.

Again, we will use the Dyson equation to compute the Green’s function. Consider the corresponding single-body Hamiltonian: \( \hat{H} = \hat{H}_0 + \hat{V} \) where \( \hat{H}_0 \) is the Hamiltonian of a free-particle and the scattering potential is given by \( \hat{V} = V_0 \sum_i \delta(\hat{r} - \hat{r}_i) \) with \( \{\hat{r}_i\} \) representing the locations of the impurities. Proceeding in the same fashion as before, we insert this potential into the Dyson equation. Integrating over the resulting delta functions yields

\[ G(r, r'; \omega) = G_0(r, r'; \omega) + \sum_i G_0(r, r_i; \omega) V_0 G(r_i, r'; \omega). \]  

(2.12)

Introduce the following vectors:

\[ \overline{G}(r; \omega) := \begin{pmatrix} G(r_1, r; \omega) \\ G(r_2, r; \omega) \\ \vdots \end{pmatrix}, \quad \overline{G}_0(r; \omega) := \begin{pmatrix} G_0(r_1, r; \omega) \\ G_0(r_2, r; \omega) \\ \vdots \end{pmatrix}. \]  

(2.13)

Writing the Dyson equation in terms of these vectors gives

\[ G(r, r'; \omega) = G_0(r, r'; \omega) + \overline{G}_0^T(r; \omega) V_0 \overline{G}(r'; \omega). \]  

(2.14)

where we used that \( G_0(r, r'; \omega) = G_0(r', r; \omega) \) (Appendix D). In order to obtain an explicit
expression for the Green’s function, analyze the Dyson equation at \( r = r_i \). Carrying out this procedure for every impurity site and organizing the results as a matrix yields

\[
\overline{G}(r'; \omega) = \overline{G}_0(r'; \omega) + \hat{G}_0(\omega)V_0\overline{G}(r'; \omega)
\]  

(2.15)

where the matrix \( \hat{G}_0(\omega) \) has been defined as

\[
\hat{G}_0(\omega) := \begin{pmatrix}
G_0(r_1, r_1; \omega) & G_0(r_1, r_2; \omega) & \ldots \\
G_0(r_2, r_1; \omega) & G_0(r_2, r_2; \omega) & \ldots \\
\vdots & \vdots & \ddots
\end{pmatrix}.
\]  

(2.16)

One can obtain a solution for the vector of Green’s functions by solving Eq. 2.15:

\[
\overline{G}(r'; \omega) = \left[I - \hat{G}_0(\omega)V_0\right]^{-1}\overline{G}_0(r'; \omega)
\]  

(2.17)

Inserting the solution back into the Dyson equation gives an explicit expression for the Green’s function. Namely,

\[
G(r, r'; \omega) = G_0(r, r'; \omega) + \overline{G}_0^T(r; \omega)\hat{T}(\omega)\overline{G}_0(r'; \omega) \\
= G_0(r, r'; \omega) + \sum_{i,j} G_0(r, r_i; \omega)\hat{T}_{i,j}(\omega)G_0(r_j, r'; \omega)
\]  

(2.18)

where the T-matrix has been defined as

\[
\hat{T}(\omega) := V_0\left[I - \hat{G}_0(\omega)V_0\right]^{-1}.
\]  

(2.19)

From Eq. 2.10 (a single scatterer) and Eq. 2.18 (multiple scatterers) it is clear that the Green’s function is constructed using the free-particle Green’s function. Computing the free-particle Green’s function in two-dimensions (or the Green’s function of a 2DEG) yields (Appendix D)

\[
G_0(r, r'; \omega) = \begin{cases}
-i(\pi \rho_0)H_0^{(1)}(k|r - r'|) & , r \neq r' \\
-i(\pi \rho_0) + \rho_0 \ln \left(\frac{E_F + \omega}{D - \omega}\right) & , r = r'
\end{cases}
\]  

(2.20)

where \( k = \sqrt{2m(E_F + \omega)} \), \( \rho_0 \) is the electron density of states, \( D \) is an ultraviolet cutoff,
and $H_0^{(1)}(x)$ is a Hankel function.[26]

2.2 Quantum Corrals

The formalism discussed so far is suitable to describe the results of quantum corral (QC) experiments.[12] Similar to what has been realized experimentally, we consider the case of 40 impurity atoms arranged in an ellipse, $(x/a)^2 + (y/b)^2 = 1$, where $a/b = 1.5$ with $a = 8.583$[nm] on a Cu(111) surface – $E_F = 0.45$[eV] and $m = 0.38m_e$.[17, 18]

We apply Eq. 2.18 to obtain the Green’s function of the QC. To do this, as discussed in Chapter 1, we treat the s-wave scattering phase shift in the black-dot approximation.[12] By computing the LDOS from the Green’s function via Eq. 2.2, we obtain the spatial map in Fig. 2.1. In agreement with experiment, our calculations produce distinct standing wave patterns inside the walls of the corral.[17, 27]

![Figure 2.1: The local density of states of an elliptical quantum corral.](image-url)
Chapter 3

Signal Control and Transmission
Using Magnetic Atoms

Seminal experiments have shown how a magnetic impurity can be used to transmit a signal between distinct points in a quantum corral: the Kondo mirage.[17] In this Thesis, we are interested in the prospect of controlling the transmitted signal.

In this Chapter, we review key properties/results of the Kondo problem; we then discuss a formalism to treat the Kondo model and, in particular, its infrared properties. We also review key properties of the mirage experiment. Finally, we discuss how two magnetic impurities in a quantum corral can be used to control transmitted signals.

3.1 The Kondo Problem

3.1.1 Background

The Kondo problem deals with a single magnetic impurity in a metal host. Investigations of this problem began by trying to understand the resistivity minimum displayed by dilute magnetic alloys[28] – as the temperature is lowered, one finds a metal’s resistivity decreases because electron-phonon scattering becomes less of a burden;[28–30] however, in the 1930s experiments revealed that doping a metal with magnetic impurities introduces a minimum
in the resistivity as a function of temperature (Fig. 3.1).[28]

![Figure 3.1: The resistivity of a dilute magnetic alloy, R vs. T. As T is lowered, R decreases; after passing a critical value, R rises again. Shown with a dotted black line is the resistivity of a metal without magnetic impurities; in this case, R vs. T is monotonic.](image)

The first satisfactory explanation of the resistivity minimum was given by Jun Kondo in 1964.[31] Kondo considered the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}$$

(3.1)

where $\hat{H}_0$ is the Hamiltonian of the metal and $\hat{V}$ is the potential that arises from the coupling of the spin degree of freedom of the magnetic atom (MA) to those of the metal. Explicitly,

$$\hat{H}_0 = \sum_{\mathbf{p},s} \varepsilon_{\mathbf{p}} c_{\mathbf{p},s}^\dagger c_{\mathbf{p},s}$$

(3.2)

where $c_{\mathbf{p},s}$ destroys an electron of momentum $\mathbf{p}$ and spin-$s$ in the metal and the single-particle dispersion is $\varepsilon_{\mathbf{p}} = \mathbf{p}^2/2m - E_F$. The potential was taken as

$$\hat{V} = J \vec{\tau} \cdot \mathbf{S}(\mathbf{r}_0)$$

(3.3)

where $J$ is a (positive) coupling constant, $\vec{\tau}$ is the MA’s spin operator, and $\mathbf{S}(\mathbf{r}_0)$ is the spin density operator of the metal (evaluated at the location of the MA): $\mathbf{S}(\mathbf{r}) = (1/2) \sum_{s,s'} \psi_{s}^\dagger(\mathbf{r}) \vec{\sigma}_{s,s'} \psi_{s'}(\mathbf{r})$ where $\psi_{s}(\mathbf{r})$ is the electron field operator of the metal at position $\mathbf{r}$ with spin-$s$ and $\{\sigma^\mu\}$ are Pauli matrices in spin space (Appendix F). Using perturbation theory, Kondo computed the resistivity $R(T)$ and obtained

$$R(T) = R_0 + aT^5 - bJ^3 \ln(k_B T/D)$$

(3.4)
where the first term is due to scattering from inert impurities, the second term is the phonon
contribution, and the final term is due to scattering from the MAs. [In Eq. 3.4, $D$ is the
bandwidth of the conduction electrons and $a$ and $b$ are (positive) constants.]

While Kondo’s calculation was able to explain the resistivity minimum (through the log-
arithmic term arising from the scattering off of magnetic impurities), it also signaled that
this (seemingly) simple Hamiltonian (Eq. 3.1) has highly nontrivial physics buried in it –
the logarithm diverges as $T \to 0$; therefore, perturbation theory breaks down and the
ground state is a strongly correlated state. After much struggle, it came to be understood
this strongly correlated state consists of a cloud of conduction electrons locked in a singlet
with the impurity.[28] The state manifests itself via a resonance in the density of states at
(or near) the Fermi energy, known as the Kondo resonance (KR).

![Figure 3.2: The density of states of a magnetic impurity in a metal host, $\rho_{\text{imp}}$ vs. $\omega$. Due to the interaction between conduction electrons and the magnetic atom, one observes a resonance in the impurity density of states at the Fermi energy.](image)

3.1.2 The Infrared Fixed Point

We will be interested in utilizing the strongly correlated ground state of the Kondo Hamil-
tonian for signal transmission; hence, we need to develop an approach appropriate for low-
energies. To this end, we employ a fermionic representation for the MA’s spin operator[28]

$$\bar{\tau} = \frac{1}{2} \sum_{s,s'} f_s^\dagger \bar{\sigma}_{s,s'} f_{s'}$$

(3.5)

where $f_s$ is a (fermionic) annihilation operator for the impurity spin. [As before, $\{\sigma^\mu\}$
are Pauli matrices.] In writing the spin operator in terms of fermion operators, we have
enlarged the Hilbert space. To obtain a proper description of the spin, we must project onto
the spin’s physical Hilbert space; namely, there is always a single (spin-up or spin-down) fermion on the impurity site. We achieve this by imposing the constraint

$$\sum_s f_s^\dagger f_s = 1.$$  \hspace{1cm} (3.6)

Using Eq. 3.5, one can show the spin-spin coupling can be written as (Appendix F)

$$\vec{\tau} \cdot \mathbf{S}(\mathbf{r}_0) = -\frac{1}{2} \sum_{s,s'} [\psi_s^\dagger(\mathbf{r}_0) f_s] [f_{s'}^\dagger \psi_{s'}(\mathbf{r}_0)] + \text{const.}$$  \hspace{1cm} (3.7)

By inserting Eq. 3.7 into the Hamiltonian one obtains

$$\hat{H} = \sum_{\mathbf{p},s} \varepsilon_{\mathbf{p}} c_{\mathbf{p},s}^\dagger c_{\mathbf{p},s} - J \sum_{s,s'} [\psi_s^\dagger(\mathbf{r}_0) f_s] [f_{s'}^\dagger \psi_{s'}(\mathbf{r}_0)]$$  \hspace{1cm} (3.8)

where the unimportant constant value has been removed for convenience (i.e. we have shifted our energy scale); then, to enforce the constraint on the Hilbert space (Eq. 3.6), we employ a Lagrange multiplier, $\lambda$ – we arrive at the effective Hamiltonian

$$\hat{H}_{\text{eff}} = \sum_{\mathbf{p},s} \varepsilon_{\mathbf{p}} c_{\mathbf{p},s}^\dagger c_{\mathbf{p},s} - J \sum_{s,s'} [\psi_s^\dagger(\mathbf{r}_0) f_s] [f_{s'}^\dagger \psi_{s'}(\mathbf{r}_0)] + \lambda \left( \sum_s f_s^\dagger f_s - 1 \right).$$  \hspace{1cm} (3.9)

To proceed, we use that our interests are solely in the infrared properties of the system. Guided by the physics, we analyze Eq. 3.9 using mean-field theory. Specifically, using that the infrared fixed point of the Kondo model is such that a cloud of conduction electrons is locked in a singlet with the impurity spin, we approximate

$$[\psi_s^\dagger(\mathbf{r}_0) f_s] [f_{s'}^\dagger \psi_{s'}(\mathbf{r}_0)] \rightarrow \langle \psi_s^\dagger(\mathbf{r}_0) f_s \rangle f_s^\dagger \psi_{s'}(\mathbf{r}_0) + \psi_s^\dagger(\mathbf{r}_0) f_s \langle f_{s'}^\dagger \psi_{s'}(\mathbf{r}_0) \rangle.$$  \hspace{1cm} (3.10)

Furthermore, we treat the constraint on average – we demand that $\partial_\lambda \langle \hat{H} \rangle = 0$ where $\langle \cdots \rangle$ represents a thermal average. Doing so yields

$$\sum_s \langle f_s^\dagger f_s \rangle = 1.$$  \hspace{1cm} (3.11)
By inserting Eq. 3.10 into Eq. 3.9 and removing the unimportant constants, one obtains the mean-field Hamiltonian:

\[
\hat{H}_{\text{MF}} = \sum_{p,s} \varepsilon_p c_{p,s}^\dagger c_{p,s} + \lambda \sum_s f_s^\dagger f_s - \chi \sum_s f_s^\dagger \psi_s(r_0) - \chi^* \sum_s \psi^\dagger_s(r_0) f_s
\]  

(3.12)

where we have defined

\[
\chi := \frac{J}{2} \sum_s \langle \psi^\dagger_s(r_0) f_s \rangle .
\]

(3.13)

In treating the Hamiltonian, we introduced the quantities \( \lambda \) and \( \chi \); these are determined self-consistently via Eqs. 3.11 and 3.13. Explicitly, one obtains

\[
\frac{\pi}{2} = \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\Gamma}{(\omega - \lambda)^2 + \Gamma^2}
\]

(3.14a)

\[
-\frac{1}{J \rho_0} = \int_{-\infty}^{\infty} d\omega f(\omega) \frac{(\omega - \lambda)}{(\omega - \lambda)^2 + \Gamma^2}
\]

(3.14b)

where \( \Gamma = \pi \rho_o \chi^2 \) and \( f(\omega) \) is the Fermi function. [These calculations are detailed in Appendix G.]

In general, Eqs. 3.14a and 3.14b must be solved numerically; however, they can be solved analytically at zero temperature. In this case, \( f(\omega) \) becomes a step function. Carrying out the integral in Eq. 3.14a yields \( \lambda = 0 \) and from Eq. 3.14b one finds \( \Gamma = T_K \) where we have introduced the Kondo temperature:[28]

\[
T_K := De^{-1/J \rho_0}
\]

(3.15)

where \( D \) is an ultraviolet cutoff. \( T_K \) represents the dynamically generated energy scale in the Kondo problem – physically, it describes the size of the cloud of electrons which screen the impurity’s spin; it governs the width of the KR. [Note the structure of the impurity atom’s Green’s function in Appendix G.]
3.2 The Kondo Mirage

Seminal experiments performed by Manoharan, Lutz, and Eigler found that introducing a MA into a quantum corral (QC) built on a surface containing a two-dimensional electron gas (2DEG) can remarkably change the system’s wave function.\[17\] By placing a cobalt atom at one focus of an elliptical QC they showed, using scanning tunneling microscope (STM) differential conductance measurements, that a “mirage” appears at the other focus of the ellipse (Fig. 3.4) – the information about the MA was transmitted from one focus to another. Notice that, in contrast to conventional technology where information is carried by currents (a consequence of the wave function), here the medium carrying the information is the wave function (of the QC) itself.

To describe the system, we consider the Kondo Hamiltonian derived above (Eq. 3.12); however, the eigenstates of the bare Hamiltonian will no longer be plane-waves, but they will be eigenstates of the QC.\[1\] Namely,

\[
\hat{H} = \sum_{n,s} \varepsilon_n c_{n,s}^\dagger c_{n,s} + \lambda \sum_s f_s^\dagger f_s - \chi \sum_s f_s^\dagger \psi_s(r_0) - \chi^* \sum_s \psi_s^\dagger(r_0)f_s 
\]

(3.16)

where \(\{c_{n,s}\}\) are annihilation operators for the QC (with eigenvalues \(\{\varepsilon_n\}\)), \(\psi_s(r_0)\) is the field operator for an electron of spin-\(s\) at the position of the MA, and \(\{f_s\}\) are annihilation operators for the impurity spin. As before, the constants \(\lambda\) and \(\chi\) are determined self-consistently via Eq. 3.11 and Eq. 3.13.

Figure 3.3: The system under consideration – a magnetic atom in a quantum corral.

\[\text{\footnotesize\cite[Specifically, they will be the eigenstates of the 2DEG in the presence of the s-wave scatterers comprising the wall of the QC.}]\]
Our goal is to compute the Green’s function for the conduction electrons:

\[ G(r, r'; t) = -i \Theta(t) \langle \{ \psi_s(r; t), \psi_s^\dagger(r') \} \rangle . \]  \hspace{1cm} (3.17)

By carrying out the calculation, one obtains (Appendix G)

\[ G(r, r'; \omega) = G_0(r, r'; \omega) + G_0(r, r_0; \omega) T(\omega) G_0(r_0, r'; \omega) . \]  \hspace{1cm} (3.18)

In Eq. 3.18, \( G_0(r, r'; \omega) \) is the Green’s function of the QC (as derived in Chapter 2); furthermore, the influence of the MA is described by the T-matrix:

\[ T(\omega) = |\chi|^2 G(\omega) \]  \hspace{1cm} (3.19)

with \( G(\omega) = -i \Theta(t) \langle \{ f_s(t), f_s^\dagger \} \rangle (\omega) \) being the impurity atom’s Green’s function.

\[ \text{Figure 3.4: The Kondo mirage. A magnetic impurity sits at the left focus of an elliptical quantum corral. By subtracting off the local density of states of the corral with no impurity present one sees the presence of the magnetic atom (in the local density of states) around the filled focus; at the unfilled focus (on the right) a signal is also visible – the magnetic atom's existence has been broadcast to the other end of the corral.} \]

The quantity measured experimentally is the local density of states (LDOS), Eq. 2.2. [Recall that the LDOS is proportional to the differential conductance measured by an STM.[12]]

Similar to what has been realized experimentally, we consider the case of 40 impurity
atoms arranged in an ellipse, \((x/a)^2 + (y/b)^2 = 1\), where \(a/b = 1.5\) with \(a = 8.583\text{[nm]}\) on a Cu(111) surface – \(E_F = 0.45\text{[eV]}\) and \(m = 0.38m_e\).\[17, 18]\ We place the MA at one foci of the elliptical QC, \(f = \sqrt{a^2 - b^2}\).

Computing the LDOS using Eq. 3.18 gives the results in Figure 3.5. In the density plot, the LDOS of the QC has been subtracted off to display the effect the MA has on the electronic properties of the system. As done in [17], a line of constant slope has been subtracted off the LDOS data at both the filled and mirage focus. One readily verifies the agreement between our calculation and the experimental data.\[17\] At the site of the MA (the filled focus), a prominent KR is observed in the electron density of states; this signal is the experimental signature of Kondo physics.\[17\] Furthermore, a clear KR is observed at the unfilled focus (i.e. the mirage signal) in both spatial and energy sweeps of the LDOS. These results confirm that the theory we developed in the previous sections is suitable to describe the physics contained in the mirage experiment.

\textbf{Figure 3.5:} The mirage signal. A single magnetic impurity sits at the left focus of a quantum corral. Top image: A spatial plot of the local density of states evaluated at the Fermi energy (with the bare density of states subtracted off) showing the Kondo mirage. Bottom image: Energy sweep of the local density of states \(A(r;\omega)\) at the filled focus (left) and unfilled focus (right). At the filled focus, one sees the characteristic Kondo resonance of a magnetic impurity; a faithful representation of this signal is produced at the unfilled (mirage) focus. [Note: a line of constant slope has been subtracted off the bottom images.]
3.3 Signal Control and Transmission

The mirage experiment is particularly interesting because it exploits the electron’s spin degree of freedom. There is currently interest in exploring technologies that take advantage of this intrinsic electron property (the field of spintronics).[32–35] The mirage experiment showed how the KR signal could be transmitted between spatially distinct points via the eigenstates of the QC, but here we ask the question: can we control this signal?

To this end, we consider the system shown in Fig. 3.6 – an elliptical QC with two MAs: the first MA is located at one focus of the QC with the other atom free to be moved about within the walls of the corral. We describe the system by the two-impurity Kondo Hamiltonian

\[
\hat{H} = \hat{H}_0 + \hat{V}
\]

(3.20)

where \( \hat{H}_0 = \sum_{n,s} \varepsilon_n c_{n,s}^\dagger c_{n,s} \) is the Hamiltonian of the bare system, and \( \hat{V} \) describes the coupling of the MAs to the 2DEG and to each other. The interaction between the MAs is taken into account by including the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction in the potential.[29, 30, 36] Specifically,

\[
\hat{V} = J_1 \vec{\tau}_1 \cdot \vec{S}(\vec{r}_1) + J_2 \vec{\tau}_2 \cdot \vec{S}(\vec{r}_2) + K \vec{\tau}_1 \cdot \vec{\tau}_2
\]

(3.21)

where \( \vec{\tau}_i \) is the spin operator for MA \( i \) (located at position \( \vec{r}_i \)), \( \vec{S}(\vec{r}_i) = (1/2) \sum_{s,s'} \psi_{s}^\dagger(\vec{r}_i) \sigma_{s,s'} \psi_{s'}(\vec{r}_i) \) is the spin density operator of the 2DEG at \( \vec{r}_i \), and \( J_1, J_2, \) and \( K \) are the couplings. [K is the
RKKY interaction; namely, the effective interaction between the MAs via the 2DEG.\[36\]

In what follows, we will focus on the case of antiferromagnetic interimpurity interaction, \(K > 0\).

**Figure 3.7:** The system under consideration – two magnetic atoms in a quantum corral.

In the two impurity Kondo problem, there are two important energy scales: the single-impurity Kondo temperature \(T_K\) (Eq. 3.15) and the interimpurity interaction \(K\). For \(K \ll T_K\), the interimpurity interaction is unimportant and the system behaves as two independent impurities. For \(K \gg T_K\), the Kondo effect will be inhibited as the two impurities will lock into a singlet. In general, there is competition/interplay between the Kondo effect and the interimpurity interaction.

Motivated by this physics, we treat Eq. 3.21 by employing a fermionic representation for each MA’s spin operator:\[28\]

\[
\tau_i = \frac{1}{2} \sum_{s,s'} f^\dagger_{i,s} \sigma_{s,s'} f_{i,s'}
\]

(3.22)

where, as before, we have a constraint on the Hilbert space \(\sum_s f^\dagger_{i,s} f_{i,s} = 1\). Then, the coupling between spin operators can be written as (Appendix F)

\[
\tau_i \cdot \mathbf{S}(r_i) = -\frac{1}{2} \sum_{s,s'} [\psi^\dagger_{s,s'}(r_i) f_{i,s} f^\dagger_{i,s'} \psi_{s'}(r_i)] + \text{const.}
\]

(3.23a)

\[
\tau_1 \cdot \tau_2 = -\frac{1}{2} \sum_{s,s'} [f^\dagger_{2,s} f_{1,s} f^\dagger_{1,s'} f_{2,s'}] + \text{const.}
\]

(3.23b)

Guided by the physics, we treat the spin-spin couplings in mean-field theory. We handle the constraints placed on the Hilbert space using Lagrange multipliers \(\{\lambda_i\}\) and treat the constraints on average (as in the single-impurity Kondo model). Doing this leads to the
effective Hamiltonian

\[
\hat{H} = \sum_{n,s} \varepsilon_n c_{n,s}^\dagger c_{n,s} + \sum_{i=1}^{2} \left[ \lambda_i \sum_s f_{i,s}^\dagger f_{i,s} - \chi_i \sum_s \psi_s^\dagger(\mathbf{r}_i) \psi_s - \chi_i^* \sum_s \psi_s^\dagger(\mathbf{r}_i) f_{i,s} \right]
- \Phi \sum_s f_{1,s}^\dagger f_{2,s} - \Phi^* \sum_s f_{2,s}^\dagger f_{1,s}
\]

(3.24)

where the parameters \(\{\chi_i, \Phi, \lambda_i\}\) are determined (self-consistently) by

\[
\chi_i := \frac{J_i}{2} \sum_s \langle \psi_s^\dagger(\mathbf{r}_i) f_{i,s} \rangle \quad (3.25a)
\]

\[
\Phi := \frac{K}{2} \sum_s \langle f_{2,s}^\dagger f_{1,s} \rangle \quad (3.25b)
\]

\[
\sum_s \langle f_{i,s}^\dagger f_{i,s} \rangle = 1 \quad (3.25c)
\]

The physical quantity of interest is once again the LDOS: \(A(\mathbf{r}; \omega) = -(1/\pi) \text{Im}[G(\mathbf{r}, \mathbf{r}; \omega)]\) where \(G(\mathbf{r}, \mathbf{r}; \omega)\) is the Fourier transform of the conduction electrons’ Green’s function (Eq. 3.17).\[12\] Computing the Green’s function yields (Appendix G)

\[
G(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}, \mathbf{r}'; \omega) + \sum_{i,j=1}^{2} G_0(\mathbf{r}, \mathbf{r}_i; \omega) \hat{T}_{i,j}(\omega) G_0(\mathbf{r}_j, \mathbf{r}'; \omega) \quad (3.26)
\]

where \(G_0(\mathbf{r}, \mathbf{r}'; \omega)\) is the Green’s function of the QC (as derived in Chapter 2), \(\mathbf{r}_i\) is the position of MA \(i\), and the T-matrix is \(\hat{T}_{i,j}(\omega) = [-i\Theta(t) \langle \{f_{i,s}(t), f_{j,s}^\dagger(t)\} \rangle(\omega)] \chi_i^* \chi_j\).

Using the same structural and surface parameters as in the previous section (the case of a single MA in a QC), we introduce the second MA into the Green’s function via Eq. 3.26. The LDOS for different distances between the MAs is shown in Fig. 3.8. In the density plot, the LDOS of the QC along with the off-focus MA is subtracted from the total electron LDOS to emphasize the change in the mirage signal due to interference caused by the off-focus MA. Also, as done previously, a line of constant slope has been subtracted off the LDOS data at the filled and mirage focus.

From the spatial (energy) sweep of the LDOS shown in the density (mirage) plot, it is clear that the KR at the mirage focus can persist even in the presence of a second MA; thus, the superposition of many-body states due to each MA can coherently interfere. Remarkably, one finds that by varying the position of the off-focus MA, one can tune the KR signal
FIGURE 3.8: Signal control and transmission using magnetic atoms. Two magnetic atoms sit inside a quantum corral with one of the impurities located at the left focus of the corral. Top image: A spatial plot of the local density of states evaluated at the Fermi energy (with the density of states of the quantum corral and off-focus magnetic atom subtracted off). In this image one sees that the corral’s wave function has been modified by the presence of the second magnetic impurity (see Fig. 3.5); however, the Kondo mirage still persists. Bottom image: Energy sweep of the local density of states \( A(\mathbf{r}; \omega) \) at the filled focus (left) and unfilled focus (right) for various position configurations. While doing little to the filled focus, small translations of the “free” magnetic atom greatly change the signal observed at the mirage focus. [Note: a line of constant slope has been subtracted off the bottom images.]

from an anti-resonance (black curve) to a resonance (red curve). The other coloured lines show the evolution of this signal as the off-focus MA is moved from a distance of 6.69[\text{nm}] (black curve) to 0.96[\text{nm}] (red curve) away from the filled focus MA. At the filled focus, the LDOS changes very little as the off-focus MA is relocated; however, the signal changes drastically at the mirage focus. Hence, the two MA QC device can be thought of as a signal modulator\[37\] – the original KR signal at the mirage focus (due to the filled focus MA) is modified or \emph{modulated} by translations of the off-focus MA.
Chapter 4

Atomic-Scale Engineering of Superconducting Nanostructures

We now consider engineering superconducting nanostructures atom-by-atom. Our system is a metal film deposited on top of a bulk superconductor. As we will see in the ensuing discussion, superconductivity is induced in the bulk states of the film via the proximity effect, but not the surface states – a two-dimensional electron gas persists on the surface. However, an impurity atom on the surface strongly couples the surface state to the bulk states.[12] This process induces superconductivity in the region of the impurity, making the atom behave as a superconducting impurity.

In this Chapter, we review key properties and features of superconducting systems and introduce the concept of superconducting atoms; we then extend the scattering formalism to treat superconducting impurities. Finally, we discuss the engineering of superconducting nanostructures and, in particular, display precise control over Andreev bound states.
4.1 Superconductivity

4.1.1 Background

When certain materials are cooled down below some critical temperature, $T_c$, they transition into the remarkable superconducting (SCing) state of matter.[38] A material in this phase has zero electrical resistance or infinite conductance – i.e. the material superconducts. Besides electrical currents flowing unimpeded inside a SC, these materials also expel external magnetic fields up to a small length called the penetration depth.[39] Namely, the bulk of a SC is perfectly diamagnetic – a characteristic feature known as the Meissner effect$^1$.\[38, 40\] Fig. 4.1 shows the change in resistivity from the normal to SCing region as the temperature is lowered as well as the Meissner effect inside a SC slab of length $L$.

![Figure 4.1: Defining properties of superconductors. Left image: The resistivity of a superconductor, $R$ vs. $T$ – the resistivity is zero in the superconducting state (below the critical temperature $T_c$). Right image: The Meissner effect – when immersed in a weak magnetic field $B_0$, a superconductor expels the field in its bulk.]

An acceptable microscopic theory of superconductivity did not emerge for nearly 50 years from its discovery in 1911 by Onnes\[41, 42\] to the theory developed by Bardeen, Cooper, and Schrieffer (BCS) in 1957.\[43\] As such, in this intermediate period many physicists tried and failed to explain the phenomenon of superconductivity$^2$.\[42\] However, prior to the BCS theory, powerful phenomenological approaches emerged that could reproduce essential features of superconductors, namely the London and Ginzburg-Landau theories.\[39, 44\]

$^1$Note that the Meissner effect is different from Lenz’s law: the Meissner effect persists even in equilibrium, whereas Lenz’s law is a dynamical effect only.

$^2$As an example, Nobel Prize winning physicist Richard Feynman spent much of the 1950s trying to explain superconductivity to no success.\[42\]
To develop a meaningful microscopic theory of superconductivity it is essential to determine the operative physics. Namely, one must determine the essential interactions that account for the features of a SC, but also what interactions can be safely disregarded in the Hamiltonian. Several important discoveries/observations were made in the years leading up to 1957 that were crucial in making these choices.

First was the experimental discovery of the \textit{Isotope effect}, where it was found that the superconducting critical temperature (from the normal state to the SC state) was inversely proportional to the mass of ions in the underlying lattice: $T_c \propto \frac{1}{\sqrt{M}}$.\cite{45, 46} This result hinted that it would be necessary to consider interactions between conduction electrons and phonon excitations in the vibrating lattice. This coupling was first explored by Herbert Fröhlich\textsuperscript{3} in 1950\cite{47} as well as Bardeen and Pines in 1955.\cite{48}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{An attractive interaction between electrons. An illustration of how two electrons elude the repulsive Coulomb interaction via the lattice. Top image: The outgoing electron (on the left) creates a phonon. Bottom image: The incoming electron “feels” an attractive interaction \textit{at a later time} due to the phonon.}
\end{figure}

It was determined that in certain systems, mediated by lattice vibrations, electrons are able to evade the repulsive Coulomb interaction.\cite{39} The essence of this interaction is shown in Fig. 4.2: an electron in the Fermi sea attracts nearby positively charged ions in the lattice; then, the resulting phonon excitation attracts another conduction electron. The net result is that in such materials one can integrate out the Coulomb and electron-phonon interactions replacing them with an effective \textit{attractive} electron-electron interaction.\cite{49}

The final key insight came from the \textit{Cooper problem}. In 1956, Leon Cooper considered the problem of two electrons interacting through an attractive interaction above a filled

\textsuperscript{3}Fröhlich's work actually preceded the experimental discover of the isotope effect; however, he was unaware that he had predicted it.\cite{42}
noninteracting Fermi sea.[50] The electrons of momentum $p_1$ and $p_2$ (Fig. 4.3) interact with the Fermi sea only through the Pauli principle; i.e. only states with $E > E_F$ are available to the two electrons.

By considering the case of a spin-singlet with zero center-of-mass momentum one can show that the energy of the electron pair becomes $E = 2E_F - 2\Delta$ where $\Delta > 0$. Therefore, two particles of opposite momentum and spin interacting near a filled Fermi surface will form a bound state for an arbitrarily weak attractive interaction, referred to as a Cooper pair (Fig. 4.4). Therefore, the Fermi sea is unstable – a collection of electrons interacting through an arbitrarily weak attractive interaction will form (energetically favourable) Cooper pairs; this results in an energy gap between the ground state and the excited states.

Equipped with these insights (affording a mechanism to produce the SCing state), BCS developed a successful microscopic theory of superconductivity in 1957.[43] Consequently, they were awarded the Nobel prize in 1972.[51]

In Appendix C, we review key elements of the theory of superconductivity.
4.1.2 Superconducting Atoms

The defining traits of SCs (perfect conductance and diamagnetism) lend themselves to a myriad of technological applications: SCing wires in power lines, strong magnetic fields for magnetic levitation, sensitive magnetometers, and more.\[52–57\] SCing structures built on the nanoscale – SCing nanostructures – further open up the potential for unique device applications.\[58–61\]

In particular, there is interest in superconductivity on the atomic scale with experiments showing the state exists in atomically thin films,\[62, 63\] small chains of molecules,\[64\] and isolated nanoparticles.\[65\] Such SCing nanostructures could be used to replace the ordinary conductors needed to fabricate interconnect wires in electronics.\[64\] Thus, a fundamental question arises: is there a limit to the number of atoms required to produce the many-body SCing state? It turns out the answer is yes – a material ceases to superconduct below a certain size, namely when the system’s level spacing becomes comparable to the (bulk) superconducting gap.\[65–67\] Here, we demonstrate a novel mechanism which allows one to circumvent this limit, enabling single atoms to exhibit superconducting properties; we utilize this mechanism to create SCing nanostructures with a bottom-up approach.

An important, but subtle, feature of superconductivity and hence SCing nanostructures is the proximity effect.\[68\] This effect occurs when a SC is placed in good electrical contact with a normal material; specifically, Cooper pairs tunnel from the SC to the normal material inducing superconductivity.\[68, 69\] The induced SCing state only persists so far into the bulk of the normal material before it is lost and the sample retains its standard properties. Only recently have the microscopic principles behind this effect been explored in detail.\[69, 70\]

As a result, one can consider the setup shown in Fig. 4.5 – a thin metal layer is deposited on top of a bulk SC. For concreteness consider a Cu(111) film deposited on a SCing crystal, as this surface harbours a two-dimensional electron gas (2DEG). Because of the proximity effect, superconductivity will be induced in the bulk of the film, but not on the surface.\[Recall, surface electrons in Cu(111) are orthogonal to bulk electrons.\] Furthermore, recall that an impurity atom on the surface strongly couples the surface and bulk states.\[12\] Remarkably, this means an impurity can induce superconductivity at a specific location on the surface – one can create a superconducting impurity.
The effect of placing an impurity atom in this system will again be described by Eq. 1.2.
Written explicitly in terms of Nambu spinors, one has
\[
\hat{V} = U \Psi_S^\dagger(r_0) \tau^3 \Psi_S(r_0) + C \left[ \Psi_S^\dagger(r_0) \tau^3 \Psi_B(r_0) + \Psi_B^\dagger(r_0) \tau^3 \Psi_S(r_0) \right]
\] (4.1)

where \( \Psi_S(r_0) \) (\( \Psi_B(r_0) \)) is the Nambu spinor for the surface (bulk) at the location of the impurity, and \( \tau^\mu \) are Pauli matrices (in Nambu space).

4.2 Scattering Formalism: Superconducting Impurities

We start by considering a single SCing impurity on the metal surface at position \( r_0 \). As discussed in Appendix E, an inert scatterer gives rise to a “scattering potential” of the form
\[
\hat{V} = V_0(\omega) \delta(\hat{r} - r_0)
\]
where \( V_0(\omega) = \frac{1}{\pi \rho_0} \left( \begin{array}{cc} Q & D \\ D & Q \end{array} \right) \) (4.2)

with \( \rho_0 \) being the surface electron density of states and
\[
Q = C \frac{-(\omega + i\Gamma)}{\sqrt{\Delta^2 - (\omega + i\Gamma)^2}}
\]
and
\[
D = C \frac{-\Delta}{\sqrt{\Delta^2 - (\omega + i\Gamma)^2}}.
\]

This potential is characterized by a superconducting energy gap \( \Delta \) and a broadening \( \Gamma \) (Appendix C) with dimensionless parameter \( C \) (Appendix E).
The Green’s function for this system is obtained from the Dyson equation:

\[
G(\mathbf{r},\mathbf{r}';\omega) = G_0(\mathbf{r},\mathbf{r}';\omega) + G_0(\mathbf{r},\mathbf{r}_0;\omega)V_0(\omega)G(\mathbf{r}_0,\mathbf{r}';\omega)
\] (4.4)

where \(G_0(\mathbf{r},\mathbf{r}';\omega)\) is the bare Green’s function of the 2DEG. [Note: for a SCing system, the Green’s function is a 2x2 matrix (Appendix C).] To solve Eq. 4.4, first let \(\mathbf{r} = \mathbf{r}_0\). One can then find an expression for \(G(\mathbf{r}_0,\mathbf{r}';\omega)\) which can be placed back into Eq. 4.4 to obtain

\[
G(\mathbf{r},\mathbf{r}';\omega) = G_0(\mathbf{r},\mathbf{r}';\omega) + G_0(\mathbf{r},\mathbf{r}_0;\omega)\hat{T}(\omega)G_0(\mathbf{r}_0,\mathbf{r}';\omega)
\] (4.5)

where the T-matrix has been defined as

\[
\hat{T}(\omega) := V_0(\omega)[I - G_0(\mathbf{r}_0,\mathbf{r}_0;\omega)V_0(\omega)]^{-1}.
\] (4.6)

To proceed, it is useful to know that the bare Green’s function of a 2DEG is (Appendix D)

\[
G_0(\mathbf{r},\mathbf{r}';\omega) = \begin{pmatrix} G_{11}^0(\mathbf{r},\mathbf{r}';\omega) & 0 \\ 0 & G_{22}^0(\mathbf{r},\mathbf{r}';\omega) \end{pmatrix}.
\] (4.7)

The elements of the bare Green’s function are

\[
G_{11}^0(\mathbf{r},\mathbf{r}';\omega) = \begin{cases} -i(\pi \rho_0)H_0^{(1)}(k_+|\mathbf{r} - \mathbf{r}'|), & \mathbf{r} \neq \mathbf{r}' \\ -i(\pi \rho_0) + \rho_0 \ln \left( \frac{E_F + \omega}{D - \omega} \right), & \mathbf{r} = \mathbf{r}' \end{cases} \tag{4.8a}
\]

\[
G_{22}^0(\mathbf{r},\mathbf{r}';\omega) = \begin{cases} -i(\pi \rho_0)H_0^{(2)}(k_-|\mathbf{r} - \mathbf{r}'|), & \mathbf{r} \neq \mathbf{r}' \\ -i(\pi \rho_0) - \rho_0 \ln \left( \frac{E_F - \omega}{D + \omega} \right), & \mathbf{r} = \mathbf{r}' \end{cases} \tag{4.8b}
\]

where \(k^2_\pm = 2m(E_F \pm \omega)\), \(\rho_0\) is the 2D electron density of states, \(D\) is an ultraviolet cutoff, and \(H_0^{(i)}\) is a Hankel function.[26]

Now, consider a collection of SCing impurities on the surface of the thin metal film. The Hamiltonian of the system is \(\hat{H} = \hat{H}_0 + \hat{V}\) where \(\hat{H}_0\) is the Hamiltonian of the system in the absence of the the SC impurities (i.e. a 2DEG) and \(\hat{V}\) is the “scattering potential” arising from the coupling of the impurity atoms to the bulk SC as a result of the proximity effect. Namely, the single-body operator is \(\hat{V} = V_0(\omega)\sum_i \delta(\mathbf{r} - \mathbf{r}_i)\) where \(V_0(\omega)\) is given by Eq. 4.2 and \(\{\mathbf{r}_i\}\) represent the locations of the SC impurities.
The Green’s function is obtained from the Dyson equation (Eq. 2.8). Integrating over the delta functions gives

\[ G(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}, \mathbf{r}'; \omega) + \sum_i G_0(\mathbf{r}, \mathbf{r}_i; \omega) V_0(\omega) G(\mathbf{r}_i, \mathbf{r}'; \omega) \]  

(4.9)

where \( G_0(\mathbf{r}, \mathbf{r}'; \omega) \) is the system’s bare Green’s function. To move forward, it will prove useful to write the sum above as a matrix multiplication. It is straightforward to show

\[ G(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}, \mathbf{r}'; \omega) + \overline{G}_0^T(\mathbf{r}; \omega) \hat{V}(\omega) \overline{G}(\mathbf{r}'; \omega) \]  

(4.10)

where we have introduced the vectors

\[ \overline{G}(\mathbf{r}; \omega) := \begin{pmatrix} G_{11}(\mathbf{r}_1, \mathbf{r}; \omega) & G_{12}(\mathbf{r}_1, \mathbf{r}; \omega) \\ G_{11}(\mathbf{r}_2, \mathbf{r}; \omega) & G_{12}(\mathbf{r}_2, \mathbf{r}; \omega) \\ \vdots & \vdots \\ G_{21}(\mathbf{r}_1, \mathbf{r}; \omega) & G_{22}(\mathbf{r}_1, \mathbf{r}; \omega) \\ G_{21}(\mathbf{r}_2, \mathbf{r}; \omega) & G_{22}(\mathbf{r}_2, \mathbf{r}; \omega) \\ \vdots & \vdots \end{pmatrix}, \quad \overline{G}_0(\mathbf{r}; \omega) := \begin{pmatrix} G^0_{11}(\mathbf{r}_1, \mathbf{r}; \omega) & 0 \\ G^0_{11}(\mathbf{r}_2, \mathbf{r}; \omega) & 0 \\ \vdots & \vdots \\ 0 & G^0_{22}(\mathbf{r}_1, \mathbf{r}; \omega) \\ 0 & G^0_{22}(\mathbf{r}_2, \mathbf{r}; \omega) \\ \vdots & \vdots \end{pmatrix} \]

(4.11)

with \( G_{ij}(\mathbf{r}, \mathbf{r}'; \omega) \) being a matrix element of the Green’s function and introduced the potential matrix defined as

\[ \hat{V}(\omega) := \frac{1}{\pi \rho_0} \begin{pmatrix} Q & 0 & \ldots & D & 0 & \ldots \\ 0 & Q & \ldots & 0 & D & \ldots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots \\ D & 0 & \ldots & Q & 0 & \ldots \\ 0 & D & \ldots & 0 & Q & \ldots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots \end{pmatrix}. \]

(4.12)

[Note: above we utilized that \( G_0(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}', \mathbf{r}; \omega) \).] It is our intention to obtain an explicit expression for the Green’s function from the Dyson equation. To that end, we analyze Eq. 4.10 at the location of an impurity: \( \mathbf{r} = \mathbf{r}_i \). Doing this for every SC impurity
and arranging the result as a matrix yields

\[ \overline{G}(r'; \omega) = \overline{G}_0(r'; \omega) + \hat{G}_0(\omega)\hat{\mathcal{V}}(\omega)\overline{G}(r'; \omega) \]  

(4.13)

where we have defined the matrix

\[ \hat{G}_0(\omega) := \begin{pmatrix}
G_{11}^0(\mathbf{r}_1, \mathbf{r}_1; \omega) & G_{11}^0(\mathbf{r}_1, \mathbf{r}_2; \omega) & \ldots & 0 & 0 & \ldots \\
G_{11}^0(\mathbf{r}_2, \mathbf{r}_1; \omega) & G_{11}^0(\mathbf{r}_2, \mathbf{r}_2; \omega) & \ldots & 0 & 0 & \ldots \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots \\
0 & 0 & \ldots & G_{22}^0(\mathbf{r}_1, \mathbf{r}_1; \omega) & G_{22}^0(\mathbf{r}_1, \mathbf{r}_2; \omega) & \ldots \\
0 & 0 & \ldots & G_{22}^0(\mathbf{r}_2, \mathbf{r}_1; \omega) & G_{22}^0(\mathbf{r}_2, \mathbf{r}_2; \omega) & \ldots \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots 
\end{pmatrix}. \]  

(4.14)

Rearranging Eq. 4.13 gives an explicit equation for the vector of Green’s functions:

\[ \overline{G}(r'; \omega) = \left[ I - \hat{G}_0(\omega)\hat{\mathcal{V}}(\omega) \right]^{-1}\overline{G}_0(r'; \omega). \]  

(4.15)

Inserting Eq. 4.15 into the Dyson equation returns the Green’s function. Namely,

\[ G(\mathbf{r}, \mathbf{r}'; \omega) = G_0(\mathbf{r}, \mathbf{r}'; \omega) + \overline{G}_0^T(\mathbf{r}; \omega)\hat{T}(\omega)\overline{G}_0(\mathbf{r}'; \omega) \]  

(4.16)

where the T-matrix has been defined as

\[ \hat{T}(\omega) := \hat{\mathcal{V}}(\omega) \left[ I - \hat{G}_0(\omega)\hat{\mathcal{V}}(\omega) \right]^{-1}. \]  

(4.17)

### 4.3 Engineering Superconducting Nanostructures

Equipped with this formalism, we are now in a position to consider atomically engineered SCing nanostructures. Recall that in quantum systems closed geometries lead to discrete states; in SCing systems, such states are known as Andreev bound states (ABS).[71, 72] To that end, we consider an elliptical quantum corral (QC) constructed using SC impurities – a superconducting quantum corral.
To investigate this system, consider the configuration shown in Fig. 4.6. Here, we probe the nanostructure using a scanning tunneling microscope (STM) built with a SCing tip. We are interested in computing experimentally observable quantities of the SCing system. To that end, it can be shown that the tunneling current between the surface and the STM tip is given by the superposition of currents from single-particle tunneling and pair tunneling;[73] the current due to pairs, known as the Josephson current, is a signature of the SCing state. The amplitude of the dc Josephson current is given by\(^4\)

\[
J_S = \frac{G_0}{\pi e} \Delta \int_0^{\infty} d\omega \ \text{Im} \left[ f_{\text{ret,nano}}(\omega) - f_{\text{ret,nano}}(-\omega) \right] F_{\text{STM}}(\omega; \Delta)
\]

(4.18)

where \(G_0(= e^2 4\pi \rho_{\text{nano}} \rho_{\text{STM}} T_0^2)\) is the normal state conductance between the STM and the surface with \(\rho_{\text{nano}} (\rho_{\text{STM}})\) being the nanostructure’s (STM’s) electron density of states (evaluated at the Fermi energy) and with \(T_0\) being the matrix element for an electron to tunnel from STM to surface, \(\Delta\) is the SCing gap of the STM tip, \(f_{\text{ret,nano}}(\omega)[= G_{12}(\mathbf{r}, \mathbf{r}; \omega)/\pi \rho_0]\) is the dimensionless anomalous (retarded) function of the nanostructure, and

\[
F_{\text{STM}}(\omega; \Delta) = \begin{cases} 
\frac{2}{\sqrt{\Delta^2 - \omega^2}} \arctan \left( \frac{\sqrt{\Delta^2 - \omega^2}}{\omega + \Delta} \right), & |\Delta| > |\omega| \\
\frac{1}{\sqrt{\omega^2 - \Delta^2}} \ln \left( \frac{\omega + \Delta + \sqrt{\omega^2 - \Delta^2}}{\omega + \Delta - \sqrt{\omega^2 - \Delta^2}} \right), & |\Delta| < |\omega|
\end{cases}
\]

(4.19)

Similar to experiments, we consider the following structural and material properties for the QC: 44 impurity atoms arranged in an ellipse, \((x/a)^2 + (y/b)^2 = 1\), where \(a/b = 2\) with \(a = 7.92[\text{nm}]\) on a Cu(111) surface – \(E_F = 450[\text{meV}]\) and \(m = 0.38 m_e;[17, 18]\) For simplicity, we consider the case where both the material inducing superconductivity on the surface and the STM tip are the same (e.g. niobium) – \(\Delta_{\text{nano}} = \Delta_{\text{STM}} \approx 2[\text{meV}]\).

\(^4\)E. H. Kim, unpublished
We compute the Green’s function of the QC from Eq. 4.16. To do this, we must assign numeric values to the broadening and ultraviolet cutoff. It is reasonable to take $\Gamma \approx 0.01\Delta$ and $D \approx E_F$. Computing the amplitude of the system’s Josephson current $J_S$ as a function of position (via Eq. 4.18) results in the plot shown in Fig. 4.7.

An initial observation is that we do obtain a Josephson current – the impurities are indeed inducing superconductivity on the surface of the metal. Also, much like the QCs built with “ordinary” impurities, standing wave patterns emerge inside the wall of the SCing QC; however, here these standing waves are ABS. Thus, the SCing QC is capable of confining/harbouring ABS – this confinement is not perfect though, as we do not have a solid wall.

Therefore, we have demonstrated how to control superconductivity on the scale of single atoms; furthermore, we have shown that confinement gives rise to ABS. Now, we seek to control the ABS inside the QC. To that end, we consider the single-atom gating techniques used in [18]; namely, by translating a single SCing impurity inside the SCing QC, we seek to modify the particle/hole wave functions of the system. We will observe such changes by computing the local density of states (LDOS) – for a SCing system Eq. 2.2 becomes $A(\mathbf{r}; \omega) = -(1/\pi)\text{Im}[G_{11}(\mathbf{r}, \mathbf{r}; \omega)]$.  

\textbf{Figure 4.7:} Josephson current for a superconducting quantum corral. The blue (red) regions represent areas of high (low) current with white regions being in-between. Regions outside the corral have minimal signs of superconductivity, whereas regions with tightly packed superconducting impurities exhibit a large Josephson current.
Figure 4.8: Atomically engineered Andreev bound states. Spatial maps of the local density of states (evaluated at $E_F$) for a superconducting quantum corral with an extra superconducting atom inside its wall. All images have the same length scale and the bare superconducting quantum corral density of states has been subtracted off (white regions represents areas where the local density of states is equal to the bare values). As the images progress from left to right and top to bottom, the impurity inside the corral moves closer to the left wall. Drastic changes occur in the corral’s particle/hole wave functions as this additional atom is moved.

Similar to [18], consider an elliptical QC composed of 44 atoms with semi-major axis $a = 7.92$[nm] and semi-minor axis $b = a/1.43$ on a Cu(111) surface; however, here the bulk material will be a SC (e.g. Nb). Density plots of the LDOS for various locations of the trapped impurity are shown in Fig. 4.8. As the SCing impurity changes position, one can see remarkable changes in the LDOS – hence, with this technique, one can manipulate the superposition of SCing QC eigenstates revealed by the LDOS. Namely, tailor-made wave functions are possible through judicious choice of SCing impurity location. This work establishes a method to control ABS on the smallest of scales.
Chapter 5

Conclusion

In this Thesis, motivated by interest in bottom-up technologies, we considered atomically engineered nanostructures built using individual atoms on a metal surface. In the course of the Thesis, we considered atoms with different properties: we started by considering the simplest case of s-wave point-scatterers i.e. inert impurities; we then progressed to atoms with partially filled d or f shells i.e. magnetic impurities; finally, we considered atoms capable of producing superconductivity on the metal’s surface i.e. superconducting (SCing) impurities.

In Chapter 2, we developed the scattering formalism in order to compute experimentally observable quantities for adatoms on a metal surface. We introduced general concepts used in the analysis throughout the Thesis; furthermore, we confirmed these methods provide a quantitative description of quantum corral (QC) experiments.

The problem of magnetic atoms (MAs) in a metal was considered in Chapter 3 and, in particular, we considered how the Kondo effect could be utilized for signal control and transmission. We reviewed the Kondo mirage experiments and discussed a formalism to describe the physics. Then, by introducing a second MA we showed that it is possible to control the Kondo mirage measured at the empty focus of a QC. In contrast to conventional technology where information is carried by currents (a consequence of the wave function), here the medium carrying the information is the wave function (of the QC) itself. With the interest in exploring technologies that take advantage of the electron’s spin degree of
freedom, these results could find utility in the field of spintronics.

Finally, in Chapter 4 we introduced/considered “superconducting atoms”. We implanted superconductivity onto the atoms by exploiting the coupling that arises between surface and bulk electrons when an impurity atom is present. As an example of the myriad of possible structures offered by this mechanism, we considered a QC made with SCing impurities. We verified that the QC does, in fact, superconduct by showing it exhibits a Josephson effect; furthermore, we demonstrated atomic-scale control over Andreev bound states by manipulating a single SCing impurity inside the QC. This degree of precision over what is (traditionally) a macroscopic phenomenon is exciting and should lend itself to novel technologies in moving forward.

This Thesis has only scratched the surface on the possibilities afforded by atomic-scale engineering. Here we focused on utilizing elliptical QCs; however, a natural extension would be to consider other structures, particularly open structures. Another natural extension would be the inclusion of the spin-orbit coupling that arises on some surfaces (e.g. Au(111) surfaces).[74] One could also consider magnetically ordered nanostructures built on the surface, particularly on surfaces with spin-orbit coupling.[75, 76]

This Thesis was motivated by experiments where structures were engineered by using a scanning tunneling microscope; however, another interesting/important area of investigation would be fabrication methods – it will be crucial to develop methods that efficiently produce larger and more complex structures if useful devices are to be fabricated. To accomplish this, self-assembly techniques seem to provide a natural means;[77–80] namely, techniques in which ordered structures naturally emerge from disordered ones when exposed to the right environmental variables.[81] Some structures have been fabricated using this approach; it would be worthwhile to further develop this approach to realize structures with precise functionalities (such as those described in this Thesis).
Appendices
Appendix A

Momentum Sums

A.1 Two Dimensions

Consider a sum over momentum states \( \mathbf{p} = (p_x, p_y) \) of the form \( \frac{1}{A} \sum \mathbf{p} F(\varepsilon_{\mathbf{p}}) \) where \( F \) is solely a function of the dispersion relation: \( \varepsilon_{\mathbf{p}} = (1/2m)p^2 - E_F. \) [Note: we are measuring energies with respect to the Fermi energy \( E_F. \)] For normalization purposes, we put our system in a large box \( (A = L^2) \) and impose periodic boundary conditions \( (\mathbf{p} = 2\pi \mathbf{n}/L \text{ where } \mathbf{n} \in \mathbb{Z}^2). \) To proceed we will take the thermodynamic limit – namely, take the limit as \( L \to \infty. \) In this limit, \( (p_x, p_y) \) approach continuous variables and we approximate the sums as integrals. Furthermore, by working in polar coordinates \( \mathbf{p} = (p, \theta) \) and appreciating that \( F \) is only a function of the energy (and therefore \( p \)), one can write the sum as an integral over energy. This process is summarized as

\[
\frac{1}{A} \sum \mathbf{p} F(\varepsilon_{\mathbf{p}}) \approx \int \frac{dp}{(2\pi)^2} F(\varepsilon_{\mathbf{p}}) = \rho_0 \int_{-E_F}^{D} d\varepsilon F(\varepsilon) \tag{A.1}
\]

where we have defined the density of states as \( \rho_0 := m/2\pi \) and introduced an ultraviolet cutoff \( D. \) Physically, \( D \simeq \) the electrons' bandwidth.
A.2 Three Dimensions

Consider a sum over momentum states $p = (p_x, p_y, p_z)$ of the form $1/V \sum_p F(\varepsilon_p)$ where $F$ is solely a function of the dispersion relation: $\varepsilon_p = (1/2m)p^2 - E_F$. [Again, we are measuring energies with respect to the Fermi energy $E_F$.] We put our system in a large box ($V = L^3$) and impose periodic boundary conditions ($p = 2\pi n/L$ where $n \in \mathbb{Z}^3$). To proceed, take the thermodynamic limit ($L \to \infty$) and approximate the sums as integrals. Furthermore, by working in spherical coordinates, write the sum as an integral over energy. This process is summarized as

$$\frac{1}{V} \sum_p F(\varepsilon_p) \approx \int \frac{d\mathbf{p}}{(2\pi)^3} F(\varepsilon_p) \approx \rho_0 \int_{-E_F}^{D} d\varepsilon F(\varepsilon) \quad (A.2)$$

where $\rho_0 := (1/2\pi)^2(2m)^{3/2}/\sqrt{E_F}$ is the density of states (evaluated at the Fermi energy) and we have introduced an ultraviolet cutoff $D$. Replacing the density of states by its value evaluated at the Fermi energy is an accurate approximation because the density of states is a slowly varying function of energy and the physics is dominated by processes near the Fermi energy.

A.3 Examples

Here we explicitly evaluate two momentum sums of particular importance for this Thesis.

First, we evaluate the following sum in the thermodynamic limit:

$$\frac{1}{L^d} \sum_p \frac{1}{\omega - \varepsilon_p + i\delta} \approx \rho_0 \int_{-E_F}^{D} d\varepsilon \frac{1}{\omega - \varepsilon + i\delta} .$$

where $d$ is the dimension of the system, $\omega$ is the energy value we are interested in probing ($-E_F < \omega < D$), and $\delta(= 0^+)$ is a convergence factor. [Note: We are only interested in processes near the Fermi energy: $\omega \ll D$.] To proceed, we use that for $\delta = 0^+$ one can write

$$\frac{1}{x + i\delta} = \mathcal{P} \left( \frac{1}{x} \right) - i\pi \delta(x) \quad (A.3)$$
Momentum Sums

where $P(\ldots)$ denotes the principal value. Carrying out the integral yields

$$
\frac{1}{L^d} \sum_{\mathbf{p}} \frac{1}{\omega - \varepsilon_{\mathbf{p}} + i\delta} \approx -i(\pi \rho_0) + \rho_0 \ln \left( \frac{E_F + \omega}{D - \omega} \right). \tag{A.4}
$$

Often times, one can treat the sum in the \textit{wide-band limit} – one can approximate the integral by taking $-E_f \to -D$ and then taking $D \to \infty$. In the wide-band limit the logarithm vanishes and we obtain

$$
\frac{1}{L^d} \sum_{\mathbf{p}} \frac{1}{\omega - \varepsilon_{\mathbf{p}} + i\delta} \approx -i(\pi \rho_0). \tag{A.5}
$$

Next, we consider the following sum evaluated in the thermodynamic limit:

$$
\frac{1}{L^d} \sum_{\mathbf{p}} \frac{1}{-\beta^2 - \varepsilon_{\mathbf{p}}^2} \approx -\rho_0 \int_{-\infty}^{\infty} d\varepsilon \frac{1}{(\varepsilon - i\beta)(\varepsilon + i\beta)}. \tag{A.6}
$$

In the above equation, we have used the wide-band limit and taken $D \to \infty$, as the integral is convergent. We see the integrand has poles at $\pm i\beta$. To evaluate the integral we use the Residue theorem:

$$
\oint_{\gamma} dz F(z) = 2\pi i \sum_j \text{Res}(z_j) \tag{A.6}
$$

where $\{z_j\}$ are the poles of $F(z)$ and $\gamma$ is the contour of integration. We choose as our contour the real line and a semicircle of infinite radius in the upper half-plane – this picks up the pole at $+i\beta$ when $\text{Re}[\beta] > 0$. The integral over the semicircle vanishes and one obtains

$$
\frac{1}{L^d} \sum_{\mathbf{p}} \frac{1}{-\beta^2 - \varepsilon_{\mathbf{p}}^2} \approx -\frac{(\pi \rho_0)}{\beta}. \tag{A.7}
$$
Appendix B

Second Quantization

B.1 Identical particles

Consider a collection of identical particles – particles with no intrinsic difference between them. In classical mechanics, such particles are distinguished by their trajectories in phase space; however, in quantum mechanics identical particles are indistinguishable because any measurement of the system disturbs the state in an uncontrolled fashion.

For concreteness, consider $N$ identical particles. The Hilbert space of the system will be the tensor product of the spaces for the individual particles: $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \cdots \otimes \mathcal{H}_N$. A valid state vector in $\mathcal{H}$ is $|\psi\rangle = |n_1\rangle \otimes |n_2\rangle \otimes \cdots \otimes |n_N\rangle$ where $|n_i\rangle$ is a state in $\mathcal{H}_i$. Define the permutation operator as $\hat{P}_{i,j}|\ldots n_i\ldots n_j\ldots\rangle := |\ldots n_j\ldots n_i\ldots\rangle$ (the operator has the properties $\hat{P}_{i,j} = \hat{P}_{i,j}^{-1} = \hat{P}^\dagger_{i,j}$). Specifically, the permutation operator swaps the state that two particles occupy.

Because no interactions can distinguish between identical particles, an operator $\hat{O}$ describing a physical observable must be invariant under permutation of the particles: $[\hat{O}, \hat{P}_{i,j}] = 0$. This means we can simultaneously diagonalize both operators; one finds the eigenvalues of $\hat{P}_{i,j}$ are $\pm 1$. A collection of identical particles will always be found in a state that is also an eigenstate of the permutation operator:

$$\hat{P}_{i,j} |\psi\rangle = \pm |\psi\rangle . \quad (B.1)$$
Namely, physical states are either completely symmetric or antisymmetric with respect to permutation of the particles.\[44]\] Identical particles with symmetric (antisymmetric) states under particle exchange are known as bosons (fermions).

**B.2 Second Quantization**

Consider the Hamiltonian of a many-body system composed of \( N \) identical particles

\[
\hat{H} = \sum_{i=1}^{N} \hat{H}_i^0 + \frac{1}{2} \sum_{i,j=1, i \neq j}^{N} \hat{V}_{i,j}
\]

(B.2)

where \( \hat{H}_i^0 \) is the Hamiltonian of particle \( i \) in the absence of the other bodies and \( \hat{V}_{i,j} \) represents the interaction between particle \( i \) and \( j \). The state of the system, \( |\psi(t)\rangle \), obeys the Schrödinger equation

\[
i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle .
\]

(B.3)

In position space, the system’s wave function is

\[
\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; t) = \langle \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N | \psi(t) \rangle .
\]

(B.4)

Consider the set of orthonormal basis states \( \{ |n\rangle \} \) in the Hilbert space of particle \( i \) with wave function \( \phi_n(\mathbf{r}_i) = \langle \mathbf{r}_i | n \rangle \). These single-particle states could correspond to energy states, momentum states, and so on; in principle we can uniquely label each state \( (n = 0, 1, 2, \ldots) \) allowing us to work without reference to specific quantum numbers. Expanding the system’s wave function in the \( \{ |n\rangle \} \) states for each particle gives

\[
\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N; t) = \sum_{n_1, n_2, \ldots, n_N} C(n_1, n_2, \ldots, n_N; t) \phi_{n_1}(\mathbf{r}_1) \phi_{n_2}(\mathbf{r}_2) \cdots \phi_{n_N}(\mathbf{r}_N)
\]

(B.5)

where \( C(n_1, n_2, \ldots, n_N; t) := \langle n_1, n_2, \ldots, n_N | \psi(t) \rangle \).
Writing the Schrödinger equation in terms of these coefficients yields

\[
ih\frac{\partial}{\partial t}C(n_1, n_2, \ldots, n_N; t) = \sum_{i=1}^{N} \sum_{m_i} \langle n_i | \hat{H}_i^0 | m_i \rangle C(n_1, n_2, \ldots, m_i, \ldots, n_N; t) + \frac{1}{2} \sum_{i,j=1}^{N} \sum_{m_i, m_j} \langle n_i, n_j | \hat{V}_{i,j} | m_i, m_j \rangle C(n_1, n_2, \ldots, m_i, \ldots, m_j, \ldots, n_N; t).
\]

Therefore, to determine the wave function of a many-body system, one must solve the set of coupled differential equations given by Eq. B.6 for each combination of \( n_1, n_2, \ldots, n_N \). Most systems of interest contain so many particles that solving Eq. B.6 is not feasible. Thus, it is crucial to find an approach which makes such systems manageable.

Because physical states are either completely symmetric or antisymmetric with respect to permutation of the particles, the coefficients have the property

\[
C(\ldots n_i \ldots n_j \ldots; t) = \pm C(\ldots n_j \ldots n_i \ldots; t)
\]

where + (−) is for the case of bosons (fermions) (which implies the Pauli principle: no two fermions can occupy the same state). This property allows us to order the argument in each coefficient from lowest to highest quantum number. Following an approach similar to that of [44] we write

\[
C(n_1, n_2, \ldots, n_N; t) = \pm \sqrt{\frac{N!}{N_0!N_1!\cdots}} \sum_{N_0, N_1, \ldots} \phi_{n_1}(r_1) \phi_{n_2}(r_2) \cdots \phi_{n_N}(r_N)
\]

where the sum is over all occupation numbers such that there is \( N \) total particles and we have defined the coefficients \( A(N_0, N_1, \ldots; t) := \sqrt{N!/N_0!N_1!\cdots} C(N_0, N_1, \ldots; t) \) and the (normalized) wave function

\[
\Psi_{N_0, N_1, \ldots}(r_1, r_2, \ldots, r_N) := \sqrt{\frac{N_0!N_1!\cdots}{N!}} \sum_{n_1, n_2, \ldots, n_N} \phi_{n_1}(r_1) \phi_{n_2}(r_2) \cdots \phi_{n_N}(r_N)
\]

where the sum is restricted to terms with \( N_0 \) particles in state 0, \( N_1 \) particles in state 1, and so on.
Notice that Eq. B.7 is the expansion of the wave function in terms of occupation numbers. To that end, we introduce an occupation number basis with a complete set of orthonormal states $|N_0, N_1, \ldots \rangle$. Therefore the coefficients and basis functions in Eq. B.7 are the inner products $A(N_0, N_1, \ldots; t) = \langle N_0, N_1, \ldots | \psi(t) \rangle$ as well as $\Psi_{N_0, N_1, \ldots}(r_1, r_2, \ldots, r_N) = \langle r_1, r_2, \ldots, r_N | N_0, N_1, \ldots \rangle$.

To preserve the correct symmetry under particle exchange when using occupation number states, one introduces creation and annihilation operators $\{c_n\}$. These operators have the property that $c_n^\dagger c_n |N_0, N_1, \ldots \rangle = N_n |N_0, N_1, \ldots \rangle$ and, in the case of bosons (fermions), obey the following commutation (anticommutation) relations:

\begin{align*}
\text{Bosons:} & \quad [c_n, c_m^\dagger] = \delta_{n,m} \quad , \quad [c_n, c_m] = 0 \quad \text{(B.9a)} \\
\text{Fermions:} & \quad \{c_n, c_m^\dagger\} = \delta_{n,m} \quad , \quad \{c_n, c_m\} = 0 \quad \text{(B.9b)}
\end{align*}

where $[\ldots] \ (\{\ldots\})$ is the commutator (anticommutator). This Thesis is only concerned with fermionic systems so it is always implied that the $\{c_n\}$ operators obey Eq. B.9b.

The combined effect of working in an occupation number representation with the creation and annihilation operators is that one can rewrite the many-body Hamiltonian as

\[ \hat{H} = \int dr \ \psi^\dagger(r) H_0(r) \psi(r) + \frac{1}{2} \int dr dr' \ \psi^\dagger(r) \psi^\dagger(r') V(r, r') \psi(r') \psi(r) \quad \text{(B.10)} \]

where $H_0(r) \ (V(r, r'))$ is the position representation of the operator $\hat{H}_i^0 \ (\hat{V}_{i,j})$ and we have introduced the field operators defined by

\[ \psi(r) := \sum_n \phi_n(r) c_n \quad \text{(B.11)} \]

with $\phi_n(r)$ being the single-body wave functions discussed earlier. Because the field operators resemble a wave function in form, but with the expansion coefficients $c_n$ having been promoted to operators, this formalism is known as second quantization; however, this is only an appearance. We are still considering the original problem, only now with a language better equipped to handle many identical particles.

As a quick example, consider a system of noninteracting identical particles – the second
quantized Hamiltonian is \( \hat{H}_0 = \int dr \, \psi^\dagger (r) H_0 (r) \psi (r) \). Expanding the field operators in the eigenstates of \( H_0 (r) \) \( [H_0 (r) \phi_n (r) = \varepsilon_n \phi_n (r)] \) and recognizing that the resulting integral is a Kronecker delta returns \( \hat{H}_0 = \sum_n \varepsilon_n \hat{c}_n^\dagger \hat{c}_n \).

### B.3 Thermal Expectation Values of Fermion Bilinears

Consider a system of fermions with second quantized Hamiltonian \( \hat{H} = \sum_n E_n \hat{c}_n^\dagger \hat{c}_n \). An eigenstate of \( \hat{H} \) is \( |N_0, N_1, \ldots \rangle \) where \( N_n (= 0, 1) \) is the number of particles occupying single-particle state \( n \); therefore, the eigenvalues of the Hamiltonian are \( \sum_n E_n N_n \). In this case, the thermal expectation value of an operator \( \hat{O} \) describing some observable is

\[
\langle \hat{O} \rangle = \frac{1}{Z} \sum_{N_0, N_1, \ldots} e^{-\beta \sum_n E_n N_n} \langle N_0, N_1, \ldots | \hat{O} | N_0, N_1, \ldots \rangle \tag{B.12}
\]

where \( \beta (= 1/T) \) is the inverse temperature and \( Z \) is the partition function

\[
Z = \prod_n (1 + e^{-\beta E_n}) \tag{B.13}
\]

We are particularly interested in expectation values of creation and annihilation operator bilinears. First, consider the annihilation of a particle in state \( m \) followed by the creation of a particle in state \( n \): \( \langle \hat{c}_m^\dagger \hat{c}_n \rangle \). The inner product in Eq. B.12 returns \( N_n \) if \( n = m \), otherwise it returns zero. Carrying out the resulting sum over occupation numbers and utilizing Eq. B.13 gives

\[
\langle \hat{c}_m^\dagger \hat{c}_n \rangle = \delta_{n,m} f(E_n) \tag{B.14}
\]

where \( f \) is the Fermi function: \( f(\omega) = (e^{\beta\omega} + 1)^{-1} \). Second, we switch the roles of creation and annihilation operators: \( \langle \hat{c}_n \hat{c}_m^\dagger \rangle \). Using the fermion anticommutation relation \( \{ \hat{c}_n, \hat{c}_m^\dagger \} = \delta_{n,m} \) one can write the expectation value in terms of Eq. B.14. One finds

\[
\langle \hat{c}_n \hat{c}_m^\dagger \rangle = \delta_{n,m} [1 - f(E_n)] \tag{B.15}
\]
Next, consider the combination of two creation (annihilation) operators: $\langle c^\dagger_n c^\dagger_m \rangle (\langle c_n c_m \rangle)$. The inner product in Eq. B.12 will always return zero. Therefore

$$\langle c^\dagger_n c^\dagger_m \rangle = 0 \quad (B.16)$$
$$\langle c_n c_m \rangle = 0 . \quad (B.17)$$

### B.4 Green’s Functions

Define the Green’s function for a many-body system composed of identical fermions as

$$G(r, r'; t) := -i\Theta(t) \langle \{\psi(r; t), \psi^\dagger(r')\} \rangle \quad (B.18)$$

where $\psi(r; t)$ is the system’s field operator at position $r$ and time $t$, $\langle \cdots \rangle$ denotes a thermal expectation value, $\{\cdots\}$ is the anticommutator, and $\Theta(t)$ is the Heaviside step function.

Consider a system with Hamiltonian $\hat{H} = \sum_n E_n c^\dagger_n c_n$. Expanding the field operator as $\psi(r) = \sum_n \phi_n(r) c_n$, the Green’s function becomes

$$G(r, r'; t) = -i\Theta(t) \sum_n \phi_n(r) \phi^*_n(r') e^{-iE_nt} . \quad (B.19)$$

Introducing the Fourier transform of a function $f(t)$ as

$$f(\omega) = \int_{-\infty}^\infty dt \ e^{i\omega t} f(t) , \quad (B.20)$$

one obtains

$$G(r, r'; \omega) = \sum_n \frac{\phi_n(r) \phi^*_n(r')}{\omega - E_n + i\delta} \quad (B.21)$$

where $\delta(= 0^+)$ is a convergence factor.
B.5 The Spectral Representation

Consider operators $\hat{A}$ and $\hat{B}$ for a system with time-independent Hamiltonian $\hat{H}$ – our goal is to determine the thermal expectation value $\langle \hat{B} \hat{A} \rangle$. In what follows, we will focus on the case where $\langle \hat{B} \hat{A} \rangle \in \mathbb{R}$. To that end, consider the Green’s function

$$G(t) = -i \Theta(t) \langle \{ \hat{A}(t), \hat{B} \} \rangle . \quad (B.22)$$

By inserting the identity operator in terms of the eigenstates of $\hat{H}$, denoted by $\{|N\rangle\}$ (with eigenvalues $E_N$), one obtains the Fourier transform of Eq. B.22

$$G(\omega) = \frac{1}{Z} \sum_{N,M} (e^{-\beta E_N} + e^{-\beta E_M}) \langle N | \hat{A} | M \rangle \langle M | \hat{B} | N \rangle \frac{1}{\omega - (E_M - E_N) + i\delta}$$

where $Z$ is the partition function, $\beta$ is the inverse temperature, and $\delta(= 0^+)$ is a convergence factor. The *spectral function* is defined as

$$A(\omega) := \frac{1}{\pi} \text{Im} [G(\omega)] . \quad (B.23)$$

By using Eq. A.3 and that $\langle \hat{B} \hat{A} \rangle \in \mathbb{R}$, one readily obtains

$$\langle \hat{B} \hat{A} \rangle = \int_{-\infty}^{\infty} d\omega f(\omega) A(\omega) \quad (B.24)$$

where $f$ is the Fermi function: $f(\omega) = \left( e^{\beta \omega} + 1 \right)^{-1}$. 
Appendix C

Theory of Superconductivity

C.1 Mean-Field Superconducting Hamiltonian

Consider a Hamiltonian which is capable of describing a superconductor (SC); namely, consider \( \hat{H} = \hat{H}_0 + \hat{V} \) where \( \hat{H}_0 \) is the Hamiltonian of a three-dimensional electron gas and \( \hat{V} \) describes the interaction between electrons. In second quantized form, the Hamiltonian is written as

\[
\hat{H} = \sum_{p,s} \varepsilon_p c^\dagger_{p,s} c_{p,s} + \frac{1}{2} \sum_{s,s'} \int d\mathbf{r} d\mathbf{r}' \psi^\dagger_s(\mathbf{r}) \tilde{\psi}^\dagger_{s'}(\mathbf{r}') V(\mathbf{r}, \mathbf{r}') \psi_{s'}(\mathbf{r}') \psi_s(\mathbf{r})
\]  

(C.1)

where \( c_{p,s} \) annihilates an electron of momentum \( p \) and spin-\( s \), \( \varepsilon_p = p^2/2m - E_F \) is the single-particle dispersion with \( E_F \) being the Fermi energy, and \( \psi_s(\mathbf{r}) \) are the electron field operators. As discussed in Chapter 4, an attractive interaction gives rise to a superconducting instability. To proceed, we consider the simplest case; namely, an attractive contact interaction – the electron-electron interaction is taken to be \( (U > 0) \)

\[
V(\mathbf{r}, \mathbf{r}') = -U \delta(\mathbf{r} - \mathbf{r}')
\]  

(C.2)
Inserting this potential into the Hamiltonian and expanding the field operators in a plane wave basis, $\psi_s(\mathbf{r}) = (1/\sqrt{V}) \sum_p e^{i \mathbf{p} \cdot \mathbf{r}} c_{p,s}$, returns

$$\hat{V} = -\frac{U}{2V} \sum_{s,s'} \sum_{p,k,q} c_{k+q,s'}^\dagger c_{p-q,s} c_{p,s'} c_{k,s} \quad (C.3)$$

Because of the insight gained from the Cooper problem, namely that electrons want to form Cooper pairs in the presence of an attractive interaction, we make the following mean-field approximation:

$$\psi_\uparrow^\dagger(\mathbf{r}) \psi_\uparrow(\mathbf{r}) \psi_\downarrow(\mathbf{r}) \psi_\downarrow^\dagger(\mathbf{r}) \rightarrow \langle \psi_\uparrow^\dagger(\mathbf{r}) \psi_\uparrow^\dagger(\mathbf{r}) \psi_\downarrow(\mathbf{r}) \psi_\downarrow^\dagger(\mathbf{r}) \rangle + \langle \psi_\downarrow^\dagger(\mathbf{r}) \psi_\downarrow^\dagger(\mathbf{r}) \psi_\uparrow(\mathbf{r}) \psi_\uparrow^\dagger(\mathbf{r}) \rangle \quad (C.4)$$

where $\langle \cdots \rangle$ represents a thermal average. Inserting this approximation into the potential returns the mean-field Hamiltonian for a SC:

$$\hat{H}_{MF} = \sum_{p,s} \varepsilon_p c_{p,s}^\dagger c_{p,s} - \sum_{p} \left( \Delta c_{p,\uparrow}^\dagger c_{-p,\downarrow} + \Delta^* c_{-p,\downarrow} c_{p,\uparrow} \right) \quad (C.5)$$

where we have defined the parameter $\Delta$ via

$$\Delta := U \langle \psi_\downarrow(\mathbf{r}) \psi_\uparrow^\dagger(\mathbf{r}) \rangle \quad (C.6)$$

Due to the structure of Eq. C.5, it is convenient to introduce the Nambu spinor:

$$\Psi_p := \begin{pmatrix} c_{p,\uparrow} \\ c_{-p,\downarrow}^\dagger \end{pmatrix} \quad (C.7)$$

In terms of $\Psi_p$, the Hamiltonian is

$$\hat{H} = \sum_p \Psi_p^\dagger H_{p}^{BdG} \Psi_p \quad (C.8)$$

where $H_{p}^{BdG}$ is the Bogoliubov-deGennes (BdG) Hamiltonian/matrix

$$H_{p}^{BdG} = \begin{pmatrix} \varepsilon_p & -\Delta \\ -\Delta^* & -\varepsilon_p \end{pmatrix} \quad (C.9)$$

[Note: an unimportant constant has been removed in Eq. C.8.]
To diagonalize Eq. C.8, we consider the Bogoliubov transformation

\[
\begin{pmatrix}
c_{p,\uparrow} \\
c_{-p,\downarrow}^\dagger
\end{pmatrix} =
\begin{pmatrix}
u_p & -v_p^* \\
v_p & u_p
\end{pmatrix}
\begin{pmatrix}
\gamma_{p,\uparrow} \\
\gamma_{-p,\downarrow}^\dagger
\end{pmatrix}.
\]  

(C.10)

In Eq. C.10, \(\gamma_{p,s}\) is a fermionic operator which destroys a superconducting quasiparticle of momentum \(p\) and spin-\(s\). Furthermore, \((u_p v_p)^T ((-v_p^* u_p^*)^T)\) is the eigenvector of \(H_p^{\text{BdG}}\) corresponding to the eigenvalue \(E_p := \sqrt{\epsilon_p^2 + |\Delta|^2} (-E_p)\); explicitly,

\[
u_p = \sqrt{\frac{1}{2} \left(1 + \frac{\epsilon_p}{E_p}\right)}
\]  

(C.11a)

\[
v_p = -e^{-i \text{arg} (\Delta)} \sqrt{\frac{1}{2} \left(1 - \frac{\epsilon_p}{E_p}\right)}.
\]  

(C.11b)

Inserting this transformation into the mean-field Hamiltonian (Eq. C.8) and using that the eigenvectors of the (Hermitian) BdG matrix are orthogonal, one obtains \((E_p > 0)\)

\[
\hat{H} = \sum_{p,s} E_p \gamma_{p,s}^\dagger \gamma_{p,s}.
\]  

(C.12)

[As before, an unimportant constant has been removed.]  

C.2 The Gap Equation

In writing down the mean-field superconducting Hamiltonian, we introduced the parameter \(\Delta\) via Eq. C.6 – \(\Delta\) is known as the SCing gap, as this is what gives rise to the gap in the density of states (see next section). Expanding the field operators in a plane wave basis, Eq. C.6 becomes

\[
\Delta = \frac{U}{V} \sum_p \langle c_{-p,\downarrow} c_{p,\uparrow}\rangle.
\]  

(C.13)

Writing the \(\{c_{p,s}\}\) in terms of the \(\{\gamma_{p,s}\}\) (via the Bogoliubov transformation) and using the
properties of thermal expectation values of fermion bilinears (Appendix B) gives

\[ \Delta = -\frac{U}{V} \sum_p u_p v_p^* \tanh \left( \frac{E_p}{2T} \right) . \]  

(C.14)

Inserting the explicit form of the \((u_p, v_p)\) into Eq. C.14 gives an equation to determine \(\Delta\) self-consistently – the gap equation:

\[ 1 = \frac{U}{2V} \sum_p \frac{1}{E_p} \tanh \left( \frac{\beta E_p}{2} \right) \]  

(C.15)

In the thermodynamic limit \((V \to \infty)\) the equation becomes

\[ 1 = \frac{U \rho_0}{2} \int_{-D}^{D} d\epsilon \frac{1}{E_p} \tanh \left( \frac{\beta E_p}{2} \right) \]  

(C.16)

where \(\rho_0\) is the electron’s density of states (evaluated at the Fermi energy) and we have introduced an ultraviolet cutoff \(D\) (using the wide-band limit).

In general, Eq. C.16 must be solved numerically; however, it is readily solved analytically in two limits: first, at zero temperature \(T=0\) and also at the critical temperature \(T_c\) where superconductivity is lost. To solve Eq. C.16 at \(T=0\), we use that \(\tanh (\beta \omega/2) = 1 - 2f(\omega)\) (\(f\) is the Fermi function). Using that \(f(\omega)\) is a step function at \(T=0\), one obtains \([39]\)

\[ \Delta = 2D e^{-1/U \rho_0}. \]  

(C.17)

To solve Eq. C.16 at \(T_c\), we use that \(\Delta \to 0\); one obtains

\[ T_c = \frac{2e^\gamma}{\pi} D e^{-1/U \rho_0} \approx 1.13 D e^{-1/U \rho_0} \]  

(C.18)

where \(\gamma\) is Euler’s constant.[39] This leads to a simple relationship between the (zero temperature) gap and the critical temperature: \(\Delta = 1.764 T_c\).
C.3 Superconducting Density of States

Consider a sum over momentum states of the form \( \frac{1}{V} \sum_{\mathbf{p}} F(E_{\mathbf{p}}) \) where \( F \) is solely a function of the superconducting dispersion: \( E_{\mathbf{p}} = \sqrt{\varepsilon_{\mathbf{p}}^2 + |\Delta|^2} \). For normalization purposes, we put our system in a large box \( (V = L^3) \) and impose periodic boundary conditions \( (\mathbf{p} = 2\pi \mathbf{n}/L \text{ where } \mathbf{n} \in \mathbb{Z}^3) \). In the thermodynamic limit \( (L \to \infty) \) one writes

\[
\frac{1}{V} \sum_{\mathbf{p}} F(E_{\mathbf{p}}) \approx \int \frac{d\mathbf{p}}{(2\pi)^3} F(E_{\mathbf{p}}) \approx \rho_0 \int_{-D}^{D} d\varepsilon_{\mathbf{p}} F(E_{\mathbf{p}}) \tag{C.19}
\]

where \( \rho_0 \) is the electron’s density of states (evaluated at the Fermi energy) and we have introduced an ultraviolet cutoff \( D \) (using the wide-band limit). To proceed, use that

\[
1 = \int_{0}^{\infty} dE \, \delta \left( E - \sqrt{\varepsilon_{\mathbf{p}}^2 + |\Delta|^2} \right). \tag{C.20}
\]

Inserting this form of unity into Eq. C.19 and switching the order of integration yields

\[
\frac{1}{V} \sum_{\mathbf{p}} F(E_{\mathbf{p}}) \approx \int_{0}^{\infty} dE \, D(E) F(E) \tag{C.21}
\]

where we have defined the superconducting density of states as

\[
D(E) := \rho_0 \int_{-D}^{D} d\varepsilon_{\mathbf{p}} \, \delta \left( E - \sqrt{\varepsilon_{\mathbf{p}}^2 + |\Delta|^2} \right). \tag{C.22}
\]

The Dirac delta of an analytic function can be written as \( \delta \left[ f(x) \right] = \sum_i \delta(x - x_i)/|\partial_x f(x_i)| \) where \( \{x_i\} \) are the zeros of the function \( f(x) \). Applying this identity gives

\[
\delta \left( E - \sqrt{\varepsilon_{\mathbf{p}}^2 + |\Delta|^2} \right) = \frac{|E|}{\sqrt{E^2 - |\Delta|^2}} \left[ \delta \left( \varepsilon_{\mathbf{p}} - \sqrt{E^2 - |\Delta|^2} \right) + \delta \left( \varepsilon_{\mathbf{p}} + \sqrt{E^2 - |\Delta|^2} \right) \right]. \tag{C.23}
\]
Inserting this formula into Eq. C.22 gives the superconducting density of states:

\[
D(E) = \begin{cases} 
0, & |E| < |\Delta| \\
2\rho_0 \frac{|E|}{\sqrt{E^2 - |\Delta|^2}}, & |E| > |\Delta|
\end{cases}
\]  
(C.24)

Notice the gap in the spectrum from 0 to $|\Delta|$ (Fig. C.1) – there are no states available to the superconducting quasiparticles below a certain energy. For this reason $\Delta$ is referred to as the superconducting gap.\[39\]

![Figure C.1: The superconducting density of states.](image)

### C.4 Green’s Function for a Superconductor

When the system is superconducting, we define the Green’s function as

\[
G(r, r'; t) := \begin{pmatrix} 
G_{11}(r, r'; t) & G_{12}(r, r'; t) \\
G_{21}(r, r'; t) & G_{22}(r, r'; t)
\end{pmatrix}
\]  
(C.25)

where the matrix exists in Nambu space and the elements are

\[
G_{11}(r, r'; t) = -i\Theta(t) \langle \{ \psi_\uparrow(r, t), \psi_\uparrow(r') \} \rangle
\]  
(C.26a)

\[
G_{12}(r, r'; t) = -i\Theta(t) \langle \{ \psi_\uparrow(r, t), \psi_\downarrow(r') \} \rangle
\]  
(C.26b)

\[
G_{21}(r, r'; t) = -i\Theta(t) \langle \{ \psi_\downarrow(r, t), \psi_\uparrow(r') \} \rangle
\]  
(C.26c)

\[
G_{22}(r, r'; t) = -i\Theta(t) \langle \{ \psi_\downarrow(r, t), \psi_\downarrow(r') \} \rangle
\]  
(C.26d)
In the above equations, \( \psi_s(\mathbf{r}; t) \) is the system’s field operator at position \( \mathbf{r} \) and time \( t \), \( \langle \cdots \rangle \) denotes a thermal average, \( \{\cdots\} \) is the anticommutator, and \( \Theta(t) \) is the Heaviside step function.\[38\] [Note: if the system we are considering is not superconducting, we obtain the usual Green’s function (Eq. B.18) by taking the \((1, 1)\) element of Eq. C.25.]

As an example, we determine the Green’s function of a SC described by the mean-field Hamiltonian, Eq. C.5. To this end, we expand the field operator in a plane-wave basis,

\[
\psi_s(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_p e^{i \mathbf{p} \cdot \mathbf{r}} c_{p,s}^\dagger
\]

using the Bogoliubov transformation, we write the \(\{c_{p,s}\}\) in terms of the \(\{\gamma_{p,s}\}\). Fourier transforming the resulting equations in time gives

\[
G_{11}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{V} \sum_p e^{i \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} \frac{|u_p|^2}{\omega - E_p + i\delta} + \frac{|\nu_p|^2}{\omega + E_p + i\delta} 
\]

(C.27a)

\[
G_{12}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{V} \sum_p e^{i \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} \frac{u_p \nu_p^*}{\omega - E_p + i\delta} - \frac{\nu_p u_p^*}{\omega + E_p + i\delta} 
\]

(C.27b)

\[
G_{21}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{V} \sum_p e^{i \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} \frac{\nu_p u_p^*}{\omega - E_p + i\delta} - \frac{u_p \nu_p^*}{\omega + E_p + i\delta} 
\]

(C.27c)

\[
G_{22}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{V} \sum_p e^{i \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} \frac{|\nu_p|^2}{\omega - E_p + i\delta} + \frac{|u_p|^2}{\omega + E_p + i\delta} 
\]

(C.27d)

where \(\delta = 0^+\) is a convergence factor. Inserting the wave functions (Eqs. C.11a and C.11b) into the Green’s function gives a succinct expression:

\[
G(\mathbf{r}, \mathbf{r}'; \omega) = \frac{1}{V} \sum_p e^{i \mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')} G_p(\omega) 
\]

(C.28)

where we have defined the momentum space Green’s function

\[
G_p(\omega) := \frac{1}{(\omega + i\delta)^2 - E_p^2} \begin{pmatrix}
\omega + \epsilon_p + i\delta & -\Delta \\
-\Delta^* & \omega - \epsilon_p + i\delta
\end{pmatrix} . 
\]

(C.29)

Of particular interest is the case \(\mathbf{r} = \mathbf{r}'\) – in the thermodynamic limit

\[
G(\mathbf{r}, \mathbf{r}; \omega) = \rho_0 \int_{-D}^D d\epsilon \frac{1}{-\beta^2 - \epsilon^2} \frac{1}{(\omega + \epsilon + i\delta - \Delta)} \begin{pmatrix}
\omega + \epsilon + i\delta & -\Delta \\
-\Delta^* & \omega - \epsilon + i\delta
\end{pmatrix} 
\]

(C.30)

where \(\beta^2 := |\Delta|^2 - (\omega - i\delta)^2\). For every term in the matrix, excluding those with \(\epsilon\) in the numerator, the integral is precisely the same one we evaluated to obtain Eq. A.7. The
integrals with $\varepsilon$ in the numerator vanish, because the integrand is odd. Finally, care must be taken when setting $\delta = 0^+$ in the final expression, because doing so introduces a singularity at $\omega = 0$. To handle the singularity we introduce a broadening $\Gamma$. Physically, the broadening can be used to describe the effects of disorder in the superconductor.[82]

Therefore, the Green’s function of a SC for $\mathbf{r} = \mathbf{r}'$ is

$$G(\mathbf{r}, \mathbf{r}; \omega) = -\left(\pi \rho_0\right) \frac{1}{\sqrt{|\Delta|^2 - (\omega + i \Gamma)^2}} \begin{pmatrix} \omega + i \Gamma & -\Delta \\ -\Delta^* & \omega + i \Gamma \end{pmatrix}. \quad (C.31)$$
Appendix D

Green’s Function for a Two-Dimensional Electron Gas

Consider a two-dimensional electron gas (2DEG) with Hamiltonian

\[ \hat{H} = \sum_{p,s} \varepsilon_p c_{p,s}^\dagger c_{p,s} \]  \hspace{1cm} (D.1)

where \( \varepsilon_p = (1/2m)p^2 - E_F \) and \( \{c_{p,s}\} \) are creation and annihilation operators for an electron with momentum \( p \) and spin \( s \). [Note: we are measuring energies with respect to the Fermi energy \( E_F \).]

Consider the (superconducting) Green’s function of such a system (Eq. C.25). To proceed, expand the field operators in a plane wave basis: \( \psi_s(r) = (1/\sqrt{A}) \sum_p e^{ip \cdot r} c_{p,s} \). Carrying out the expansion and Fourier transforming the equations in time gives

\[ G_{11}(r, r'; \omega) = \frac{1}{A} \sum_p \frac{e^{ip \cdot (r-r')}}{\omega - \varepsilon_p + i\delta} \]  \hspace{1cm} (D.2a)

\[ G_{12}(r, r'; \omega) = 0 \] \hspace{1cm} (D.2b)

\[ G_{21}(r, r'; \omega) = 0 \] \hspace{1cm} (D.2c)

\[ G_{22}(r, r'; \omega) = \frac{1}{A} \sum_p \frac{e^{-ip \cdot (r-r')}}{\omega + \varepsilon_p + i\delta} \] \hspace{1cm} (D.2d)

where we have inserted a convergence factor \( \delta(= 0^+) \).
We will evaluate the Green’s function in the thermodynamic limit. To that end, start by considering the \((1, 1)\) element of the Green’s function, Eq. D.2a. Go to an integral over momentum states and write the variables in polar coordinates \(p = (p, \theta)\) with \((r - r') := R = (R, \phi)\). One obtains

\[
G_{11}(r, r'; \omega) = \frac{1}{(2\pi)^2} \int_0^\infty dp \frac{p}{(k^2 - p^2)/2m + i\delta} \int_0^{2\pi} d\theta e^{ipR\cos(\theta - \phi)}
\]

where \(k := \sqrt{2m(E_F + \omega)}.\) Since the angular integrand has a period of \(2\pi\), \(\phi\) has no effect on the result (there is no preferred direction for the system): set \(\phi = 0\) for convenience. By use of Eq. 3.339 in [26] one finds

\[
\int_0^{2\pi} d\theta e^{ipR\cos(\theta)} = 2\pi J_0(pR)\]

where \(J_0\) is a Bessel function of first kind.[26] Thus

\[
G_{11}(r, r'; \omega) = -2\rho_0 \int_0^\infty dp \frac{pJ_0(pR)}{p^2 + (-k^2 - i2m\delta)}
\]

where \(\rho_0 = m/2\pi\) is the 2D electron density of states. Consider equation 6.532-4 in [26]:

\[
\int_0^\infty dp \frac{pJ_0(pa)}{p^2 + \beta^2} = K_0(\alpha\beta), \quad [\alpha > 0, \text{Re}[\beta] > 0]
\]

where \(K_0\) is a modified Bessel function.[26] One must be careful to ensure that the necessary conditions for Eq. D.5 to hold are met. In this case, we can only apply the formula if \(R > 0\) and \(\text{Re}[\pm i\sqrt{k^2 + i2m\delta}] > 0\).

\(R > 0\): Since \(R = |r - r'|\) we have \(R \geq 0\). Thus the condition is met so long as \(r \neq r'\). For the case of \(R = 0\) (or \(r = r'\)) the Green’s function element must be handled separately (see below).

\(\text{Re}[\pm i\sqrt{k^2 + i2m\delta}] > 0\): Since \(k > 0\) and \(\delta = 0^+\), the location of \(\pm i\sqrt{k^2 + i2m\delta}\) in the complex plane has the form shown in Fig. D.1. Therefore to ensure the condition is met one must take \(\pm \rightarrow -\).

This gives

\[
G_{11}(r, r'; \omega) = -2\rho_0 K_0(-iR\sqrt{k^2 + i2m\delta}).
\]

(D.6)
Figure D.1: Arguments for the Green’s function – the phase $\pm i\sqrt{k^2 + i2m\delta}$ is shown in the complex plane to ensure the proper Hankel function is chosen.

Notice how this result is only valid because of the convergence factor $\delta$. Without it, the real part would be zero and the result would be ill-defined. Now, depending on the phase of the variable, one can write the modified Bessel function in terms of Hankel functions two different ways:[26]

$$K_0(z) = i(\pi/2) H_0^{(1)}(iz) \quad , \quad [-\pi < \arg(z) \leq \pi/2] \quad (D.7a)$$

$$K_0(z) = -i(\pi/2) H_0^{(2)}(-iz) \quad , \quad [-\pi/2 < \arg(z) \leq \pi] . \quad (D.7b)$$

Only Eq. D.7a remains well-defined as we take $\delta \to 0^+$ (see Fig. D.1). Thus, for $\mathbf{r} \neq \mathbf{r}'$

$$G_{11}(\mathbf{r}, \mathbf{r}'; \omega) = -i(\pi\rho_0) H_0^{(1)}(k|\mathbf{r} - \mathbf{r}'|) \quad (D.8)$$

where $\delta$ was formally taken to zero. For the case that $\mathbf{r} = \mathbf{r}'$ we return to Eq. D.2a – in the thermodynamic limit this sum becomes Eq. A.4. Therefore, the first element of the Green’s function is

$$G_{11}(\mathbf{r}, \mathbf{r}'; \omega) = \begin{cases} 
-i(\pi\rho_0) H_0^{(1)}(k|\mathbf{r} - \mathbf{r}'|) & , \quad \mathbf{r} \neq \mathbf{r}' \\
-i(\pi\rho_0) + \rho_0 \ln \left( \frac{E_F + \omega}{\Delta - \omega} \right) & , \quad \mathbf{r} = \mathbf{r}' .
\end{cases} \quad (D.9)$$

Now, only the $(2, 2)$ element remains to be determined. To do this, we follow the same procedure used to compute the previous element. Start by working in the thermodynamic
limit and writing the variables in polar coordinates \( p = (p, \theta) \) with \((r - r') := R = (R, \phi)\). Using the same arguments above, we arrive at

\[
G_{22}(r, r'; \omega) = 2 \rho_0 \int_0^\infty dp \frac{p J_0(pR)}{p^2 + (-k^2 + i2m\delta)}
\]

where \( k := \sqrt{2m(E_F - \omega)} \), \( \rho_0 \) is the electron’s density of states, and \( J_0 \) is a Bessel function.[26]

Again make use of Eq. D.5; however, in this case, the equation is only valid if \( R > 0 \) and \( \text{Re}[\pm i\sqrt{k^2 - i2m\delta}] > 0 \). This means we have to consider the case of \( R = 0 \) separately and we’re forced to take \( \pm \to + \). Therefore the element is \( G_{22}(r, r'; \omega) = 2 \rho_0 K_0(iR\sqrt{k^2 - i2m\delta}) \)

where \( K_0 \) is a modified Bessel function.[26] We write the equation in terms of the Hankel functions using Eq. D.7b (because the result remains well-defined when we take \( \delta \to 0^+ \)):

\[
G_{22}(r, r'; \omega) = -i(\pi \rho_0) H_0^{(2)}(k|r - r'|)
\]

For the case \( r = r' \) we return to Eq. D.2d and compute the sum in the thermodynamic limit. [The integral is almost identical to the example considered in Appendix A.] Therefore, one finds the last element of the Green’s function is

\[
G_{22}(r, r'; \omega) = \begin{cases} 
-\i\pi \rho_0 H_0^{(2)}(k|r - r'|) & , \ r \neq r' \\
-i\pi \rho_0 - \rho_0 \ln\left(\frac{E_F - \omega}{E_F + \omega}\right) & , \ r = r' 
\end{cases}
\]

To summarize, the (superconducting) Green’s function of a 2DEG is

\[
G(r, r'; \omega) = \begin{pmatrix} 
G_{11}(r, r'; \omega) & 0 \\
0 & G_{22}(r, r'; \omega)
\end{pmatrix}
\]

where

\[
G_{11}(r, r'; \omega) = \begin{cases} 
-\i\pi \rho_0 H_0^{(1)}(k_+|r - r'|) & , \ r \neq r' \\
-i\pi \rho_0 + \rho_0 \ln\left(\frac{E_F + \omega}{E_F - \omega}\right) & , \ r = r'
\end{cases}
\]

\[
G_{22}(r, r'; \omega) = \begin{cases} 
-\i\pi \rho_0 H_0^{(2)}(k_-|r - r'|) & , \ r \neq r' \\
-i\pi \rho_0 - \rho_0 \ln\left(\frac{E_F - \omega}{E_F + \omega}\right) & , \ r = r'
\end{cases}
\]

and we have defined \( k_\pm := \sqrt{2m(E_F \pm \omega)} \).
Appendix E

Effective Scattering Potentials

Consider a system with an impurity atom on the surface at position $r_0$. As discussed in Chapter 1, the bare system (i.e. the system without the impurity) has bulk states which are orthogonal to the surface state; however, the impurity couples the surface and bulk.[12] The Hamiltonian for the system is (see Chapter 1)

$$
\hat{H} = \hat{H}_0 + U \sum_s \psi_s^\dagger(r_0)\psi_s(r_0) + C \sum_s \left[ \psi_s^\dagger(r_0)\chi_s(r_0) + \chi_s^\dagger(r_0)\psi_s(r_0) \right]
$$

(E.1)

where $\hat{H}_0$ is the system’s bare Hamiltonian, $U$ is the strength of potential scattering (in the s-wave channel), $C$ is the strength of the coupling between the surface and the bulk, and $\psi_s(r)$ ($\chi_s(r)$) are the electron field operators for the surface (bulk).

As we are interested in the physics of the surface, and ultimately surface Green’s functions, we integrate out the bulk – for the case of a superconducting bulk, one obtains a Dyson equation for the surface\textsuperscript{1}

$$
G_{\text{surface}}(r, r'; \omega) = G_{\text{surface}}^0(r, r'; \omega) + G_{\text{surface}}^0(r, r_0; \omega)V_0(\omega)G_{\text{surface}}(r_0, r'; \omega)
$$

(E.2)

where $G_{\text{surface}}^0(r, r'; \omega)$ is the bare Green’s function for the surface electrons and the effective

\textsuperscript{1}E. H. Kim, unpublished
scattering potential is given by

\[
V_0(\omega) = U\tau^3 + C^2\tau^3 G^0_{\text{bulk}}(r_0, r'_0; \omega)\tau^3.
\]  

(E.3)

In the above equation, \(\tau^\mu\) are Pauli matrices in Nambu space and \(G^0_{\text{bulk}}(r, r'; \omega)\) is the bare Green’s function for the bulk electrons. Inserting Eq. C.31 into Eq. E.3 gives

\[
V_0(\omega) = (U\tau^3 + QI + D\tau^1)/\pi \rho_{\text{surface}}
\]  

(E.4)

where we introduced dimensionless quantities \(U := \pi \rho_{\text{surface}} U\) and \(C := (\pi \rho_{\text{surface}} C)(\pi \rho_{\text{bulk}} C)\) using the surface (bulk) electron density of states \(\rho_{\text{surface}} (\rho_{\text{bulk}})\) and defined

\[
Q := C\frac{-(\omega + i\Gamma)}{\sqrt{\Delta^2 - (\omega + i\Gamma)^2}} \]  

(E.5a)

\[
D := C\frac{-\Delta}{\sqrt{\Delta^2 - (\omega + i\Gamma)^2}}.
\]  

(E.5b)

For the case of an ordinary metallic bulk, we take \(\Delta \to 0\) and focus on the elements in the \((1, 1)\) block of the Green’s function, \(G_{11}^{\text{surface}}(r, r'; \omega)\). The effective potential is then

\[
V_0(\omega) = (U - iC)/\pi \rho_{\text{surface}}.
\]  

(E.6)

**E.1 Black-dot Approximation**

It has been shown that one achieves quantitative agreement with experiment by treating an impurity in the *black-dot approximation* – one takes the coupling between the surface and the bulk (due to the atom) to be so strong that “ordinary” scattering can be ignored, \(U \to 0\); the strength of the coupling between surface and bulk states is chosen to give half the amplitude of the T-matrix for a unitary scatterer.[12]
Appendix F

Spin Operators

F.1 Spin Density Operator

For an $N$ particle spin−1/2 system, the spin density operator at position $r$ is

$$S(r) = \sum_{i=1}^{N} \frac{1}{2} \sigma \delta(\hat{r}_i - r)$$  \hspace{1cm} (F.1)

where $\hat{r}_i$ is the position operator of particle $i$ and $\{\sigma^\mu\}$ are Pauli matrices in spin space. Writing Eq. F.1 in second quantized form gives

$$S(r) = \sum_{s,s'} \frac{1}{2} \psi^\dagger_s(r) \bar{\sigma}_{s,s'} \psi_{s'}(r)$$  \hspace{1cm} (F.2)

where $\{\psi_s(r)\}$ are the system’s field operators. Succinctly, $S(r) = (S^x(r), S^y(r), S^z(r))$ where

$$S^x(r) = \frac{1}{2} \left[ \psi^\dagger_\uparrow(r) \psi^\downarrow(r) + \psi^\dagger_\downarrow(r) \psi^\uparrow(r) \right]$$  \hspace{1cm} (F.3a)

$$S^y(r) = -\frac{i}{2} \left[ \psi^\dagger_\uparrow(r) \psi^\downarrow(r) - \psi^\dagger_\downarrow(r) \psi^\uparrow(r) \right]$$  \hspace{1cm} (F.3b)

$$S^z(r) = \frac{1}{2} \left[ \psi^\dagger_\uparrow(r) \psi^\uparrow(r) - \psi^\dagger_\downarrow(r) \psi^\downarrow(r) \right]$$  \hspace{1cm} (F.3c)
The angular momentum raising and lowering operators for $S(r)$ are then

$$ S^+(r) = \psi^\dagger_\downarrow(r) \psi_\uparrow(r) $$  \hspace{1cm} (F.4a)  

$$ S^-(r) = \psi^\dagger_\uparrow(r) \psi_\downarrow(r) $$  \hspace{1cm} (F.4b)  

where $S^\pm = S^x \pm i S^y$.\textsuperscript{[24]}

### F.2 Spin-Spin Coupling

Consider the coupling between two spin operators: $\bar{\tau} \cdot S$. It is readily shown that

$$ \bar{\tau} \cdot S = \frac{1}{2}(\tau^+ S^- + \tau^- S^+) + \tau^z S^z. \hspace{1cm} (F.5) $$

Employing a fermionic representation for the spin operators gives $\bar{\tau} = (1/2) \sum_{s,s'} f^\dagger_s \sigma_{s,s'} f_{s'}$ (S = $(1/2) \sum_{s,s'} \psi^\dagger_s \sigma_{s,s'} \psi_{s'}$) where $\{f_s\}$ ($\{\psi_s\}$) are fermionic annihilation operators and $\{\sigma^\mu\}$ are the Pauli matrices. Eq. F.5 is then

$$ \bar{\tau} \cdot S = \frac{1}{2} \left( f^\dagger_\uparrow f_\downarrow \psi^\dagger_\uparrow \psi_\downarrow + f^\dagger_\downarrow f_\uparrow \psi^\dagger_\downarrow \psi_\uparrow \right) + \frac{1}{4} \left( f^\dagger_\uparrow f_\uparrow - f^\dagger_\downarrow f_\downarrow \right) \left( \psi^\dagger_\uparrow \psi_\uparrow - \psi^\dagger_\downarrow \psi_\downarrow \right). \hspace{1cm} (F.6) $$

Using the fact that fermions for $\bar{\tau}$ are a different species than those for $S$, the $\{f_s\}$ and $\{\psi_s\}$ operators anticommute. By using the fermion anticommutation relations, one can write Eq. F.6 as

$$ \bar{\tau} \cdot S = -\frac{1}{2} \sum_{s,s'} (\psi^\dagger_\downarrow f_s)(f^\dagger_\uparrow \psi_{s'}) + \frac{1}{4} (2 - \sum_s f^\dagger_\downarrow f_s) \sum_{s'} \psi^\dagger_\downarrow \psi_{s'}. \hspace{1cm} (F.7) $$

In this Thesis, we are interested in the case where $\bar{\tau}$ describes a magnetic impurity. In this case, there is a constraint on the Hilbert space; namely, that there is always a single (spin-up or spin-down) fermion on the impurity site: $\sum_s f^\dagger_\downarrow f_s = 1$. Hence, the second term in Eq. F.7 reduces to $(1/4) \sum_s \psi^\dagger_\downarrow \psi_s$. Furthermore, $S$ will represent the electrons’ spin density operator at the impurity site – $\sum_s \psi^\dagger_\downarrow \psi_s$ is a local potential scattering term (at the impurity site). As this term simply gives a small renormalization of the density of states at the impurity site, it is typically ignored.
Appendix G

Green’s Functions with Magnetic Impurities

G.1 Green’s Functions for the Magnetic Atom

Recall from Chapter 3 the mean-field Hamiltonian suitable to describe a magnetic atom (MA) in a bare system (namely, a metal or quantum corral) is

\[ \hat{H} = \sum_{n,s} \varepsilon_n c_{n,s}^\dagger c_{n,s} + \lambda \sum_s f_s^\dagger f_s - \chi \sum_s f_s^\dagger \psi_s(\mathbf{r}_0) - \chi^* \sum_s \psi_s^\dagger(\mathbf{r}_0) f_s \]  

(G.1)

where \( \{c_{n,s}\} \) are creation and annihilation operators for the bare system (with eigenvalues \( \{\varepsilon_n\} \)), \( \psi_s(\mathbf{r}_0) \) is the bare system’s electron field operator at the position of the MA with spin-\( s \), and \( \{f_s\} \) are creation and annihilation operators for the impurity spin.

Consider the Green’s functions

\[ G(t) = -i\Theta(t) \langle \{f_s(t), f_s^\dagger\} \rangle \]  

(G.2a)

\[ F(t) = -i\Theta(t) \langle \{\psi_s(\mathbf{r}_0; t), f_s^\dagger\} \rangle . \]  

(G.2b)

To compute these, we employ the equations of motion method[28] – we differentiate \( G(t) \) and \( F(t) \) with respect to time and obtain the (differential) equations satisfied by these
functions. Starting with $G(t)$, one obtains

$$i\partial_t G(t) = \delta(t) - i\Theta(t) \langle \{i\partial_t f_s(t), f_s^\dagger \} \rangle$$  \hfill (G.3)

where it was used that $\partial_t \Theta(t) = \delta(t)$, $\{f_s, f_s^\dagger\} = 1$, and that the Hamiltonian is time-independent. Then, the derivative of the magnetic atom’s annihilation operator is computed using the Heisenberg equation of motion: $i\partial_t f_s(t) = [f_s(t), \hat{H}].$ Since the $\{f_s\}$ and $\{c_n,s\}$ represent different species of fermions, the operators anticommute; using this one obtains $i\partial_t f_s(t) = \lambda f_s(t) - \chi \psi_s(r_0; t)$. Then Eq. G.3 becomes

$$i\partial_t G(t) = \delta(t) + \lambda G(t) - \chi F(t) .$$  \hfill (G.4)

To proceed, expand the field operators in the eigenstates of the bare system:

$$F(t) = \sum_n \phi_n(r_0) F_n(t)$$  \hfill (G.5)

where we have introduced the Green’s function $F_n(t) := -i\Theta(t) \langle \{c_{n,s}(t), f_s^\dagger \} \rangle$. Taking the derivative of $F_n(t)$ with respect to time, one obtains

$$i\partial_t F_n(t) = \varepsilon_n F_n(t) - \chi^* \phi_n^*(r_0) G(t) .$$  \hfill (G.6)

Fourier transforming Eq. G.4, G.5, and G.6 gives

$$1 = (\omega - \lambda) G(\omega) + \chi F(\omega)$$  \hfill (G.7a)

$$F(\omega) = \sum_n \phi_n(r_0) F_n(\omega)$$  \hfill (G.7b)

$$F_n(\omega) = -\chi^* \frac{\phi_n^*(r_0)}{\omega - \varepsilon_n} G(\omega)$$  \hfill (G.7c)

By inserting Eq. G.7c into Eq. G.7b one obtains a linear system of equations:

$$\begin{pmatrix} \omega - \lambda & \chi \\ \chi^* G_0(r_0, r_0; \omega) & 1 \end{pmatrix} \begin{pmatrix} G(\omega) \\ F(\omega) \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$  \hfill (G.8)
where $G_0(r_0, r_0; \omega)$ is the bare Green’s function of the system. Inverting the matrix gives

$$G(\omega) = \frac{1}{\omega - \lambda + i\Gamma}$$  \hspace{1cm} (G.9a)

$$F(\omega) = \frac{i(\Gamma/\chi)}{\omega - \lambda + i\Gamma}$$ \hspace{1cm} (G.9b)

where the broadening has been defined as $\Gamma := i|\chi|^2G_0(r_0, r_0; \omega)$.

### G.1.1 Mean-Field Equations

These Green’s functions allow one to compute $\lambda$ and $\chi$ (or $\Gamma$) self-consistently via Eqs. 3.11 and 3.13. We compute the expectation values, using the spectral representation (Appendix B); this is allowed because $\langle f_s^\dagger f_s \rangle \in \mathbb{R}$ and we will take $\langle \psi_s^\dagger(r_0)f_s \rangle \in \mathbb{R}$ (which means $\chi \in \mathbb{R}$). $G(t)$ ($F(t)$) is used to obtain an expression for $\langle f_s^\dagger f_s \rangle$ ($\langle \psi_s^\dagger(r_0)f_s \rangle$). It is straightforward to show that the spectral functions are

$$-\frac{1}{\pi} \text{Im}[G(\omega)] = \frac{1}{\pi} \frac{\Gamma}{(\omega - \lambda)^2 + \Gamma^2}$$ \hspace{1cm} (G.10a)

$$-\frac{1}{\pi} \text{Im}[F(\omega)] = -\frac{1}{\pi} \frac{\Gamma}{\chi} \frac{(\omega - \lambda)}{(\omega - \lambda)^2 + \Gamma^2}$$ \hspace{1cm} (G.10b)

From here, one can write the expectation values in the spectral representation. By inserting these results into Eq. 3.11 and Eq. 3.13 one obtains the mean-field equations

$$\frac{\pi}{2} = \int_{-\infty}^{\infty} d\omega f(\omega) \frac{\Gamma}{(\omega - \lambda)^2 + \Gamma^2}$$ \hspace{1cm} (G.11a)

$$\frac{i\pi}{\mathcal{F}G_0(r_0, r_0; \omega)} = \int_{-\infty}^{\infty} d\omega f(\omega) \frac{(\omega - \lambda)}{(\omega - \lambda)^2 + \Gamma^2}$$ \hspace{1cm} (G.11b)

where $f(\omega)$ is the Fermi function.

For the case that the bare system is a metal, the bare Green’s function is given by Eq. A.5 in the wide-band limit: $G_0(r_0, r_0; \omega) = -i\pi\rho_0$ where $\rho_0$ is the electron density of states. This simplifies the broadening to $\Gamma = \pi\rho_0\chi^2$ as well as the mean-field equations above.
G.2 Green’s Function for the Conduction Electrons

Once again, consider the mean-field Hamiltonian for a MA in a bare system (Eq. G.1).

Now, we want the Green’s function for the conduction electrons

\[ G(r, r'; t) = -i\Theta(t) \langle \{\psi_s(r; t), \psi^\dagger_s(r')\} \rangle. \] (G.12)

As before, we will obtain \( G(r, r'; t) \) using the equations of motion method; however, it will prove useful to first expand the field operators in the eigenstates of the bare system: \( \psi_s(r) = \sum_n \phi_n(r)c_{n,s}. \) Doing so yields

\[ G(r, r'; t) = \sum_{n,m} \phi_n(r)\phi^*_m(r')G_{n,m}(t) \] (G.13)

where we have defined the following Green’s function

\[ G_{n,m}(t) := -i\Theta(t) \langle \{c_{n,s}(t), c^\dagger_{m,s}(t')\} \rangle. \] (G.14)

To aid in the analysis, we introduce a secondary time[28] by letting \( t \to t - t' \) and using that \( G(t - t') = G(t, t') \); namely, \( G_{n,m}(t, t') = -i\Theta(t - t') \langle \{c_{n,s}(t), c^\dagger_{m,s}(t')\} \rangle. \) We now employ the equations of motion by differentiating this Green’s function with respect to the first time variable, \( t \):

\[ i\partial_t G_{n,m}(t, t') = \delta_{n,m}\delta(t - t') + \varepsilon_n G_{n,m}(t, t') - \chi^*\phi^*_n(r_0)F_m(t, t') \] (G.15)

where \( F_m(t) \) is defined as

\[ F_m(t) := -i\Theta(t) \langle \{f_s(t), c^\dagger_{m,s}\} \rangle. \] (G.16)

To proceed, differentiate this equation with respect to the second time variable, \( t' \):

\[ i\partial_{t'} F_m(t, t') = -\varepsilon_m F_m(t, t') + \chi\phi_m(r_0)G(t, t') \] (G.17)
where \( G(t) = -i\Theta(t) \langle \{ f_s(t), f_s^\dagger \} \rangle \). Fourier transforming equations G.15 and G.17 gives

\[ \delta_{n,m} = (\omega - \varepsilon_n)G_{n,m}(\omega) + \chi^* \phi_n^\ast(r_0)F_m(\omega) \]  

\[ 0 = (\omega - \varepsilon_m)F_m(\omega) + \chi \phi_m(r_0)G(\omega) \]  

(Solving Eq. G.18b for \( F_m(\omega) \) and inserting the result into Eq. G.18a gives

\[ G_{n,m}(\omega) = \delta_{n,m} \frac{\phi_n^\ast(r_0)}{\omega - \varepsilon_n} + \frac{\phi_n^\ast(r_0)}{\omega - \varepsilon_n} \chi^2 G(\omega) \frac{\phi_m(r_0)}{\omega - \varepsilon_m}. \]  

From Eq. G.19 one obtains the system’s Green’s function as

\[ G(r, r'; \omega) = G_0(r, r'; \omega) + G_0(r, r_0; \omega)T(\omega)G_0(r_0, r'; \omega) \]  

where \( G_0(r, r'; \omega) \) is the system’s bare Green’s function, and we have defined the T-matrix \( T(\omega) := |\chi|^2 G(\omega) \).

### G.3 Green’s Function for Two Magnetic Atoms in a Metal

Consider the mean-field Hamiltonian for two MAs in a bare system (namely, a metal or quantum corral):

\[ \hat{H} = \sum_{n,s} \varepsilon_n c_n^\dagger c_{n,s} + \sum_{i=1}^2 \left[ \lambda_i \sum_s f_{i,s}^\dagger f_{i,s} - \chi_i \sum_s f_{i,s}^\dagger \psi_s(r_i) - \chi_i^* \sum_s \psi_s^\dagger(r_i) f_{i,s} \right] - \Phi \sum_s f_{1,s}^\dagger f_{2,s} - \Phi^* \sum_s f_{2,s}^\dagger f_{1,s} \]  

where \( \{ c_{n,s} \} \) are creation and annihilation operators for the bare system (with energy eigenvalues \( \{ \varepsilon_n \} \)), \( \psi_s(r_i) \) is the bare system’s electron field operator at the position of MA \( i \) with spin-\( s \), and \( \{ f_{i,s} \} \) are creation and annihilation operators for MA \( i \). Consider the Green’s function of the system:

\[ G(r, r'; t) = -i\Theta(t) \langle \{ \psi_s(r; t), \psi_s^\dagger(r') \} \rangle. \]
Our goal is to compute its Fourier transform. To proceed, use the exact same approach outlined in the previous section for a single MA. Start by expanding the field operators in the eigenstates of the bare system. Doing so yields

\[
G(r, r'; t) = \sum_{n,m} \phi_n(r) \phi^*_m(r') G_{n,m}(t) \tag{G.23}
\]

where we have defined the following Green’s function

\[
G_{n,m}(t) := -i\Theta(t) \langle \{ c_{n,s}(t), c_{m,s}^\dagger(t) \} \rangle . \tag{G.24}
\]

Once again, we introduce a secondary time \( t \rightarrow t - t' \). Employ the equations of motion by differentiating the Green’s function with respect to the first time variable, \( t \):

\[
i\partial_t G_{n,m}(t, t') = \delta_{n,m}(t - t') + \varepsilon_n G_{n,m}(t, t') - \sum_i \chi_i^* \phi_n^*(r_i) F_{i,m}(t, t') \tag{G.25}
\]

where \( F_{i,m}(t) \) is defined as

\[
F_{i,m}(t) := -i\Theta(t) \langle \{ f_{i,s}(t), c_{m,s}^\dagger(t) \} \rangle . \tag{G.26}
\]

To proceed, differentiate this equation with respect to the second time variable, \( t' \):

\[
i\partial_{t'} F_{i,m}(t, t') = -\varepsilon_m F_{i,m}(t, t') + \sum_j \chi_j \phi_m(r_j) G_{i,j}(t, t') \tag{G.27}
\]

where

\[
G_{i,j}(t) := -i\Theta(t) \langle \{ f_{i,s}(t), f_{j,s}^\dagger(t) \} \rangle \tag{G.28}
\]

Fourier transforming equations G.25 and G.27 yields

\[
\delta_{n,m} = (\omega - \varepsilon_n) G_{n,m}(\omega) + \sum_i \chi_i^* \phi_n^*(r_i) F_{i,m}(\omega) \tag{G.29a}
\]

\[
0 = (\omega - \varepsilon_m) F_{i,m}(\omega) + \sum_j \chi_j \phi_m(r_j) G_{i,j}(\omega) \tag{G.29b}
\]
Solving Eq. G.29b for $F_{i,m}(\omega)$ and inserting the result into Eq. G.29a gives

$$G_{n,m}(\omega) = \frac{\delta_{n,m}}{\omega - \varepsilon_n} + \sum_{i,j} \frac{\phi_n^*(r_i)}{\omega - \varepsilon_n} \chi_i^* G_{i,j}(\omega) \chi_j \frac{\phi_m(r_j)}{\omega - \varepsilon_m}. \quad (G.30)$$

From Eq. G.30 one obtains the system’s Green’s function as

$$G(r, r'; \omega) = G_0(r, r'; \omega) + \sum_{i,j=1}^{2} G_0(r, r_i; \omega) \hat{T}_{i,j}(\omega) G_0(r_j, r'; \omega) \quad (G.31)$$

where $G_0(r, r'; \omega)$ is the bare system’s Green’s function and the T-matrix has been defined as $\hat{T}_{i,j}(\omega) := G_{i,j}(\omega) \chi_i^* \chi_j$. 
Bibliography


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