Local Electronic Structure of Defects in Superconductors

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I. Introduction .................................................................................................................. 138
   1. The Importance of Defects in Understanding Homogeneous Systems .................... 138
   2. Introduction to Scanning Tunneling Microscopy ..................................................... 140
   3. Atomic-Scale Structure in Condensed Electron Systems ....................................... 141
   4. The Koster-Slater Technique ................................................................................. 142
   5. Outline of This Chapter ........................................................................................ 143

II. Bulk Properties of Defects in Superconductors ...................................................... 144
   6. Models of the Formation of a Magnetic Moment in a Superconductor .................... 144
   7. Defects in Isotropic Order-Parameter Superconductors ........................................ 146
   8. Defects in Anisotropic Order-Parameter Superconductors .................................. 150

III. Techniques for Calculating the Local Properties of Defects in Superconductors ...... 152
   9. Coarse-Grained Theories of Local Properties ...................................................... 152
   10. Bogoliubov-de Gennes Equations ........................................................................ 154
   11. Koster-Slater Inversion Formalism ..................................................................... 164

IV. Analytic Solution of the Point Potential .................................................................. 171
   12. Particle-Hole Symmetry in the Normal State ....................................................... 173
   13. Magnetic and Nonmagnetic Point Potentials in a Superconductor with an Isotropic Order Parameter ................................................................. 176
   14. Anisotropic Order Parameters ............................................................................ 179
   15. Connection to the Born Approximation ................................................................ 181

V. Impurities in Superconductors with Isotropic Order Parameters ............................ 184
   16. Nonmagnetic Impurity ....................................................................................... 184
   17. Magnetic Impurity ............................................................................................... 189
   18. Combined Magnetic and Nonmagnetic Potentials ................................................ 204
   19. Connection to Normal-State df/dV Spectra .......................................................... 206
   20. Pairing Suppression ............................................................................................. 208
   21. Comparison of Local Electronic Structure Near Impurities with That Near Vortices ................................................................................................................. 210

VI. Impurities in Superconductors with Anisotropic Order Parameters ....................... 212
   22. Energy and Character of Resonances ................................................................... 212
   23. Differential Conductance and Local Density of States ......................................... 215
   24. Local Distortion of the Order Parameter ............................................................. 219
   25. Planar Tunneling .................................................................................................. 223

VII. Brief Discussion of Recent Results for Dynamical Spins ........................................ 224
I. Introduction

1. The Importance of Defects in Understanding Homogeneous Systems

Condensed matter physics is largely based on relating atomic-scale properties to macroscopic properties. The probes available to the field have favored this approach. For instance, x-ray diffraction provides detailed information about the Fourier transform of lattice positions averaged over many lattice spacings. Such diffraction techniques have atomic-scale resolution only to the extent that structures are periodic, or, such as in the case of liquids, quasi-homogeneous. Macroscopic measurements (e.g., of thermodynamic quantities) are easiest to analyze in terms of homogeneous (clean) samples. Areas of intensive research have focused on making systems more and more homogeneous, primarily by removing defects from the crystalline matrix. As a result, momentum-based perspectives have dominated condensed matter theory, due to the nature of the available experimental techniques and the technological importance of clean crystalline structures.

The advent of scanning probe microscopies offers a new way to directly examine the local properties without a need for periodicity or homogeneity. Many materials of current interest are not periodic or homogeneous, and as a result momentum is not a good quantum number. Important examples include some solids, such as glasses, disordered alloys, and amorphous silicon. Examples of phenomena in these systems that are best described in real space include variable-range hopping, localization, and long-range (RKKY) interactions. Soft condensed matter systems, such as polymers, membranes, or vortex phases in superconductors, are also systems where momentum-based perspectives can be clumsy. The physics of the entanglement of vortices or polymers, and of the constrained geometry of membranes, is more naturally explored in real space.

Additional important areas of interest where a local perspective is useful concern situations where translational symmetry is broken at an interface. In this category are real-space models of the proximity effect at the interface of a superconductor. Local probes based on scanning tunneling microscopy (STM) have been used recently to probe the details of the proximity effect, such as the order parameter suppression induced by gold islands on a niobium surface. In semiconductor heterostructures, where interfaces are important, the dominant physical picture is a real-space-based envelope function model. Traditional experimental information about such systems, however, has involved that which can be measured far from the interface, such as the current through the structure.

Even when momentum is a good quantum number there are advantages to the real-space viewpoint if interactions are localized. This is the case for Cooper pairs in a superconductor. Whereas the ordinary isotropic order parameter superconductor is usually modeled with an interaction of zero range, anisotropic superconductors are naturally modeled by interactions with finite but small range. An example is the $d_{xy}$ order parameter believed to dominate in high-temperature superconductors, which can be produced by nearest-neighbor interactions on a square lattice.

Scanning probe microscopies place more of an emphasis on real-space concepts and, thereby, help redefine what materials and situations are of interest. In this chapter the focus will be on the ability of a scanning tunneling microscope to probe the local density of states in a superconductor when translational symmetry is broken. The pump-probe language of driven systems can be appropriated to understand this type of physical situation. Consider an impurity, step-edge, or grain boundary as a local pump that perturbs the otherwise homogeneous material; the STM in spectroscopic mode serves as a probe that examines the local response to reveal length-dependent properties on the atomic scale. Traditional techniques lose this information due to the inhomogeneous broadening of features in experimental data, thus driving the need for sample purity. In contrast, scanning probe microscopies use the pervasive inhomogeneity of real materials to their advantage. An elegant example is the use of STM to measure the electronic structure near individual impurity atoms or step edges on noble-metal surfaces.

From information on the local electronic structure near these defects the dispersion relation of the surface state present on the homogeneous metal surface can be obtained.

The interplay of interactions and disorder has been a recurring theme in condensed matter physics. Here we will describe the use of the localized spectroscopic capabilities of STM to study how the best understood of interacting elec-

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2. See, for example, P. G. de Gennes, Superconductivity of Metals and Alloys, Addison-Wesley, Reading, MA (1989).
tron systems, a conventional low-$T_c$ superconductor, responds to impurities. The local structure around an impurity if the superconductor has anisotropic pairing (as in the high-$T_c$ superconducting cuprates) will also be presented. These are demonstrations of the use of real-space techniques to understand the localized spectroscopy of inhomogeneous superconductivity both for intrinsic interest and as an indicator of how STM and general scanning probe microscopies (SPM) may enhance the understanding of disordered correlated electron systems in the future.

2. INTRODUCTION TO SCANNING TUNNELING MICROSCOPY

The scanning tunneling microscope$^8$-$^{10}$ is an atomically sharp wire that can be positioned close enough to a surface for electrons to tunnel across the energy barrier constituted by the work function of the STM tip and sample surface. The tip can be scanned over the surface via a piezolectric “walker” or other mechanical means. The STM current $I$ is related to the tip height $z$ and the tip-surface voltage $V$, by

$$ I \propto e^{2\kappa z} \int d\omega \{1 - n(\omega - eV)\} \sum_{\sigma, \eta} |\psi_{\sigma, \eta}(\mathbf{r})|^2 \delta(\omega - E_\eta), \hspace{1cm} (2.1) $$

where $e$ is the charge of the electron, $n(\omega)$ is the Fermi function in the sample, and

$$ n(\omega - eV) = n_{STM}(\omega) = \left[ 1 + \exp\left(\frac{\omega - eV}{k_B T}\right) \right]^{-1} \hspace{1cm} (2.2) $$

is the Fermi function in the STM tip. $T$ is the temperature and $k_B$ is Boltzmann’s constant. The $\psi_{\sigma, \eta}(\mathbf{r})$ are the wavefunctions of the sample surface with $E_\eta$ their corresponding energy eigenvalues and $\sigma$ their spins. $\mathbf{x}$ is the position on the surface below the STM tip. With two out of the three quantities $I$, $z$, and $V$ fixed, the third can be imaged as a function of surface position $\mathbf{x}$. For our purposes, the STM as a probe can be understood as operating in one of three modes: constant current, constant resistance, or constant height.

In the constant-current mode, a feedback loop is maintained between the height and the current. The current is fixed by varying the height of the STM tip above the surface. A two-dimensional mapping of variation in height is the resulting data. If the voltage between the tip and surface is a large constant value (typically 500 mV–2 V) a significant amount of the total density of states under the tip is sampled. When operating in this manner the height data can be interpreted as a topographic image of the surface. The STM is most often used in this mode due to the simplicity of the measurement and the direct interpretation of the data.

An additional powerful attribute of the STM is its ability to measure local spectra. One spectroscopic technique, the constant resistance mode, is to set the tip height based on a constant current at some relatively large voltage, then open the feedback loop (fixing the height) and measure the current as a function of voltage. This method has the advantage that when adatoms are present on the surface the tip height is adjusted up to prevent the tip from hitting them. Another spectroscopic method is the constant-height mode, which requires that the initial height be maintained without feedback throughout the measurement. This approach allows the current to be measured as a function of voltage as the tip is scanned across the surface. In either spectroscopic mode the differential conductance is obtained either by differentiating a collection of $I - V$ curves or through the use of more direct (and more accurate) lock-in techniques. Either of these modes of spectroscopic operation can be termed scanning tunneling spectroscopy (STS).

Tersoff and Hamann have identified the local density of states (LDOS) at the surface of the sample as the measured quantity in STS.$^{11, 12}$ The differential conductance can be written at finite temperature in the following form, which depends on the local density of states (LDOS) at the tip location:

$$ \frac{dI(\mathbf{x}, V, T)}{dV} \propto \int_{-\infty}^{\infty} d\omega \frac{\partial n_{STM}(\omega)}{\partial \omega} \sum_{\sigma, \eta} |\psi_{\sigma, \eta}(\mathbf{x})|^2 \delta(\omega - E_\eta), $$

$$ \propto \int_{-\infty}^{\infty} d\omega \frac{\partial n_{STM}(\omega)}{\partial \omega} \sum_{\sigma} \left( \frac{\text{Im} \; G_{\sigma}(\mathbf{x}, \omega)}{\pi} \right). \hspace{1cm} (2.3) $$

The differential conductance is thus proportional to the imaginary part of the retarded Green’s function fully dressed by the interaction of the electronic system with the impurity, which is the LDOS of the interacting system.

3. ATOMIC-SCALE STRUCTURE IN CONDENSED ELECTRON SYSTEMS

The traditional perspective on the importance of band structure on the properties of condensed electron systems is that only low-energy properties (such as the density of states at the Fermi level) are relevant. The argument for this perspective relies on small order parameter energies (typically of the order of meV) compared to the energy scale of important band structure features (typically of the order of eV).

Our purpose will be to extend this argument to inhomogeneous systems, where the energy scale of the inhomogeneity is very large compared to the order parameter energy. The new low-energy quantities of importance in the condensate are the low-energy LDOS of the inhomogeneous system. Due to the energy scale of the inhomogeneity, however, the low-energy LDOS depends on mixed-in high-energy features of the homogeneous material’s band structure. This picture of inhomogeneous systems immediately suggests that caution must be exercised when making the common assumption that the electronic structure of a correlated electronic system is particle-hole symmetric. This assumption is usually justified with the argument that the electronic structure of the homogeneous system is particle-hole symmetric over the small energy range of interest (e.g., the energy scale of the order parameter or the temperature). The inhomogeneity, however, has a large energy scale, so the assumption of particle-hole symmetry in the homogeneous system produces serious errors in the low-energy LDOS of the inhomogeneous system.

Section 16 demonstrates the importance of the low-energy inhomogeneous electronic structure by using it to provide a direct way to visualize Anderson’s argument for the stability of the superconducting state in the presence of nonmagnetic impurities. Superconductivity opens up a low-energy gap in the normal-state LDOS induced by the strong impurity; however, neither the gap nor $T_c$ is reduced.

Section 17 extends this use of the normal-state LDOS to construct the superconductor’s LDOS near a magnetic impurity. In a host superconductor with an anisotropic order parameter, however, the momentum-resolved density of quasiparticle states differs substantially from that of the normal state, so the connection between the normal-state and superconducting LDOS becomes less simple and direct.

4. THE KOSTER-SLATER TECHNIQUE

The local electronic properties of defects such as magnetic or nonmagnetic impurities in the superconductor can be calculated self-consistently from the Gor’kov equation without further approximation with a new technique introduced in Refs. 14 and 15. This technique for calculating the electronic structure around a defect in a superconductor is related to the Koster-Slater inversion techniques for determining the local electronic structure of impurities in metals.16,17

Since its original application to localized vibrational modes, this algorithm has been applied to numerous problems including deep levels in semiconductors and impurity states in magnets.20

The new Koster-Slater technique takes advantage of the short-ranged nature of the impurity potential by formally separating space around the defect into two regions: the near field and the far field. The far field is a region distant enough from the defect that the potential is insignificant and the order parameter has relaxed back to its homogeneous value. The near field is the region close to the defect where the potential is finite or the order parameter is distorted. In essence, the Gor’kov equation that determines the Green’s functions of the inhomogeneous superconductor is inverted in real space within the near-field region.

5. OUTLINE OF THIS CHAPTER

Part II provides a brief guide to the most important bulk characteristics of impurities in superconductors with either isotropic or anisotropic order parameters. Part III presents a survey of calculational techniques of the local properties of defects in superconductors, including coarse-grained approaches such as Ginzburg-Landau and Eilenberger theory, the quasiparticle-based method of the Bogoliubov-de Gennes equations, and the more recently developed Koster-Slater Green’s function technique.

Part IV describes an analytic model, based on a delta-function potential, which reproduces some of the quantitative behavior obtained from the Koster-Slater calculations presented in Parts V and VI. For clarity when discussing the numerical calculations for various impurities, as well as the heuristic pictures of the electronic structure near the impurities, the presentation has been separated into two parts depending on whether the order parameter is isotropic or anisotropic. Part V discusses the results of the numerical calculations for magnetic impurities, nonmagnetic impurities, impurities incorporating both magnetic and nonmagnetic potentials, and inhomogeneities in the pairing interaction, all in superconductors with isotropic order parameters, such as the low-temperature superconductors. Part VI discusses similar results for superconductors with anisotropic order parameters and quasi-two-dimensional electronic structure, characteristic of the high-temperature superconductors. Comparisons with the analytic results of Part IV will be made in Parts V and VI. Part VII provides some very recent results for dynamical spins, which may be relevant to recent tunneling experiments on the edges of the high-temperature superconductor YBa$_2$Cu$_3$O$_{7−\delta}$.

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19 For example, M. Jaros, Deep Levels in Semiconductors, Adam Hilger, Bristol (1982).
II. Bulk Properties of Defects in Superconductors

6. MODELS OF THE FORMATION OF A MAGNETIC MOMENT IN A SUPERCONDUCTOR

The behavior of magnetic impurities in metals is a rich area in its own right, and the models developed there have been applied at various times to the problem of magnetic impurities in superconductors. The basic response of a superconductor to magnetic impurities is quite different than that of a metal. In a metal the magnetic moment of an impurity can disappear when that impurity atom is placed in a nonmagnetic host. Several models have been developed to describe this behavior. Excellent reviews of this topic are available in Refs. 21, 22. Here we merely provide a brief description suitable for conveying the richness and difficulty of the problem.

The model of Friedel\textsuperscript{23} requires a strong scattering potential to generate a virtual bound state near the Fermi energy, and then a sufficiently strong exchange energy to induce a local magnetic moment. The Friedel Hamiltonian is

\[ H = \sum_{k,s} E_k n_{ks} + J \sum_{k,s} \mathbf{S} \cdot \mathbf{c}_{ks}^\dagger \mathbf{c}_{ks}, \]  \hspace{1cm} (6.1)

where \( J \) is the exchange energy between the impurity spin and conduction electron spins. The condition for the formation of the local moment via \( \ell \)-channel scattering,\textsuperscript{24}

\[ 2\epsilon_{ex} \rho_i (E_F) > 1, \]  \hspace{1cm} (6.2)

is very similar to the Stoner condition for ferromagnetism. Here the exchange energy is equal to \(-\frac{1}{2} n^2 \epsilon_{ex} \), where \( n \) is the number of unpaired \( d \) electrons and \( \rho_i (E_F) \) is the density of localized states in the virtual bound state.

The method of Anderson\textsuperscript{25} relies on the now familiar model Hamiltonian,

\[ H = \sum_{\sigma} E_d n_{d\sigma} + Un_{d\uparrow} n_{d\downarrow} + \sum_{k,s} E_k n_{ks} \] 
\[ + \sum_{k_s} [V_{dk} c_{k_s}^\dagger c_{d\uparrow} + V_{dk} c_{k_s}^\dagger c_{d\downarrow}]. \]  \hspace{1cm} (6.3)

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Fig. 1. The “phase diagram” of the Anderson model in a mean-field (Hartree-Fock) treatment as a function of the separation of the \( d \)-orbital energy from the Fermi energy and the width of the resonant state. Regions where the \( d \)-orbital is magnetic or nonmagnetic are indicated. [After Ref. 25]

The hybridization between the conduction electrons and the \( d \) electrons introduces a nonmagnetic resonant state at \( E_d \) when \( U = 0 \) with a linewidth

\[ \Gamma = \pi \langle |V_{dk}|^2 \rangle_{\sigma \sigma} \rho (E). \]  \hspace{1cm} (6.4)

When \( U \neq 0 \) the system can be magnetic or nonmagnetic depending on the relative values of \( \Gamma \) and \( U \) and the separation of \( E_d \) from the Fermi energy \( \epsilon_F \). A mean-field (Hartree-Fock) treatment of the Anderson model reveals the nontrivial “phase diagram” of Fig. 1.

Although these models produce some sensible results, there are several drawbacks in their practical application. One of the key problems is the difficulty of measuring the required bare parameters of either model. Some of the bare quantities, such as \( U \), can be best extracted from information on the electronic structure far from the Fermi surface. Unfortunately other electronic features can complicate the extraction of \( U \) from these measurements. As an example, metallic oxides have a lattice arrangement of \( d \)-orbitals, and their \( U \) can be extracted from

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photoemission spectroscopy. The small additional signal from dilute magnetic impurities, however, cannot be distinguished. Given that the most common probes of electronic structure — that is, thermodynamic or transport measurements — are only sensitive to the electronic structure near the Fermi energy, consistent information about all the parameters in the Anderson or Friedel model for a particular system can be hard to obtain.

A further problem concerns the importance of correlations within the local shell in the presence of more than one $d$ electron. The Hartree-Fock theory is quite inadequate here, and explanations based on Hund’s rule must be introduced ad hoc. For impurity atoms with shells containing only one $d$ electron or missing only one $d$ electron, magnetic moments have been observed only at low impurity concentration. For shells with one or missing one $f$ electron magnetic moments have been observed in hosts, but they appear fragile — vanishing under pressure (increasing $T$). The loss of the moment appears to correlate with the movement of an electron from the $f$ state to the conduction band (with a corresponding change in the Hartree-Fock potential). Thus even the one-electron or one-hole shells cannot be described well without taking into account aspects of the system ignored in the above models, such as the orbital moment, Hund’s rule, and local effects like crystal fields.

7. Defects in Isotropic Order-Parameter Superconductors

The response of a superconductor to magnetic impurities is considerably more dramatic than that seen in metals. Matthias and coworkers noticed that magnetic impurities at a critical concentration of 1–2% could reduce the characteristic gap in the density of states and at slightly higher concentrations all superconductivity vanished. The first detailed model for magnetic impurities in a superconductor was based on incoherent spin-flip scattering from the impurity treated within the Born approximation — namely, Abrikosov-Gor’kov theory.

Before introducing Abrikosov-Gor’kov theory it is important to address the presence of nonmagnetic impurities. Low-temperature superconductors almost always have a high concentration of nonmagnetic impurities. Even in the dirty limit, however, where the elastic mean free path is shorter than the coherence length, superconductivity endures. The differing effects of magnetic and nonmagnetic impurities are directly attributable to the time-reversal invariance of a superconducting condensate formed of electrons paired in spin singlets with an isotropic wavefunction. If the pair wavefunction is triplet as in $He^3$ or anisotropic as in high-$T_c$ cuprate superconductors, the distinction between the effects of magnetic and nonmagnetic impurities is modified. The robustness of the superconductor to nonmagnetic impurities relies on an isotropic order parameter and the presence of Kramers doublets (pairs of degenerate states) in a time-reversal invariant system. The BCS pairing of states of opposite momentum is then generalized to the pairing of two members of the Kramers doublet. This argument only fails to the extent that the impurities destroy the normal-state metallic properties.

A magnetic impurity, which does break time-reversal symmetry, is described by a term $J/s\cdot\sigma$ in the Hamiltonian. A complete treatment of this term includes the possibility of flipping the quasiparticle spin and the resulting change in the impurity spin. Even in the simpler case of a normal metal a correct treatment of this situation is quite difficult. When the coupling $J$ is antiferromagnetic, this effect can give rise to Kondo physics, which is beyond the scope of our treatment of impurity spins.

One of the common approximations is to ignore the quantum mechanical operator character of the impurity spin. The impurity can then be imagined (when part of an ensemble) as an uncorrelated spin-flipping scatterer. Within the Born approximation the effect of these impurities is to induce a finite width in any quasiparticle state. This treatment forms the basis of the popular Abrikosov-Gor’kov treatment of magnetic impurities in superconductors.

The introduction of a lifetime $\tau$ to the quasiparticle smooths the gap edges at low concentrations, and eventually leads to gapless superconductivity. Fig. 2 shows a series of calculated spectra for various $\alpha = [\tau\Delta]^{-1}$. In this model, as the impurity concentration is increased, the intragap states move from the gap edge deeper into the gap. The presence of these intragap states leads to a linear suppression of $T_c$ with impurity concentration for low concentrations. A recent strong-coupling calculation yields qualitatively similar results.

Intragap states form in quite a different way in the presence of a classical spin. In this case a localized state is formed around each impurity with an energy determined by the strength of the spin-dependent potential. As the concentration of impurities increases, the individual localized states hybridize to form a band.

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similar to an impurity band in a semiconductor. As the concentration increases the intragap band broadens until it fills the energy gap, leading to gapless superconductivity. Hence a model of gapless superconductivity is possible whether the spin is dynamic (flips the quasiparticle spin) or static (and preserves the quasiparticle spin).

In the classical limit of the spin, $J(x) \to 0$ and $S \to \infty$, whereas $J(x)S \to V_g(x)$. Because the amplitude of spin-flip scattering is proportional to $J(x)$, but not to $S$, in this limit the potential is spin-dependent, but does not flip the spin of the quasiparticles. We will always take the quantization direction of the superconducting electrons’ spins to be parallel to the impurity spin, so the impurity term in the Hamiltonian will be $\sigma V_g(x)$. Thus the classical spin acts formally as a local magnetic field. The two most important qualitative differences between the Abrikosov-Gor’kov treatment and the treatment of the classical spin are that (1) for the classical spin only coherent elastic scattering is allowed, so the quasiparticle lifetimes are infinite in the absence of other phase-decohering processes, and (2) the classical spin model can be solved exactly even for strong potentials, whereas the treatment of incoherent scattering non-perturbatively is extremely difficult.

The type of model appropriate for a particular magnetic impurity can be determined from two experimental quantities: the detailed concentration dependence of the critical temperature of the superconductor and the specific heat jump of the alloy at the superconducting transition relative to that of the host at its superconducting transition. For moments whose characteristic fluctuation time is long ($\hbar \omega_c \ll \Delta$, where $\omega_c$ is the fluctuation frequency), and the impurity-conduction electron interaction ($J$) is weak the superconducting properties are well described by modeling the impurity with a classical spin. Such a system is Mn in niobium.

If the impurity-conduction electron interaction is antiferromagnetic and is treated quantum mechanically, then for sufficiently low temperature there is a competition between the formation of a Kondo-like singlet between the impurity electron and a cloud of conduction electrons that compensate it, and the formation of a BCS singlet between conduction electrons. Such a system can demonstrate reentrant superconductivity, in which the system is superconducting between two finite temperatures $T_{c1}$ and $T_{c2}$, but not at $T = 0$. Such a system is LaAl$_3$ with Ce impurities.

Considerable theoretical effort has been expended in exploring the interplay of the Kondo effect and superconductivity. Although there have been successes, such as the identification of an origin of reentrant superconductivity, the details of the Kondo effect in a superconductor should be considered an open problem. Part of the problem originates from the lack of good methods for tackling inhomogeneous frequency-dependent interacting systems. A recently developed tool for attacking such problems is dynamical mean field theory, and the quantum mechanical spin in a superconductor has been examined with that technique.

The final category of behavior is for local moments with fast timescales. For

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such impurities the localized state can be treated as a broad (wider than the superconducting gap) resonance. The depression of $T_c$ with $n$ can be described by the following form,

$$\frac{T_c(n)}{T_c(0)} = e^{-[An/(1-Dn)]},$$  \hspace{1cm} (7.1)

where the parameters $A$ and $D$ depend on the parameters of the Anderson or Friedel models of the magnetic impurity. The origin of the suppression of $T_c$ in this system is the reduction of the density of states at the Fermi level and the reduction of the effective attractive electron-electron interaction due to the Coulomb repulsion between electrons of opposite spin when they are both in the localized state.

8. Defects in Anisotropic Order-Parameter Superconductors

Extensive investigation in the high-temperature superconductors has explored the effect on the superconducting transition temperature of a wide variety of dopants. A review of this work is available in Ref. 51. As a general rule the critical temperature decreases linearly with dopant concentration, even at low concentrations. This set of results does not appear to be consistent with the robust nature of the low-temperature superconductors’ critical temperature to nonmagnetic impurities. As discussed in Sec. 7, in low-temperature superconductors $T_c$ decreases linearly with dopant density for magnetic impurities, but not for nonmagnetic impurities. The observation of linear decreases in the critical temperature with dopant concentration for a wide variety of dopants either leads one to the curious argument that almost all dopants act as magnetic impurities in the high-temperature superconductors, or indicates that the order parameter is highly anisotropic. A particularly powerful example is the use of electron irradiation to displace oxygen atoms from the copper-oxygen planes of YBa$_2$Cu$_3$O$_{7-\delta}$. The resulting defects do not have measurable local moments nor do they change the carrier concentration. Nevertheless, these nonmagnetic defects suppress the critical temperature to zero when merely 4.1% of the in-plane oxygen atoms have been displaced.

The observation that almost all impurities suppress $T_c$ linearly should not be taken as an indication that they all act the same. For example, the presence of Zn depresses $T_c$ about three times more per impurity $^{52}$ than Ni. There is currently considerable controversy over both Ni and Zn concerning whether or not they should be treated as magnetic impurities or nonmagnetic impurities when placed in the copper-oxygen planes of high-temperature superconductors.

It has taken several years for the qualitative behavior of some thermodynamic quantities in clean high-temperature superconductors to be disentangled from the effects of impurities on the superconductors. Essentially this has been achieved through the growth of extremely high-quality samples, as well as the reproduction of earlier measurements through the addition of intentional doping. An impressive example of this type of work involves the magnetic penetration depth measured on YBa$_2$Cu$_3$O$_{7-\delta}$. Here twinned single crystals were intentionally doped with Zn and Ni impurities.$^{54}$ In the undoped samples, the penetration depth exhibits a linear dependence on the temperature, which is consistent with line nodes in the order parameter. The Zn doped samples showed a low-temperature $T^2$ behavior, followed by a crossover to linear $T$ behavior at higher temperature. That nonmagnetic impurities induce the $T^2$ behavior can be viewed as support for an order parameter whose average around the Fermi surface is close to zero. If the order parameter averaged to a sizable value around the Fermi surface, the disorder would tend to average the order parameter, leading to a low-temperature exponential behavior.$^{56,57}$

In order to obtain this $T^2$ dependence and crossover behavior, it is crucial $^{58}$ to use strongly scattering impurities rather than weakly scattering ones, because concentrations of weakly scattering impurities sufficient to generate this $T^2$ dependence would also destroy the superconducting state. Within the Born approximation, which applies for weakly scattering impurities, states very near the chemical potential (which affect the low-temperature properties of the system) must originate from the smoothing of the gap edge. When there are sufficient impurities to smooth the gap edge enough to place a substantial number of states at the chemical potential, superconductivity has already been destroyed. In contrast, strongly scattering impurities can put the intragap quasiparticle states predominately very near the chemical potential, where they affect the low-energy quasiparticle properties, but do not significantly damage $T_c$. The use of strongly scattering impurities has been an extremely fruitful direction in obtaining qualitative agreement between experiment and theory in the high-temperature superconductors.

III. Techniques for Calculating the Local Properties of Defects in Superconductors

Among the first local properties calculated in the vicinity of an impurity in a superconductor were the structures of screening clouds around a charged impurity\textsuperscript{59,60} and a magnetic impurity\textsuperscript{60,61} in a superconductor (characterized by exponentially decaying Friedel-like oscillations). The oscillation of the order parameter around a magnetic impurity was first evaluated without self-consistency.\textsuperscript{52-64} A self-consistent calculation was reported for the order parameter at the impurity and very far away for weak magnetic impurity potentials by Schlottmann,\textsuperscript{65} and far away from nonmagnetic impurities by Fetter.\textsuperscript{66} All of these calculations focused on ground-state properties of the system — this chapter emphasizes the local properties of excited states as well.

9. Coarse-Grained Theories of Local Properties

Some formalisms for inhomogeneous superconductivity, such as Ginzburg-Landau theory\textsuperscript{67} or the Eilenberger equations,\textsuperscript{68} treat the spatial degrees of freedom as coarse-grained over the superconductor’s coherence length. This is sensible if the properties of interest are of that scale, such as the decay of the Gor’kov amplitude into a normal metal at an interface with a superconductor.\textsuperscript{5} If the properties of interest have atomic-scale structure the Bogoliubov-de Gennes equations, or the Koster-Slater technique presented here, must be used.

The Ginzburg-Landau theory is based on the dependence of the free energy of the superconductor on the order parameter. It can be extremely useful to identify effects in a qualitative way, but because it only holds formally near $T_c$, it has limited quantitative use at lower temperatures. Because it focuses on the order parameter and the quasiparticles themselves do not directly appear in the theory, Ginzburg-Landau theory is not appropriate for addressing the details of localized states around magnetic impurities. The parameters of Ginzburg-Landau theory either must be set empirically from the behavior of macroscopic properties near $T_c$ or must be determined from a microscopic calculation. Such calculations have been performed in anisotropic order parameter superconductors.\textsuperscript{69,70} As an additional concern, the Ginzburg-Landau theory does not produce the detailed information on the electronic structure necessary for calculating STM tunneling spectra.

The Eilenberger equations do contain information about the quasiparticles. They are obtained from the microscopic Gor’kov equations under the quasiclassical approximation that the gradients in the electron amplitudes due to the inhomogeneity are small. This approximation is not appropriate for situations where the electronic properties change considerably over a coherence length or when a local potential is large compared to the order parameter. The Eilenberger equations have been applied to the electronic structure of the vortex core in $s$-wave superconductors,\textsuperscript{71,72} in anisotropic $s$-wave superconductors (specifically NbSe$_2$),\textsuperscript{73} and in $d$-wave superconductors.\textsuperscript{74} In addition to lacking spatial information on the atomic scale, these treatments lack the ability to resolve the energies of quantized states within the vortex core (which can be picked out by STM).\textsuperscript{75,76} This inability to resolve the energies of quantized states is a fundamental difficulty with the theory, because the quantized energies of the localized states are determined by matching conditions on the quasiparticle wavefunction equations (Bogoliubov-de Gennes equations) at the boundaries of the system containing the vortex. Thus they are intrinsically atomic-scale conditions.

Atomic-scale defects also have been investigated with the Eilenberger equations. Here the validity of the theory is even more in question, due to the strength of the potential. The electronic structure of a magnetic impurity\textsuperscript{77} and the effect of pinning centers on vortices\textsuperscript{78} are such examples. When the potential is large, such as in these cases, the Eilenberger equations are appropriate only for calculating properties far from the impurity.

\textsuperscript{60} J. P. Hurault, Journal de Physique 26, 252 (1965).
\textsuperscript{63} J. Heinrichs, Phys. Rev. 168, 451 (1968).
\textsuperscript{64} R. Kummel, Phys. Rev. B 6, 2617 (1972).
\textsuperscript{68} G. Eilenberger, Z. Phys. 214, 195 (1968).

10. BOGOLOUBOV-DE GENNES EQUATIONS

The Bogoliubov-de Gennes (BdG) equations are generalized Schrödinger equations for the electron and hole wavefunctions of a quasiparticle and are valid for a superconductor with an arbitrarily-varying order parameter, only constrained by the validity of BCS theory. The inhomogeneous order parameter for a superconductor can also be determined self-consistently from these equations. Unfortunately, the BdG equations have significant practical difficulties.

Despite qualitative success modeling STM measurements of a single vortex in superconducting NbSe$_2$, calculations of the electronic structure$^{79-83}$ using the BdG equations are hampered by the difference in energy scales between the Fermi energy and the order parameter. Because the BdG equations are solved numerically for a finite system, the difficulty of the calculation is determined by the necessary spectral resolution. The key energy scale that must be resolved is the superconducting gap. Thus, the numerical difficulty increases as the ratio of the Fermi energy to the gap becomes large. For low-temperature superconductors the band structure assumed must be somewhat unrealistic (for Refs. 82 and 83 the Fermi wavelength in the calculation was approximately 100 Å, which is too large$^{84}$ for NbSe$_2$). This limitation extends to calculations of a vortex’s structure in a quasi-two-dimensional system with a square lattice,$^{85}$ calculations of the interaction between a vortex and an impurity,$^{86}$ the characteristics of the vortex lattice,$^{87,88}$ and work on a nonmagnetic impurity$^{89-92}$ and a magnetic impurity$^{93}$ in a two-dimensional s-wave or d-wave superconductor. In contrast, the computational requirements of the Koster-Slater technique (to be described in Sec. 11) are determined by the range of the impurity potential rather than the necessary spectral precision.

$^{92}$ M. E. Flatté and J. M. Byers, unpublished.

To place our new Koster-Slater formalism in context, we will contrast it with the BdG equations. This section, therefore, describes the BdG equations in several physical situations. The first is a three-dimensional continuum model of a superconductor with an isotropic order parameter. Following that description we explore a two-dimensional lattice model of a superconductor with an anisotropic order parameter. We conclude with a description of the additional formalism required in the presence of a magnetic field — and thus appropriate for the electronic structure of a vortex line.

The magnetic impurity will be modeled by a classical spin. The quantization direction of the electronic spins in the superconductor (σ = ± 1/2) can be chosen parallel to the classical spin, and spin is a good quantum number for the quasiparticles. The equations for parallel and antiparallel quasiparticle spins decouple, and we must therefore solve two equations, coupling electron and hole amplitudes of the same spin, rather than four equations coupling electron and hole amplitudes of both spins.

a. Three-Dimensional Continuum Model with an Isotropic Order Parameter

For a (normal-state) free electron band structure with mass $m$, the quasiparticles correspond to positive-energy ($E$) solutions to

$$\frac{p^2}{2m} - \mu - E + V_0(x) + \sigma V_\delta(x)\right] u_\sigma(x) + \Delta(x)v_\sigma(x) = 0,$$

$\left[ - \frac{p^2}{2m} + \mu - E - V_0(x) + \sigma V_\delta(x)\right] v_\sigma(x) + \Delta^*(x)u_\sigma(x) = 0,$

where $\mu$ is the chemical potential and $\sigma$ is the operator $-\hbar \nabla$. Here $\sigma V_\delta(x)$ is the position-dependent, spin-dependent potential of $\nu_\sigma(x)$ is a position-dependent nonmagnetic potential and $\Delta(x)$ is the inhomogeneous order parameter.

The spatially dependent order parameter is determined self-consistently:

$$\Delta(x) = \sum_{j\sigma} \gamma(x, E_{j\sigma}) [1 - 2n(E_{j\sigma})] [1 - 2n(E_{j\sigma})] = \sum_{j\sigma} \gamma(x, E_{j\sigma}) \left( \frac{E_{j\sigma}}{2k_BT} \right) \tanh \left( \frac{E_{j\sigma}}{2k_BT} \right),$$

where $j$ labels the states for each spin $\sigma$, $\gamma(x, E_{k\sigma})$ is the effective electron-electron interaction potential, which usually will be taken to be...
\[ \gamma(x, E_{\sigma\sigma}) = \gamma_{\sigma}, \quad E_{\sigma\sigma} < \hbar \omega_D, \]
\[ = 0, \quad E_{\sigma\sigma} > \hbar \omega_D. \quad (10.3) \]

These equations are derived under the assumption that the pairing potential has zero range (a delta function). A more general order parameter requires a pairing potential of greater than zero range. Furthermore, because the defect potential is real, \(\Delta(x)\) may be chosen real. In contrast, the inhomogeneous order parameter for a vortex cannot be chosen to be real everywhere.

The combinations \(\sigma V_k \pm V_0\) have straightforward physical significance: \(\sigma V_k + V_0\) is the potential felt by an electron of spin \(\sigma\), whereas \(\sigma V_k - V_0\) is the potential felt by a hole of spin \(\sigma\). The terms proportional to \(\Delta(x)\), which couple \(u(x)\) and \(v(x)\), also have straightforward interpretations: they couple spin \(\sigma\) electrons to spin \(\sigma\) holes and vice versa. A spin \(\sigma\) electron can convert to a spin \(\sigma\) hole by putting a Cooper pair into the condensate (conserving particle number), and a spin \(\sigma\) hole can convert to a spin \(\sigma\) electron by pulling a Cooper pair from the condensate.

For a spherically symmetric defect the wavefunctions are eigenstates of angular momentum with quantum numbers \(\ell\) and \(m\). Typically the defect is placed in a sphere of radius \(R\) with appropriate boundary conditions. For example, the wavefunctions may be set to zero at the boundary. Thus the solutions to Eq. (10.1) can be written as

\[ \left( \begin{array}{c} u_{j_r,l_m}(x) \\ v_{j_r,l_m}(x) \end{array} \right) = \sum_n \left( \begin{array}{c} U_{j_r,n_m} \\ V_{j_r,n_m} \end{array} \right) f_j(k_n R) Y_{l_m}(\Omega), \quad (10.4) \]

where \(f_j(k_n R) = 0\). In this Ansatz Eq. (10.1) is a matrix equation relating all the \(U_{j_r,n_m}\) and \(V_{j_r,n_m}\) with fixed \(\ell\) and \(m\).

The size of the basis is partially determined by the number of \(k_n\)'s necessary. The range of important \(k_n\) is centered around the Fermi surface, but extends above and below by energies comparable to the largest values of \(V_0(x)\) and \(V_k(x)\). Because these potentials have a characteristic scale of \(eV\), this range is of the order of the bandwidth, and therefore is quite substantial. The other requirements on the eigenstates are that their energy separation should be small enough so that both Eq. (10.2), and the spectral width of features measurable by the STM, can be accurately evaluated. Otherwise, the finite-size effects on the spectrum will limit the accuracy of these quantities. The first condition, based on Eq. (10.2), requires that the level spacing must be much smaller than \(\Delta_0\) (less than 1 meV for low-temperature superconductors). The second condition, based on resolving spectral features observable by STM, can be even more restrictive (less than 0.1 meV).

Operationally these conditions determine the minimum size \(R\) of the finite system that must be solved. The resulting computational requirements are so severe that such calculations have not been attempted for impurities. Attempts to evaluate similar equations for vortices (where the potential strengths are much smaller) will be discussed later in this section.

b. Two-Dimensional Lattice Model with a General Order Parameter

Consider now a case where the real-space locations are discrete. Such a lattice model is typically based on a tight-binding approach to the normal-state electronic properties. The focus here is on a square lattice, by virtue of its applicability to the high-temperature superconductors. The square lattice is considerably simpler than the real physical systems, and is intended to represent the important physics of the copper-oxygen planes.\(^{114}\) The lattice sites are effectively the copper sites, which are arrayed in a square pattern within each copper-oxygen plane, with oxygen sites between nearest-neighbor copper sites. The copper-oxygen electronic structure can be described near the Fermi energy with an effective one-band tight-binding model.

A treatment of high-temperature superconductors also requires the consideration of general order parameters, for the evidence of anisotropic order parameters in high-temperature superconductors is overwhelming, supported by measurements of the magnetic penetration depth,\(^{155}\) angle-resolved photoemission,\(^{156,157}\) the critical current dependence of Josephson junctions,\(^{161}\) and the presence of a half-flux quantum in certain tricrystal rings.\(^{162}\) A review of the current experimental support for various order parameter symmetries is available in Ref. 100.

The principal difference introduced by considering general order parameters in our model is the introduction of a second coordinate in the order parameter, \(\Delta(x, x')\). The BdG equations now become

\[
[\sigma V_s(\mathbf{R}_{ij}) + V_0(\mathbf{R}_{ij}) - \mu - E]u_{\sigma}(\mathbf{R}_{ij}) \\
- \sum_{ij} t_{i-i',j-j'}u_{\sigma}(\mathbf{R}_{i'j'}) + \sum_{ij} \Delta(\mathbf{R}_{ij}, \mathbf{R}_{i'j'})v_{\sigma}(\mathbf{R}_{i'j'}) = 0, \tag{10.5}
\]

\[
[\sigma V_s(\mathbf{R}_{ij}) - V_0(\mathbf{R}_{ij}) + \mu - E]v_{\sigma}(\mathbf{R}_{ij}) \\
+ \sum_{ij} t_{i-i',j-j'}v_{\sigma}(\mathbf{R}_{i'j'}) + \sum_{ij} \Delta^*(\mathbf{R}_{ij}, \mathbf{R}_{i'j'})u_{\sigma}(\mathbf{R}_{i'j'}) = 0.
\]

Lattice locations are denoted by \(\mathbf{R}_{ij}\), where \(i\) is the row and \(j\) is the column of the site. The expression for the inhomogeneous order parameter is

\[
\Delta(\mathbf{R}_{ij}, \mathbf{R}_{kl}) = \frac{\gamma(\mathbf{R}_{ij} - \mathbf{R}_{kl})}{2} \sum_{m\sigma} (u_{m\sigma}(\mathbf{R}_{ij})v^*_{m\sigma}(\mathbf{R}_{kl}) + u_{m\sigma}(\mathbf{R}_{kl})v^*_{m\sigma}(\mathbf{R}_{ij})) \\
\times [1 - 2n(E_{m\sigma})].
\tag{10.6}
\]

where the sum \(m\) is over all the positive energy solutions to Eq. (10.5). Here \(\gamma(\mathbf{R})\) is the effective electron-electron interaction potential. Unlike the effective potential considered in a superconductor with an isotropic order parameter, this interaction potential has non-zero range.

The number of parameters in Eq. (10.5) is reduced to simplify calculations. The model considered here includes nearest-neighbor and next-nearest-neighbor hopping elements \(t = 350\) meV and \(t' = -56\) meV. These values parametrize the normal-state band structure of \(\text{YBa}_2\text{Cu}_3\text{O}_{6-\delta}\). More complete tight-binding parametrizations\(^{101,102}\) are now available for \(\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8\).

Further simplification occurs when the order parameter’s range is limited. By allowing for on-site or nearest-neighbor pairing only, we allow for both \(d_{x^2-y^2}\) and anisotropic s-wave order parameters in addition to isotropic s-wave. Thus the sum over neighboring sites in Eq. (10.5) extends only to nearest neighbors for the order parameter. This restriction is more naturally guaranteed within the model by restricting the range of the pairing potential \(\gamma(\mathbf{R})\). For the isotropic s-wave order parameter considered in the previous section, \(\gamma(\mathbf{R})\) has the form of a delta function. For anisotropic order parameters we restrict \(\gamma(\mathbf{R})\) to be nonzero only for \(\mathbf{R} = 0\) and for nearest-neighbor sites.

Direct diagonalization calculations based on Eq. (10.5) have been attempted\(^{89-92}\). The rank of the matrix to be inverted scales with the number of lattice sites. If we consider a physical square of sites of linear size \(d\), the computation time scales as \(d^6\). The approximate limit, based on CPU time and memory, for current high-end desktop workstations is \(d = 50\). A quantity of critical importance, then, is the amount of broadening required to smooth the spectrum obtained from the exact diagonalization of the finite cluster into a spectrum representative of the infinite system. Unfortunately the states of the finite cluster are distributed over the entire bandwidth of the infinite system, instead of near the gap edge where good resolution is desired. The distribution of the states is highly nonuniform due to symmetry-induced degeneracies. We find that the broadening factor necessary to obtain a spectrum that does not clearly show the influence of finite-size effects is at least \(\Gamma \sim 4td\).

In order to accurately resolve the gap edge we need \(\Gamma \ll \Delta_{\text{max}}\), where \(\Delta_{\text{max}}\) is the maximum value of the order parameter on the Fermi surface. Because \(\Gamma \sim 0.1t\) for the largest possible currently accessible values of \(d\), gaps cannot be accurately resolved unless \(\Delta_{\text{max}} \sim t\). Even for the high-temperature superconductors, which have large order parameters, this is unrealistically large by a factor of ten. We show in Fig. 3(a, b) the density of states in the presence of a realistic \(d_{x^2-y^2}\) gap in a high-temperature superconductor. Figure 3(a) shows the

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spectrum over a broad energy range, whereas Fig. 3(b) shows a closeup view of the energy gap region, where the spectrum is unBroadened (solid line) and broAened by $\Gamma = 0.1t$ (dashed line).

c. Vortices in Superconductors with Isotropic Order Parameters

The electronic structure of a superconductor in the neighborhood of a vortex can be determined from the previous sections if the influence of the vector potential is also considered. In the presence of a vortex, the potential present in the Bogoliubov-de Gennes equations comes from two self-consistent quantities: the order parameter, as previously given, and the vector potential $\mathbf{A}(x)$. The new Bogoliubov-de Gennes equations are

$$
\left[ \frac{(p + \frac{i}{\hbar} \mathbf{A}(x))^2}{2m} - \mu + \frac{\hbar \Omega}{\hbar} + \sigma V_g(x) \right] u_\sigma(x) + \Delta(x) v_\sigma(x) = 0,
$$

$$
\left[ \frac{(p - \frac{i}{\hbar} \mathbf{A}(x))^2}{2m} + \mu - \frac{\hbar \Omega}{\hbar} + \sigma V_g(x) \right] v_\sigma(x) + \Delta^*(x) u_\sigma(x) = 0,
$$

where $\mathbf{A}(x)$ is determined by first calculating the current,

$$
\mathbf{j}(x) = \frac{e \hbar}{2mi} \sum_{\alpha} n(E_{m\alpha}) u_{m\alpha}^\ast \left( \nabla - \frac{i e}{\hbar c} A(x) \right) u_{m\alpha}
+ \left( 1 - n(E_{m\alpha}) \right) v_{m\alpha} \left( \nabla - \frac{i e}{\hbar c} A(x) \right) v_{m\alpha}^\ast - \text{H.c.}
$$

and then calculating $\mathbf{A}(x)$ from

$$
\nabla \times \nabla \times \mathbf{A}(x) = \frac{4\pi}{c} \mathbf{j}(x).
$$

A self-consistent solution of these equations is obtained by repeatedly solving Eq. (10.7) and calculating $\Delta(x)$ and $\mathbf{A}(x)$ using Eqs. (10.2), (10.8), and (10.9), and reinserting them into Eq. (10.7) until convergence is attained.

Caroli et al.$^{103}$ showed that the suppressed order parameter in the vicinity of the vortex core allowed for the presence of localized states. The suppressed order parameter was assumed to heal over a coherence length, and the localized states were found. Later work by Bardeen et al.$^{104}$ treated the order parameter self-consistently within a variational calculation. Motivated by the STM measurements of Hess et al.$^{75,76}$ Shore et al.$^{7}$ calculated the LDOS of the vortex core bound states, assuming a particular form for the order parameter. Gygi and Schlüter$^{81}$ were the first to directly solve Eqs. (10.7)–(10.9) in a homogeneous medium with cylindrical symmetry (around the vortex core) and calculate both the self-consistent order parameter and the LDOS.

Because the system of interest in Ref. 83 was NbSe$_2$, the electronic structure was assumed to be quasi-two-dimensional with a free-electron-like dispersion in the planes. The cylindrical symmetry allows us to write solutions of Eq. (10.7) with well-defined angular momentum around the vortex core,

$$
u(x) = u_{\mu k_z} (\rho) e^{i(\mu - \frac{1}{2})\theta} e^{ik_z z},
$$

$$v(x) = v_{\nu k_z} (\rho) e^{i(\nu + \frac{1}{2})\theta} e^{ik_z z},
$$

where $n$ is a radial quantum number, $\mu = \nu + \frac{1}{2}$ (where $\nu$ is an odd integer), and $k_z$ is the momentum parallel to the vortex line. Equations (10.7)-(10.9) simplify if the gauge is chosen$^{105}$ where $\Delta(x) = \Delta(\rho) e^{-i\theta}$. In this gauge, for cylindrical symmetry the vector potential has the form

$$
\mathbf{A}(x) = A_{\theta}(\rho) \hat{\mathbf{e}}_{\theta}.
$$

The BdG equations are then solved separately for each value of $\mu$ and $k_z$. Results from these calculations will be compared at the end of this section with results for impurities.

d. Vortices in Superconductors with Anisotropic Order Parameters

Cylindrical symmetry, which rendered numerically tractable the vortex problem in an isotropic order parameter superconductor, is not appropriate for the high-temperature superconductors with their anisotropic order parameters. Instead, further approximations to the vortex problem are required. All attempts using the BdG equations$^{69,105}$ to date have relied on the observation that the vortex core size is considerably smaller than the London penetration depth. By considering a region of the material of a size much greater than the core, but much smaller than the London penetration depth, it is possible to consider the vector potential to be very small. Because the form of the vector potential for $\xi < \rho < \lambda$ is proportional

to $\lambda^{-2} \ln(\lambda/\rho)$, and the screening current is proportional to $\lambda^{-2}$, this approximation corresponds to the $\lambda \to \infty$ limit, and has been referred to as the extreme Type II limit.

This approximation eliminates the need to calculate self-consistently $j(x)$ and $A(x)$, and eliminates $A(x)$ from Eq. (10.7). In Ref. 69, the resulting equations were solved in a quadrant with the center of the core at one corner. The presence of the vortex was enforced by establishing the proper matching conditions between the solution at the vertical and horizontal edges containing the center of the vortex. The same computational problems connected with solving for the order parameter exist for the vortex as for the impurity. This has either been finessed by taking an unrealistically large value for $\Delta_0$, or by ignoring the “spiky” nature of the sum in Eq. (10.2) and not showing the density of states.69

c. Comparison of BdG Calculations for Impurities and Vortices

A principal computational distinction between the vortex problem and the impurity problem has to do with the strength of the defect potential. In the case of the vortex the potentials, coming from the $A(x)$ terms and the $\Delta(x)$ terms in Eq. (10.7), are of the scale of meV. In contrast, the potentials $V_0(x)$ and $V_2(x)$ are of the scale of eV. It is not possible to choose a coarser energy level spacing for the impurity, however, because the separation between the energies of the eigenstates must be considerably less than $\Delta_0$ for both the impurity and vortex in order to accurately evaluate Eq. (10.2).

The BdG equations are hard to evaluate even with the smaller potential of the vortex. For example, in the calculations for the vortex in NbSe$_2$, $\epsilon_F/\Delta_0 = 32$ was the largest ratio of the Fermi energy to the homogeneous order parameter considered. This value is a result of fitting the coherence length and upper critical field of NbSe$_2$ to a free-electron model. A more realistic band structure has a bandwidth to energy gap ratio at least an order of magnitude greater, and a highly anisotropic Fermi velocity. Niobium has an $\epsilon_F/\Delta_0 = 705$, rendering its LDOS numerically inaccessible for most potentials $V_0$ and $V_2$.

The energy scales are greater for the impurity potential than the vortex, but the spatial extent of the order parameter suppression is much greater for the vortex than for the impurity. Figure 4 shows the order parameter as a function of distance from the vortex core, as calculated in Ref. 83. The length scale of the relaxation of the order parameter to its bulk value is of order $\xi$. Figure 5 shows the same situation for an impurity, as calculated with the Koster-Slater method described in the next section. For this calculation $V_0$ and $V_2$ are Gaussians of radius $k_F^{-1}$. The $\delta\Delta(x)$ for $\nu = \pi N_s \int d\mathbf{x} V_2(\mathbf{x}) = 1.75$ and $v_0 = \pi N_s \int d\mathbf{x} V_0(\mathbf{x}) = 0$ is shown in

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Fig. 5. While oscillating with wavelength $\sim \pi k_F^{-1}$, $\delta \Delta(x)$ falls off to a negligible potential within $10k_F^{-1}$. Thus, the effective range of the potential arising from the distorted order parameter is much greater for the vortex. The two types of inhomogeneities clearly have different computational requirements; the vortex requires a better treatment of length scales beyond $\xi$, whereas the impurity requires a better treatment of energy scales far exceeding $\Delta_o$. There also exist problems that share both elements of difficulty, of which the most notable is evaluating the pinning potential of an impurity for a vortex.

11. **Koster-Slater Inversion Formalism**

a. **Three-Dimensional Continuum Model with an Isotropic Order Parameter**

We now introduce a self-consistent method that works within a sphere whose radius is determined by the range of the defect's potential and utilizes the continuum spectrum of the homogeneous superconductor. Our presentation of this method will largely follow Ref. 15. In essence, we invert the Gor'kov equation in real space. The Gor'kov equation for a defect in a superconductor can be written in the Nambu formalism\(^{107}\) as:

$$
\int dx' \delta(x' - x'') - g(x', x'') \mathbf{V}(x'') \mathbf{G}(x'', x'') \omega = g(x', x') \omega, \quad (11.1)
$$

where $g$ is the homogeneous Green's function, $\mathbf{V}$ is the potential, and the inhomogeneous retarded Green's function is

$$
\mathbf{G}(x, x'; \omega) = \begin{pmatrix}
G^r(x, x'; \omega) & F(x, x'; \omega) \\
F^a(x', x; \omega) & -G^r(x', x'; -\omega)
\end{pmatrix}. \quad (11.2)
$$

If the potential can spin-flip scatter quasiparticles, a $4 \times 4$ formalism must be used.\(^{108}\) Here the assumption remains that the spin is classical (no inelastic dynamics and no spin flipping), and the quantization direction in the superconductor is chosen parallel to the impurity spin. The elements of the matrix in Eq. (11.2) are

$$
G^r(x, x'; \omega) = -i \int_{-\infty}^{\infty} dt e^{i\omega t} \langle 0 | \{ \psi^r(x'; t), \psi^r_1(x; 0) \} | 0 \rangle, \quad (11.3)
$$

$$
F(x, x'; \omega) = -i \int_{-\infty}^{\infty} dt e^{i\omega t} \langle 0 | \{ \psi^r(x'; t), \psi^a_1(x; 0) \} | 0 \rangle, \quad (11.4)
$$

$$
F^a(x', x; \omega) = -i \int_{-\infty}^{\infty} dt e^{i\omega t} \langle 0 | \{ \psi^a_1(x'; t), \psi^a_2(x; 0) \} | 0 \rangle, \quad (11.5)
$$

$$
-\mathbf{G}^r(x', x'; -\omega) = -i \int_{-\infty}^{\infty} dt e^{i\omega t} \langle 0 | \{ \psi^r_1(x'; t), \psi^r_1(x; 0) \} | 0 \rangle, \quad (11.6)
$$

where $F^\sigma(x', x; \omega)$ is an advanced Green's function.

The explicit subscripts $\uparrow$ and $\downarrow$ do not refer to the spin of the excitation in the superconductor but rather to the spin band of the normal state used to construct the excitation. The key concept is that the spin-up band contains both $\uparrow$ electrons and down holes just as the spin-down band contains both $\downarrow$ electrons and $\uparrow$ holes. The convention employed here is standard in the theory of semiconductors, where a spin-up electron excited above the Fermi energy leaves a spin-down hole below the Fermi energy. This is convenient for magnetic potentials because if spin-up electrons are attracted to a magnetic impurity, spin-down holes should be repelled by the impurity. In the presence of a single classical impurity spin, the quasiparticle spin is a good quantum number despite electron-hole mixing. Our convention determines the composition of a spin-up quasiparticle to be part spin-up electron and part spin-up hole, rather than part spin-up electron and part spin-down hole.

For $\omega > 0$, $\mathbf{G}(x, x'; \omega)$ describes spin-up excitations, including the mixing of electrons in the spin-up band with holes in the spin-down band. For $\omega < 0$, $\mathbf{G}(x, x'; \omega)$ describes spin-down excitations, including the mixing of electrons in the spin-down band with holes in the spin-up band. By calculating $\mathbf{G}(x, x'; \omega)$ for all $\omega$, information about both spin-up and spin-down quasiparticles is obtained.

The homogeneous Green's function is independent of the spin $\sigma$, and

$$
g(x, x'; \omega) = \begin{pmatrix}
g(x, x'; \omega) & f(x, x'; \omega) \\
f(x, x'; \omega) & -g^*(x, x'; -\omega)
\end{pmatrix}. \quad (11.7)
$$

The potential (when the order parameter is real),

$$
\mathbf{V}(x'') = \begin{pmatrix}
V_\uparrow(x'') + V_\downarrow(x'') & \delta \Delta(x'') \\
\delta \Delta^*(x'') & V_\uparrow(x'') - V_\downarrow(x'')
\end{pmatrix}. \quad (11.8)
$$

where $\delta \Delta(x) = \Delta(x) - \Delta_o$ and $V_\uparrow$, $V_\downarrow$, and $\Delta(x)$ have similar meaning here as in the BdG equations. The factor of one-half from the electron spin magnitude has been incorporated into the potential $V_\uparrow$. The self-consistency equation for the order parameter is

$$
\delta \Delta(x) = \int_{-\infty}^{\infty} d\omega \gamma(x, \omega) n(\omega) \text{Im}[F(x, x; \omega) - F^a(x, x; -\omega)] - \Delta_o. \quad (11.9)
$$

An error in this equation in Ref. 15 has been corrected in Eq. (11.9).

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To be concrete and without loss of generality, the spin direction attracted by the potential will be called spin up and the spin direction repelled will be called spin down. Unlike the case of the quantum spin, there is no qualitative difference between ferromagnetic and antiferromagnetic coupling for the classical spin. We therefore do not discuss the orientation of the impurity spin, but merely define a low-energy direction for the quasiparticle spin.

For a BCS superconductor with an isotropic gap in a parabolic band, for \( \omega \) much smaller than the Fermi energy, the analytic forms for the homogeneous Green's functions are

\[
g(x, x'; \omega) = \frac{-\pi N_e}{k_F \sqrt{\Delta_o - \omega^2}} e^{-i\Delta_o - \omega^2/\pi k_F \sqrt{\Delta_o - \omega^2}} \sin k_F r,\]

\[
f(x, x'; \omega) = \frac{-\pi \Delta_o N_e}{k_F \sqrt{\Delta_o - \omega^2}} e^{-i\Delta_o - \omega^2/\pi k_F \sqrt{\Delta_o - \omega^2}} \sin k_F r,\]  

where \( r = |x - x'| \) and \( N_e \) is the density of states for each spin at the Fermi level. The coherence length \( \xi = \hbar v_F / \pi \Delta_o \), where \( v_F \) is the Fermi velocity. These expressions are valid for \( \omega \) above and below \( \Delta_o \) so long as the imaginary parts of both \( f \) and \( g \) are multiplied by \( \text{sgn} \omega \).

One strength of this formalism is its reliance on the short-range nature of the impurity’s potential. Solution of Eq. (11.1) requires inverting the frequency-dependent real-space matrix

\[
M(x, x'; \omega) = \delta(x - x') - g(x, x'; \omega) V(x')
\]  

(11.11)

to obtain \( G(x, x'; \omega) \) for \( G = M^{-1} g \). The structure of \( M(x, x'; \omega) \) allows for a precise description of the difference between the near field and the far field. We require that the impurity’s potential \( V(x) \) is zero for \( |x| > R \). The space \( |x| > R \) belongs to the far field, whereas the space \( |x| \leq R \) belongs to the near field. We can then separate any real-space matrix \( M \) symbolically into four pieces:

\[
A = \begin{pmatrix} A^{n,n} & A^{n,f} \\ A^{f,n} & A^{f,f} \end{pmatrix},
\]  

(11.12)

where \( n \) and \( f \) label the near field region and far field region, respectively. The particular example of \( M \) is block-triangular:

\[
M = \begin{pmatrix} I - g^{n,n} V & 0 \\ -g^{f,n} V & I \end{pmatrix},
\]

\[
M^{-1} = \begin{pmatrix} (I - g^{n,n} V)^{-1} & 0 \\ g^{f,n} V (I - g^{n,n} V)^{-1} & I \end{pmatrix}.
\]  

(11.13)

It is clear from Eq. (11.13) that the computational effort in inverting \( M \), and thus finding the inhomogeneous electronic structure, is entirely determined by the complexity of inverting \( M^{n,n} \). The inhomogeneous Green’s functions in the near and far fields are:

\[
G^{n,n} = (I - g^{n,n} V)^{-1} g^{n,n}
\]  

(11.14)

\[
G^{n,f} = (I - g^{n,n} V)^{-1} g^{n,f}
\]  

(11.15)

\[
G^{f,n} = g^{f,n} (I - g^{n,n} V)^{-1}
\]  

(11.16)

\[
G^{f,f} = g^{f,f} + g^{f,n} V (I - g^{n,n} V)^{-1} g^{n,f}.
\]  

(11.17)

Thus we obtain the useful result that the electronic structure in the far field is easily determined once the electronic structure in the near field is known. The connection to the \( T \)-matrix formalism is straightforward, as from Eq. (11.17),

\[
T = V (I - g^{n,n} V)^{-1}.
\]  

(11.18)

Certain features of these equations simplify their numerical implementation. For spherical symmetry each angular momentum channel constitutes an independent block-diagonal submatrix in \( M(\omega) \). Because the bare Green’s functions in Eqs. (11.10) have analytic expansions in spherical harmonics, \( M(\omega) \) can be calculated quickly. These expansions are detailed in the Appendix.

The value of \( R \) is governed by the longest-range potential. For the impurities considered here that is determined, not by the shorter-ranged magnetic and nonmagnetic potentials, but by the self-consistently determined \( \delta \Delta(x) \). Figure 5 showed the order parameter around an impurity evaluated from Eq. (11.9) at \( T = 0 \). A typical radial grid of 100 points provides a numerically robust solution. While oscillating with wavelength \( \sim \pi k_F^{-1} \), \( \delta \Delta(x) \) falls off to a negligible potential within \( 10k_F^{-1} \). The self-consistent solution depends on the value of

\[
N_e \frac{\Delta_o}{k_F} = \frac{2\pi^2 \xi k_F^{-1}}{\Delta_o} = \frac{4\pi^2 \xi k_F^{-1}}{\Delta_o}.
\]  

(11.19)

which for a free-electron model of niobium \( k_F = 1.18 \text{ Å}^{-1} \) and \( \xi = 380 \text{ Å} \) is \( 3.6 \times 10^{-3} \). This is the single dimensionless parameter required to parametrize the free-electron model of a superconductor.

In contrast to the Koster-Slater technique described here, which exploits a physical distinction between the near field and the far field to accelerate the numerical calculation, the BdG equations treat the near field and the far field on the
same level. A large $R$ is desired for decent spectral resolution, but the possible size of $R$ is limited by computational constraints. Hence a numerical implementation of the BdG equations, by comparison, is typically slower and substantially less accurate than the Koster-Slater technique.

b. Two-Dimensional Lattice Model with a General Order Parameter

For the quasi-two-dimensional tight-binding model of a superconductor appropriate for high-temperature superconductors, the lattice formulation of the Gor’kov equation must be used.

\[
\sum_{ij,k'k''} [\delta_{ij,j'} \delta_{k,k''} - g(R_{ij}, R_{ij'}; \omega) V(R_{ij}, R_{k''}; \omega) G(R_{k',k''}; \omega) = g(R_{ij}, R_{k''}; \omega),
\]

(11.20)

where $ij, kl, i'j'$, and $k'l'$ label lattice sites, $g(R_{ij}, R_{ki}; \omega)$ is the Green's function of the homogeneous superconductor, $V(R_{ij}, R_{ki})$ is the self-consistent inhomogeneous potential, and $G(R_{ij}, R_{ki}; \omega)$ is the Green's function of the superconductor fully dressed by interactions with the impurity. Eq. (11.20) is written in implicit Nambu form,

\[
G(R_{ij}, R_{ki}; \omega) = \begin{pmatrix} G_T(R_{ij}, R_{ki}; \omega) & F(R_{ij}, R_{ki}; \omega) \\ F^\dagger(R_{ki}, R_{ij}; -\omega) & -G_T^\dagger(R_{ij}, R_{ki}; -\omega) \end{pmatrix},
\]

(11.21)

and

\[
V(R_{ij}, R_{ki}) = \begin{pmatrix} V_T(R_{ij}, R_{ki}) & \delta \Delta(R_{ij}, R_{ki}) \\ \delta \Delta^\dagger(R_{ij}, R_{ki}) & V_{\delta}(R_{ij}, R_{ki}) \end{pmatrix}.
\]

(11.22)

$V_T$ and $V_{\delta}$ are the potentials felt by a spin-up electron and spin-up hole, respectively, and $\delta \Delta(R_{ij}, R_{ki})$ must be self-consistently determined from

\[
\delta \Delta(R_{ij}, R_{ki}) = \frac{\gamma |R_{ij} - R_{ki}|}{2} \int_{-\infty}^{\infty} n(\omega) \text{Im}(F(R_{ij}, R_{ki}; \omega) + F(R_{ki}, R_{ij}; -\omega) - F^\dagger(R_{ki}, R_{ij}; -\omega) - F^\dagger(R_{ij}, R_{ki}; \omega) - \Delta_\sigma(R_{ij}, R_{ki}); \omega).
\]

(11.23)

Here $\Delta_\sigma(R_{ij}, R_{ki})$ is the homogeneous order parameter. For an isotropic $s$-wave superconductor, $\gamma(R) = \gamma(\tilde{R})$, whereas for our model of an anisotropic $s$-wave or $d_{x^2-y^2}$ superconductor $\gamma(\tilde{R}) = \gamma$ when the distance $R$ corresponds to a nearest-neighbor distance.

The electron and hole potentials also have two spatial position labels. For the typical magnetic and nonmagnetic potentials, as described previously in the description of isotropic order parameter superconductors, the two positions would be the same (e.g., $V_{\delta}(R_{ij}) = \delta \Delta(R_{ij})$). An example of a physically relevant two-position potential is a local change in the hopping matrix elements.

c. Self-Consistent Potentials

In addition to the self-consistent order parameter, self-consistent spin-dependent and charge-dependent potentials can also be constructed for $V(x)$ using the calculated spatial structure of the spin $s(x)$ and charge $\rho(x)$ around the defect.

\[
s(x) = \frac{1}{2} \int_{-\infty}^{\infty} \text{d}w(\omega) \left( -\frac{\text{Im}[G_T(x, x; \omega) - G_\delta(x, x; \omega)]}{\pi} \right),
\]

(11.24)

\[
\rho(x) = e \int_{-\infty}^{\infty} \text{d}w(\omega) \left( -\frac{\text{Im}[G_\sigma(x, x; \omega)]}{\pi} \right).
\]

(11.25)

Because these self-consistent quantities are not expected to change appreciably between the normal and superconducting state, no calculations are reported for such potentials here.

d. Strong-Coupling Order Parameters

A few observations are in order concerning the extension of this formalism to systems for which the homogeneous order parameter has important frequency structure. The Gor’kov equation (Eq. (11.1)) changes due to the more general form for the off-diagonal potential originating from the order parameter.

\[
\int dx dx' \int_{-\infty}^{\infty} \delta(x - x') \delta(x'' - x'') g(x, x'; \omega) V(x'', x'''; \omega) G(x'', x'''; \omega)
\]

(11.26)

where

\[
V(x'', x'''; \omega) = \begin{pmatrix} V_T(x'', x'''; \omega) & \delta \Delta(x'', x'''; \omega) \\ \delta \Delta^\dagger(x'', x'''; \omega) & V_{\delta}(x'', x'''; \omega) \end{pmatrix}.
\]

(11.27)

General frequency dependence is included in Eqs. (11.26) and (11.27). The diagonal terms are the possibly energy-dependent potentials effective on spin-up electrons ($V_T$) and spin-up holes ($V_{\delta}$) for $\omega > 0$. Because this potential is diagonal in frequency, as is the Gor’kov equation, the frequency structure of the order parameter does not add any additional complication to numerically solving the Gor’kov equation.
The order parameter’s frequency dependence complicates the self-consistency equation (Eq. (11.9)). It must now be solved for each frequency self-consistently with the quasiparticle weight $Z$:

$$\Delta(r, r'; \omega)Z(r, r'; \omega) = \int_{-\infty}^{\infty} d\epsilon \rho_\epsilon[\text{Re} \, F(r, r'; \epsilon)(K_+(r, r'; \epsilon, \omega) - U_\epsilon)$$

$$\omega[1 - Z(r, r'; \omega)] = \int_{-\infty}^{\infty} d\epsilon \rho_\epsilon[\text{Re} \, G(r, r'; \epsilon)]K_-(r, r'; \epsilon, \omega),$$

(11.28)

where $K_\pm$ are kernels of the pairing interaction and are different for each mechanism of superconductivity. They can be determined from the homogeneous solution $U_\epsilon$ is a Coulomb factor. Incorporating these strong coupling effects allows a determination of the effect of the frequency-dependence of the pairing interaction on the electronic structure around a defect. Whereas selecting the particular orientation of the STM tip is similar to selecting the momentum of the quasiparticles of interest, selecting the STM voltage indicates which order parameter frequency is probed.

c. Dynamical Spins

The ability to model dynamical spins without creating an intractable numerical problem is an additional advantage of the Koster-Slater Green’s function technique. As mentioned in Sec. 7, there are several levels of approximation that are of interest for dynamical spins. The most complete model, which is required to obtain effects such as the Kondo effect, will accurately treat inelastic scattering, spin-flipping, and the quantum nature of the impurity spin.

The next level of approximation would allow for spin flipping and inelastic scattering. A model that could include spin flipping would need to be based on a $4 \times 4$ matrix formalism containing the simultaneous coupled equations of motion for electrons and holes of both spins. A major complication introduced by inelastic processes, however, is that the Gor’kov equation, Eq. (11.1), is no longer diagonal in frequency. Inhomogeneous Green’s functions for all $\omega$ are coupled to each other by inelastic processes.

In order to make the infinite set of coupled equations that result more tractable, we model the time dependence of the dynamic spin with a harmonic potential of frequency $\omega_\phi$, such as

$$V_\phi(x, t) = V_\phi(x)\cos(\omega_\phi t).$$

(11.29)

The frequency $\omega_\phi$ is taken to be characteristic of the spin motion. Energy transfer to and from the superconductor is only possible in units of $\omega_\phi$. The more general form of Eq. (11.1) is now

$$\int d\epsilon [\delta(x - x') - g(x, x'; \omega)V(x'; n\omega_o)]G(x', x'; \omega, \omega + n\omega_o)$$

$$= g(x, x'; \omega)\delta_{\omega_0},$$

(11.30)

where in the $4 \times 4$ formalism the inhomogeneous retarded Green’s function,

$$G(x, x'; \omega) =$$

$$\begin{pmatrix}
G_+(x, x'; \omega) & F(x, x'; \omega) & 0 & 0 \\
F^a(x', x; \omega) & -G_+^a(x, x'; \omega) & 0 & 0 \\
0 & 0 & G_+(x, x'; \omega) & -F^a(x', x; \omega) \\
0 & 0 & -F(x, x'; \omega) & -G_+^a(x, x'; \omega)
\end{pmatrix},$$

(11.31)

and the potential, $V(x, \omega)$, is

$$\begin{pmatrix}
V_+(x; \omega) & \delta\Delta(x) & V_+(x; \omega) & 0 \\
\delta\Delta(x) & V_-(x; \omega) & 0 & V_+(x; \omega) \\
V_-(x; \omega) & 0 & -V_-(x; \omega) & \delta\Delta(x) \\
0 & V_-(x; \omega) & \delta\Delta(x) & -V_+(x; \omega)
\end{pmatrix},$$

(11.32)

where

$$V(x, \omega) = V(x, \omega) = V(x, \omega) = V(x, \omega).$$

(11.33)

Our numerical results will rely on further approximations as well. By setting $V_0 = V_1 = 0$, we remove the complication of mixing the quasiparticle spins, thus retaining spin as a good quantum number and reducing our problem to the $2 \times 2$ Nambu formalism. The time dependence of the potential will be assumed to be $\cos(\omega t)$, making the potential couple only “nearest neighbor” Green’s functions in frequency space. Despite these apparently serious approximations, the key known feature of dynamic spins in superconductors — the zero bias anomaly (ZBA) in tunneling — is obtained in our calculations if the timescale of the spin is fast enough.

IV. Analytic Solution of the Point Potential

The formalism we have described is extremely powerful for working with short-range potentials within mean-field theory. It has the additional advantage of yield-
ing some analytic results for more approximate models. The main feature these models share is that the potential has zero range — it is a point. Such a model for the potential, when coupled with a carefully chosen analytic expression for the Green’s function, can yield simple analytic expressions for the energies and LDOS of localized states or resonances around impurities in a superconductor.

Analytic expressions for the Green’s functions are typically limited to continuum models. A continuum model of the electronic structure, however, when combined with a delta function potential, may yield pathological results. We first explore such an analytic model and the resulting pathologies through the response of a normal metal to a spin-dependent point potential. \( \text{Re} \ g(x, x'; \omega) = 0 \) diverges as \( r = |x - x'| \to 0 \), and sensible results are not possible unless a nondiagonal Green’s function is used. It is quite common in such a situation (e.g., Ref. 37) to set \( \text{Re} \ g(x, x'; \omega) = 0 \). The \( \delta \)-function potential, however, should be considered a mathematical convenience, and successful use of a \( \delta \)-function potential is based on the ability to reproduce with it the results of more realistic potentials. Calculations of local electronic properties near a \( \delta \)-function impurity fail using this approximation for the Green’s function. As an example, a calculation using \( \text{Re} \ g(x, x'; \omega) = 0 \) for all positions within the range of the potential yields the same LDOS for both spin-up and spin-down electrons around a potential that attracts spin-up electrons and repels spin-down electrons.

Once this flaw in standard calculations is pointed out, an approximate Green’s function that does not yield such pathologies is introduced and the resulting LDOS are analyzed. The \( \text{Re} \ g(0, x; \omega) \) is averaged over the range of a physical potential to yield a single parameter \( \alpha \), which depends on the details of the band structure. This example illuminates the importance of a correct understanding of a band structure’s effects on local properties.

Section 13 treats the isotropic order parameter superconductor, obtaining the energies of localized states. The model and results are applicable to three dimensions or two dimensions — the details of the band structure are again absorbed into the phenomenological quantity \( \alpha \). The LDOS of localized states is obtained for the special case of a three-dimensional system with a (normal-state) free-electron dispersion relation.

Section 14 addresses the situation where the order parameter is anisotropic. First it is demonstrated that for any anisotropic order parameter there are always at least two intragap resonances or localized states associated with a magnetic or nonmagnetic impurity. Subsequently, the energies of the intragap resonances are determined for an analytic approximation to the Green’s functions in a two-dimensional superconductor with a \( d_{x^2-y^2} \) order parameter.

The presentation of the point potential concludes in Sec. 15 with a quite different focus, an examination of the LDOS at a fixed frequency. In the limit that the potential is a point, the spatial structure of the LDOS depends on the relative magnitude of two spatially dependent functions that depend only on the Green’s functions of the homogeneous superconductor: one depends on the normal Green’s function \( g(x, x'; \omega) \) and the other depends on the anomalous Green’s function \( f(x, x'; \omega) \). The relative magnitude of these two functions is determined in part by the potential strength of the impurity. Due to the similarities in the spatial structure of \( g(x, x'; \omega) \) and \( f(x, x'; \omega) \), the spatial structure of the LDOS is often still given by the Born approximation (weak-scattering) result.

12. Particle-Hole Symmetry in the Normal State

In the limit \( \Delta_0 \to 0 \), the Green’s functions of the normal metal can be recovered from Eq. (11.10). In particular, the anomalous Green’s function \( f(x, x'; \omega) = 0 \). For a three-dimensional free-electron metal the normal Green’s function appropriate for an outgoing wave,

\[
g(x, x'; \omega) = -\frac{\pi N_e}{k_F} e^{ik_F r},
\]

where \( \omega \) is considered close to the Fermi surface so the change in momentum due to \( \omega \neq 0 \) is negligible.

When \( \Delta_0 \) and \( f(x, x'; \omega) \) vanish, the \( 2 \times 2 \) matrix equation of Eq. (11.1) becomes diagonal. In order to focus on the spin-dependent potential, the nonmagnetic potential will be set to zero. For a spin-dependent delta-function potential, \( V^s(x) = V^z \delta(x) \), the two resulting equations are

\[
[1 - g(0, 0; \omega)V^z]G^z(0, 0; \omega) = g(0, 0; \omega),
\]

\[
[-1 - g^*(0, 0; -\omega)V^z]G^z(0, 0; -\omega) = -g^*(0, 0; -\omega).
\]

Taking the complex conjugate of Eq. (12.3) and changing \( -\omega \) to \( \omega \) yields the clearer equation

\[
[1 + g(0, 0; \omega)V^z]G^z(0, 0; \omega) = g(0, 0; \omega).
\]

These equations are not well defined for the Green’s function of Eq. (12.1), because the real part of the Green’s function diverges at \( r = 0 \). A common method of coping with this problem is to ignore the real part of \( g \). This approximation is essentially an assumption of a strict particle-hole symmetry (not merely linearizing \( \epsilon(k) \) around \( \epsilon_F \)). We can write

\[
\text{Re} \ g(x, x'; \omega) = \int \frac{A(k; \epsilon)e^{ik(x-x')}}{\omega - \epsilon + i\delta} dk d\epsilon.
\]
where $A(k; \epsilon)$ is the momentum-resolved density of states with a given energy $\epsilon$. In order for $\text{Re} \ g(x, x'; \omega = 0)$ to vanish for all $r$, we require $A(k; \epsilon) = A(k; -\epsilon)$ for all $k$ and $\epsilon$. It is this particle-hole symmetry in the momentum-resolved density of states that produces pathological results in the spatially-resolved density of states in the presence of an impurity.

The LDOS calculated with this approximate Green's function around a spin-dependent delta-function potential is

$$
-\frac{1}{\pi} \text{Im} \ G_{\sigma}(x, x; \omega) = N_0 \left( 1 - \frac{(\pi N_0 V_0)^2}{1 + (\pi N_0 V_0)^2} \right) \frac{\sin^2 k_F r}{(k_F r)^2}.
$$

(12.6)

This expression yields the pathological behavior that the local density of states near a spin-dependent potential is exactly the same for spin-up electrons as for spin-down electrons. The local density of states for $V_s = \pi N_0 |V_0| = 0.1$ is plotted in Fig. 6 as a function of distance from the potential. Although it is somewhat distorted from its homogeneous value, it does not show the spin-dependent asymmetry of a more realistic model. An exact calculation for a Gaussian of range $k_F^{-1}$ is also shown in Fig. 6 for comparison.

A more realistic approach to coping with the divergence in Eq. (12.1) without yielding the pathological result of Eq. (12.6) is to average the $\omega$-symmetric real part of $g$ over a range given by the assumed range of the potential. That yields a finite value for the local density of states at the potential, but does not control the behavior for small $r$. To perform that task, we consider a “muffin-tin” Green's function. This function has the form

$$
g(x, x'; \omega) = -\frac{\pi N_o}{k_F r} \frac{e^{ik_F r}}{r > R_o}
$$

$$
= -i\pi N_o - \pi N_o \alpha \quad r < R_o
$$

(12.7)

where $-\pi N_o \alpha$ is the average of the $\omega$-symmetric real part of $g$ over the range of the potential, and $R_o$ is chosen so that the spatially integrated spectral weight of the Green's function is unchanged (as required by probability conservation). We show in Fig. 6 the local density of states calculated with this Green’s function. In particular, the asymmetry in the response of spin-up electrons and spin-down electrons to a spin-dependent delta-function potential is governed by this phenomenological parameter $\alpha$. The agreement with the exact solution is good at the origin and far from the impurity. The muffin-tin Green's function is discontinuous, unfortunately, but yields a better approximation of the response of the system than the particle-hole symmetric approximation (discarding the $\omega$-symmetric real part of the Green’s function).

For a Gaussian potential with range $a$.

$$
\alpha = \frac{2}{\sqrt{\pi k_F a}} \left( 1 + \sum_{n=3}^{\infty} \frac{1}{(2n-3)!!} \left( \frac{(k_F a)^2}{2} \right)^{n-1} \right).
$$

(12.8)

For the Gaussian potentials numerically calculated in this paper, $a = k_F^{-1}$, so $\alpha = 0.704$.

It is also possible to generate an asymmetry between spin-up and spin-down electrons by adding a nonmagnetic potential $V_0$ with the $V_s$ to parametrize the impurity, but still maintaining a particle-hole symmetric band structure. Because the response of a particle-hole symmetric system to a potential does not depend on the sign of that potential, the $V_0$ is required to distinguish between particles and holes. A spin-up electron feels a potential $V_s + V_0$, whereas a spin-down hole feels a potential $V_s - V_0$. This additional nonmagnetic potential only breaks particle-hole symmetry locally (within the range of the potential), whereas for a realistic band structure the particle-hole symmetry is broken everywhere in the solid.
13. Magnetic and Nonmagnetic Point Potentials in a Superconductor with an Isotropic Order Parameter

a. Gor'kov Equations and Self-Consistency

Approximating the local potential by a delta function,

\[
V(x) = V\delta(x) = \begin{pmatrix} V_x + V_0 & 0 \\ 0 & V_x - V_0 \end{pmatrix} \delta(x),
\]

leads to a simple expression for Eq. (11.1),

\[
\begin{pmatrix}
1 - g(0, 0; \omega)(V_x + V_0) & -f(0, 0; \omega)(V_x - V_0) \\
-f(0, 0; \omega)(V_x + V_0) & 1 + g^*(0, 0; -\omega)(V_x - V_0)
\end{pmatrix} \mathbf{G}(0, 0; \omega)

= \mathbf{M}^{\alpha\rightarrow\beta}(\omega) \mathbf{G}(0, 0; \omega)

= \mathbf{M}^{\alpha\rightarrow\beta}(\omega) \mathbf{G}(0, 0; \omega).
\]

(13.1)

In principle \( \mathbf{M}(\omega) \) can be found from the Green's functions in Eq. (11.10), however the same divergence in the real part of \( g(r; \omega) \) as \( r \to 0 \), which is present in the normal state, is present in the superconducting state. This divergence is coped with in Ref. 37 by discarding the divergent piece. This strategy, however, yields the same pathologies in the superconducting state as were found in the normal state. Later we will introduce appropriate Green's functions for the superconducting state. First, however, our definition of the potential \( V \) in this model will be extended to include a crude form of self-consistency.

As seen from Fig. 5, the distortion of the order parameter is short-ranged around an impurity. We may then consider the effect of the order-parameter distortion on the electronic structure to be parametrized by an effective delta-function potential \( \delta \mathcal{V}(x) \) similarly motivated to the delta-function potentials for the magnetic and nonmagnetic potentials. The potential \( V(x) \) is changed in the following way:

\[
V(x) = V\delta(x) = \begin{pmatrix} V_x + V_0 & \delta \Delta \\ \delta \Delta & V_x - V_0 \end{pmatrix} \delta(x).
\]

(13.3)

The relative effect of the \( \delta \Delta \) compared to the other two potentials is likely to be small for the potentials considered in this chapter. Typically \( v_1 = \pi N_B V_x \approx 1 \) or \( V_0 = \pi N_B V_0 \approx 1 \), and for a free-electron model of niobium \( N_B \Delta_0/k_B \approx 3.6 \times 10^{-8} \). Even for a small coherence length of \( \xi = 10k_F^{-1}, N_B \Delta_0/k_B = 1.6 \times 10^{-3} \). For convenience we define \( \delta \Delta = \pi N_B \delta \Delta \).

b. Energies and Character of Localized States in the Superconductor

The energies of the localized states of angular momentum \( \ell \) correspond to the positive energies \( \omega_0 = |\Omega| \), where

\[
\det \mathbf{M}^{\alpha\rightarrow\beta}(\Omega) = 0,
\]

and the solution is traced to the \( \ell \)-channel block of \( \mathbf{M} \) (see the Appendix). For the analytic model, \( \mathbf{M}^{\alpha\rightarrow\beta}(\omega) \) is the matrix shown in Eq. (13.2), where \( g(0, 0; \omega) \) in the superconducting state is constructed similarly to that of the normal state,

\[
g(0, 0; \omega) = -\pi N_B \left( \frac{\Delta_0}{\sqrt{\Delta_0^2 - \omega^2}} \right).
\]

(13.5)

The anomalous Green's function is given by Eq. (11.10), and because it does not have a divergence problem as \( r \to 0 \),

\[
f(0, 0; \omega) = -\pi N_B \left( \frac{\Delta_0}{\sqrt{\Delta_0^2 - \omega^2}} \right).
\]

(13.6)

This analytic model only has localized states in the \( \ell = 0 \) angular momentum channel, as expected for a delta-function potential. Those energies are

\[
\omega_0 = \left| \frac{v_1 \delta_0 \pm [(v_1 \delta_0)^2 - (v_1^2 + \gamma^2)(\delta_0^2 - \gamma^2)]^{1/2}}{v_1^2 + \gamma^2} \right| \Delta_0.
\]

(13.7)

where \( \gamma = [(1 + \alpha^2)(v_1^2 - \delta_0^2 - \gamma^2) - 2 \alpha v_0 - 1]^{1/2} \).

(13.8)

Eq. (13.7) reduces to a result obtained by Shiba when \( v_0 = \alpha = \delta_0 = 0 \), a result obtained by Rusinov when \( \alpha = \delta_0 = 0 \), a result obtained by us when \( v_0 = \delta_0 = 0 \), and a result obtained by Salkola, Balatsky, and Schrieffer when \( \alpha = 0 \).

b. Energies and Character of Localized States in the Superconductor

The energies of the localized states of angular momentum \( \ell \) correspond to the positive energies \( \omega_0 = |\Omega| \), where

\[
\det \mathbf{M}^{\alpha\rightarrow\beta}(\Omega) = 0,
\]

and the solution is traced to the \( \ell \)-channel block of \( \mathbf{M} \) (see the Appendix). For the analytic model, \( \mathbf{M}^{\alpha\rightarrow\beta}(\omega) \) is the matrix shown in Eq. (13.2), where \( g(0, 0; \omega) \) in the superconducting state is constructed similarly to that of the normal state,

\[
g(0, 0; \omega) = -\pi N_B \left( \frac{\Delta_0}{\sqrt{\Delta_0^2 - \omega^2}} \right).
\]

(13.5)

The anomalous Green's function is given by Eq. (11.10), and because it does not have a divergence problem as \( r \to 0 \),

\[
f(0, 0; \omega) = -\pi N_B \left( \frac{\Delta_0}{\sqrt{\Delta_0^2 - \omega^2}} \right).
\]

(13.6)

This analytic model only has localized states in the \( \ell = 0 \) angular momentum channel, as expected for a delta-function potential. Those energies are

\[
\omega_0 = \left| \frac{v_1 \delta_0 \pm [(v_1 \delta_0)^2 - (v_1^2 + \gamma^2)(\delta_0^2 - \gamma^2)]^{1/2}}{v_1^2 + \gamma^2} \right| \Delta_0.
\]

(13.7)

where \( \gamma = [(1 + \alpha^2)(v_1^2 - \delta_0^2 - \gamma^2) - 2 \alpha v_0 - 1]^{1/2} \).

(13.8)

Eq. (13.7) reduces to a result obtained by Shiba when \( v_0 = \alpha = \delta_0 = 0 \), a result obtained by Rusinov when \( \alpha = \delta_0 = 0 \), a result obtained by us when \( v_0 = \delta_0 = 0 \), and a result obtained by Salkola, Balatsky, and Schrieffer when \( \alpha = 0 \).

The energies of Eq. (13.7) correspond to a spin-up quasiparticle and a spin-down quasiparticle. However, there may be only one real energy; then only one \( \ell = 0 \) localized state exists around the impurity, as occurs for a magnetic impurity \( (v_0 = \delta_0 = 0) \). When \( v_0 = 0 \) the localized states are due to order parameter suppression, and the energies of the two spin states are degenerate. This follows from time-reversal symmetry in the absence of a magnetic potential. For small \( v_0 \) the two energies are split by an amount

\[
\Delta \omega_0 = \frac{2v_1 \delta_0 \Delta_0}{v_1^2 + \gamma^2}.
\]

(13.9)
c. Spectral Weight Asymmetry in the Analytic Model

The spatial structure of the spectral weight as a function of the distance \( r \) from the impurity will now be addressed. A spin-up quasiparticle consists of amplitudes for a spin-up electron (electron in a spin-up state), and a spin-up hole (electron missing from a spin-down state). Therefore the spectral weight of a spin-up localized state will be divided between an electron-like pole in the spin-up band at \( \omega = \omega_+ \) (with weight \( A_+(r; \omega) \)) and a hole-like pole in the spin-down band at \( \omega = -\omega_+ \) (with weight \( A_-(r; -\omega) \)). These two types of excitation are independently resolvable by a scanning tunneling microscope because at positive sample voltage relative to the tip, the STM places electrons in the sample, whereas at negative sample voltage the STM places holes in the sample. We define the energy of the pole in the spin-up band to be \( \omega_+ \) and in the spin-down band to be \( \omega_- \). Even though \( \omega_+ \) is always positive, \( \omega_- \) can be positive or negative, and \( \omega_- = -\omega_+ \).

The spatial structure of the spectral weights of the spin-up band and spin-down band components of the localized state are given by

\[
A_+(r; \omega) = \frac{\pi N_0 \Delta^2}{2v_x} \delta(\omega - \omega_+) \left[ (v_0 - v_x) \Delta^2_0 + (v_0 + v_x) \omega^2 - (v_0 + v_x) \alpha^2 (\Delta^2_0 - \omega^2) \right] \frac{2(v_0 + v_x) \alpha \omega \sqrt{\Delta^2_0 - \omega^2} - (1 + \alpha^2)(v_0 - v_x)(\alpha (\Delta^2_0 - \omega^2) + \omega \sqrt{\Delta^2_0 - \omega^2})}{\Delta_0^2},
\]

\[
A_-(r; \omega) = \frac{\pi N_0 \Delta^2}{2v_x} \delta(\omega + \omega_+) \left[ (v_0 - v_x) \Delta^2_0 + (v_0 + v_x) \omega^2 - (v_0 + v_x) \alpha^2 (\Delta^2_0 - \omega^2) \right] \frac{2(v_0 + v_x) \alpha \omega \sqrt{\Delta^2_0 - \omega^2} - (1 + \alpha^2)(v_0 - v_x)(\alpha (\Delta^2_0 - \omega^2) + \omega \sqrt{\Delta^2_0 - \omega^2})}{\Delta_0^2},
\]

for \( r < R_o \).

For a spin-down quasiparticle there is an electron-like pole in the spin-down band and a hole-like pole in the spin-up band and the relative weight is still given by this expression (Eq. (13.11)). This expression for \( v_0 = 0 \) was reported in Ref. 14.

In Sec. 17 these results are compared with numerical calculations of properties in the superconducting state and in the normal state.

14. Anisotropic Order Parameters

a. A General Result for Anisotropic Order Parameters

In anisotropic superconductors a finite density of states remains within the energy "gap." In particular, for a \( d \)-wave order parameter the density of states remains finite down to the chemical potential. An intragap state can hybridize with this continuum of quasiparticles within the gap, producing a resonance rather than a localized state.

With a few additional approximations it can be shown that there are always at least two resonant energies for both magnetic and nonmagnetic potentials for an anisotropic superconductor. The first approximation is that impurity-induced variations in the order parameter can be neglected. A further approximation involves the condition for a resonant state, when \( \text{Re}[\text{det } M] = 0 \). For anisotropic superconductors, where there is a finite density of states within \( \Delta_{\text{max}} \) of the chemical potential, det \( M \) can have an imaginary part. This part produces a width in the resonance, and it can be argued that the resonance is poorly defined if the width is much greater than \( \Delta_{\text{max}} \). This problem is complicated by the frequency dependence of Im[det \( M \)], which can distort the shape and peak energy of the resonances. These complexities are set aside here as simpler situations are considered.

The Gor’kov equation is

\[
[1 - g(\omega)V_h][1 + g^*(-\omega)V_h] = f^2(\omega)V_hV_h = \text{det } M.
\]

We separate the particle-hole symmetric part of the Green’s function from that which is not particle-hole symmetric by assuming the following form for \( g(\omega) \):
\[ g(\omega) = \pi N_p (\alpha + \tilde{g}(\omega)). \]  

(14.2)

Here \( \tilde{g}(\omega) = -g^{*}(-\omega) \). In order to parametrize the anisotropy of the order parameter in a way still suitable to our analytic model we can make the approximation

\[ f^2(\omega) = \beta(\omega)\pi^2 N_p^2 (\tilde{g}(\omega) + 1). \]  

(14.3)

\( \beta(\omega) \) is thus a measure of the gap anisotropy. Two special cases yield simple frequency-independent values for \( \beta(\omega) \), (1) isotropic s-wave (\( \beta = 1 \)), and (2) d-wave (\( \beta = 0 \)). Using the appropriate dimensionless quantities in our lattice situation, \( v_s = \pi N_p V_s \) and \( v_0 = \pi N_p V_0 \), we can express the conditions for resonant states.

Resonances for magnetic potentials exist when

\[ \tilde{g}(\omega) = \frac{1 \pm \sqrt{v_s^2 (\alpha^2 + \beta)(1 - \beta) + \beta}}{(1 - \beta)v_s}, \]  

(14.4)

and for nonmagnetic potentials when

\[ \tilde{g}(\omega) = \pm \sqrt{[(1 - \alpha v_0)^2 + \beta v_0^2] (1 - \beta) v_0^2}. \]  

(14.5)

Because \( \tilde{g}(\omega) \) varies from \( +\infty \) to \( -\infty \) between \( \omega = -\Delta_{\text{max}} \) and \( \omega = \Delta_{\text{max}} \), and because for all order parameters except isotropic s-wave \( 0 \leq \beta(\omega) < 1 \) for \( \omega \) sufficiently close to \( \Delta_{\text{max}} \), there always are solutions to Eqs. (14.4) and (14.5). For the nonmagnetic case solutions come in pairs due to the spin degree of freedom. Note that the degeneracy of the two solutions for the magnetic potential for a particle-hole symmetric d-wave model (\( \alpha = \beta = 0 \)), which was pointed out in Ref. 93 and linked to the point-group of the lattice, actually is not directly related to the spatial symmetry of the superconductor.

b. **Energies of Resonances for a Two-Dimensional d-Wave Superconductor**

A d-wave superconductor is a special case of the previous results, and one that is likely relevant to high temperature superconductors. The on-site anomalous Green's function vanishes, hence \( \beta(\omega) = 0 \). Saikola et al.\(^{109} \) have derived the form of the ordinary Green's function for the order parameter \( \Delta(\phi) = \Delta_{\text{max}} \cos 2\phi \), where \( \phi \) is the angle of the momentum from the (10) direction. They obtain

\[ G_{\text{eff}}(\omega) = -(2\varepsilon/\pi) [\text{sgn}(\omega) K(\sqrt{1 - e^2}) + iK(\varepsilon)], \]  

(14.6)

for \( e = |\omega|/\Delta_{\text{max}} < 1 \). \( K \) is the complete elliptic integral of the first kind. Solutions to Eq. (14.5) for \( \alpha = 0 \) to logarithmic accuracy are given by\(^{110} \)

\[ \Omega_0 = \frac{\Delta_{\text{max}}}{2N_p V_0 \ln(8N_p V_0)}, \]  

(14.7)

with a linewidth

\[ \Gamma = \frac{\pi \Omega_0}{2 \ln(8N_p V_0)}. \]  

(14.8)

15. **Connection to the Born Approximation**

In Ref. 111 it was argued that calculations within the Born approximation for the spatial structure of the d\( f(r; V)/dV \) would remain accurate for strong potentials, so long as the potential was short-ranged. In this section we explicitly make the connection between the result from the Born approximation and the result from the Koster-Slater technique in the limit that self-consistency can be ignored and that the size of the potential approaches a point.

In this limit Eq. (11.17) is

\[ \frac{1}{\pi} \sum_{\mathbf{x}} \text{Im} G_\omega(\mathbf{x}, \mathbf{x}; \omega) = \frac{1}{\pi} \text{Im} \{ 2g(\mathbf{x}, \mathbf{x}; \omega) + [g(0, 0; \omega)V_{\text{eff}}(\omega)g(0, \mathbf{x}; \omega)]_{11} \}
\]

\[ - [g^*(\mathbf{x}, 0; -\omega)V_{\text{eff}}(\omega)g^*(0, \mathbf{x}; -\omega)]_{22}, \]  

(15.1)

where \( V_{\text{eff}}(\omega) \delta(\mathbf{x})\delta(\mathbf{x}') = V[1 - g(0, 0; 0; V)]^{-1} \). The inhomogeneous part of the right-hand side of Eq. (15.1) has the following form if the off-diagonal elements of \( V_{\text{eff}}(\omega) \) can be ignored (this is appropriate when self-consistency is not important):

\[ \frac{1}{\pi} \text{Im} \{ ([V_{\text{eff}}(\omega)]_{11} - [V_{\text{eff}}(\omega)]_{22})g(0, \mathbf{x}, \omega)g(0, \mathbf{x}, \omega) \}
\]

\[ - ([V_{\text{eff}}(\omega)]_{11} - [V_{\text{eff}}(\omega)]_{22})f(\mathbf{x}, 0, \omega)f(\mathbf{x}, 0, \omega) \]  

(15.2)

\[ = C(\omega)g(0, \mathbf{x}, \omega)g(0, \mathbf{x}, \omega) - C(\omega)f(\mathbf{x}, 0, \omega)f(\mathbf{x}, 0, \omega), \]  


The functions \( C_i(\omega) \) and \( C_e(\omega) \) depend on the potential strength and the frequency, but not on the position. In Ref. 111 the differential conductance near a nonmagnetic impurity in the Born approximation was found to depend on the spatial Green's functions in the same combinations as Eq. (15.2), with \( C_i(\omega) = C_e(\omega) = V_0 \).

The spatial structure of the LDOS in Eq. (15.2) depends sensitively on the order parameter anisotropy, and particularly the momenta of the minima and maxima of the order parameter on the Fermi surface. In the real-space directions corresponding to these momenta, the LDOS is enhanced. Figures 7(a, b) show the spatial structure of the differential conductance calculated in the Born approximation for a voltage just above \( \Delta_{\text{max}} \) for (a) an isotropic order parameter and (b) a \( d_{x^2-y^2} \) order parameter. The normal-state electronic structure is assumed to be that of a quasi-two-dimensional free-electron gas, and the length units are \( k_F^{-1} \). Enhancements of the LDOS along the real-space directions corresponding to gap nodes also have been found at low voltages. Figure 7(c) shows the enhancement of the LDOS at a voltage much less than \( \Delta_{\text{max}} \) along directions rotated 45° from those in

Fig. 7. Differential conductance, normalized to the normal metal's homogeneous differential conductance, near a nonmagnetic impurity (\( V_0/k_F = 1 \)) in a superconductor. The length scale is set by \( k_F^{-1} \) and the coherence length is \( \Theta(k_F) \). The range of the intensity is from \( 0.1 \) (black) to \( 0.1 \) (white):

(a) Isotropic order parameter, voltage of \( 1.1 \Delta_{\text{max}} \);
(b) \( d_{x^2-y^2} \) order parameter, voltage of \( 1.1 \Delta_{\text{max}} \);
(c) \( d_{x^2-y^2} \) order parameter, voltage of \( 0.1 \Delta_{\text{max}} \). For (c) the result has been multiplied by the radius to enhance the oscillatory features far from the impurity. (a) and (b) from Ref. 111.)
Fig. 7(b). The enhancement of the LDOS along these directions, corresponding to nodes in momentum space of the $d_{x^2-y^2}$ order parameter, occurs because most quasiparticles at low energies have group velocities perpendicular to the Fermi surface near the locations of nodes. This feature was pointed out generally in Ref. 111.

The argument was made in Ref. 111 that the spatial structure calculated in the Born approximation was essentially the same as that obtained in the strong potential limit. The derivation at the beginning of this section justifies these arguments so long as $C_3(\omega)$ is not too different from $C_2(\omega)$. In a later calculation Choi\textsuperscript{112} found these two prefactors to be similar for voltages above $\Delta_{\text{max}}$ for strongly scattering potentials as well as for weakly scattering potentials, but he did not consider the interesting case of scattering from an intragap resonance.

There are two major qualitative changes in the LDOS introduced by a strong potential. One is the relative amplitude of the LDOS at different frequencies (due to resonances or localized states). The other is the relative amplitude of $C_3(\omega)$ and $C_2(\omega)$, which can differ substantially from the Born approximation result when $\omega$ is near a resonance.

The case for a magnetic potential is slightly different. For a purely magnetic potential there would be no inhomogeneous structure in the LDOS within the Born approximation, because

$$V_{\text{eff}}(\omega) = \begin{pmatrix} V_s & 0 \\ 0 & V_s \end{pmatrix},$$

so the distortions in the LDOS of the two spin directions are equal and opposite. For a stronger magnetic potential, because $[V_{\text{eff}}(\omega)]_{11} \neq [V_{\text{eff}}(-\omega)]_{22}$, the LDOS would be spatially inhomogeneous, and would have similar spatial structure as a nonmagnetic impurity.

### V. Impurities in Superconductors with Isotropic Order Parameters

#### 16. Nonmagnetic Impurity

Even strong nonmagnetic impurities at moderate concentrations will not suppress the critical temperature of a superconductor with an isotropic order parameter.\textsuperscript{35} Nevertheless, it was recognized early on\textsuperscript{66} that the local order parameter may be affected. In Ref. 66 the effect of the nonmagnetic impurity was calculated in the far field by modeling the impurity potential with a phase shift. The phase shifts were evaluated for two models: a spherical square-well potential and a delta-shell potential. Self-consistency was ignored by only focusing on regions far from the impurity where the change in the order parameter is small compared to its homogeneous value. The order parameter change due to the impurity was found to oscillate with the Fermi wavelength, and decay as $r^{-2}$ for $r < \xi$. For $r > \xi$, expressions in Ref. 66 indicate a decay of $r^{-3}$.

Figure 8 shows the spectral weight $A(r; \omega)$ at several frequencies above the energy gap near a strong nonmagnetic impurity with a Gaussian potential of range $k_F^{-1}$ and strength $V_0 = 7/8$, calculated self-consistently for a superconductor with $\xi k_F = 449$ (a free-electron parametrization of niobium). The spectral weights are suppressed to approximately 30% of their homogeneous value at the center of the potential. Only continuum states are shown because no localized states were found for this potential. The curves showing the spectral weight have been displaced from $\Delta(r)/\Delta_0$ so that they may be distinguished. Also shown displaced in Fig. 8 is the spectral weight in the normal state, normalized to the spectral weight in the homogeneous metal. All of the quantities plotted in Fig. 8 are identical to the accuracy of the calculation. Figure 8 is an illustration of a relationship between

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the spectral weight in the normal state and the spectral weight in the superconducting state,

\[ A(r; \omega) = \frac{A_{\text{n}}(r)}{2N_o} A_{\text{n}}(\omega), \]  

where \( A_{\text{n}}(r) \) is the spectral weight in the inhomogeneous normal state for energies near the Fermi surface and \( A_{\text{n}}(\omega) \) is the homogeneous superconductor's spectral weight as a function of frequency. \( 2N_o \) is the normal state's spectral weight far from the impurity. This expression is valid for small \( r \) and small \( \omega \), the regime of interest for STM on a superconductor. For \( \omega \) of order \( \Delta_o \), Eq. (16.1) is valid for \( r \ll \xi \).

We further illustrate the relationship of Eq. (16.1) in Fig. 9(a), which shows the differential conductance near this nonmagnetic impurity, normalized by the normal-state result, as a function of voltage and position calculated from the LDOS using Eq. (2.3) with \( T = 0.13\Delta_o/k_B \). This temperature corresponds to 2 K for niobium. There is no change in the energy gap due to this nonmagnetic potential. Figure 9(a) shows that it is merely the local amplitude of the spectral weight that is reduced — this would also manifest itself as a locally reduced oscillator strength for an optical transition. Figure 9(b) is an identical calculation for a shorter coherence length, \( \xi = 10^{-6} \). There appears to be little difference, although here a localized state exists near the continuum.

Figures 8 and 9(a, b) show for the nonmagnetic impurity that the normal-state electronic structure determines the spatial dependence of the superconductor's \( A(r; \omega) \) for all frequencies including near the energy gap. The potential strength of the impurity is orders of magnitude greater than \( \Delta_o \), and thus locally mixes in states far from the Fermi surface in the homogeneous metal. These states are required to construct probability densities that are suppressed by 70% near the impurity. The spatial structure of the spectral weight in the normal state is essentially identical to that seen in Fig. 8 over an energy range around the Fermi surface that is orders of magnitude greater than \( \Delta_o \).

Once the normal-state electronic structure has been distorted by the presence of the nonmagnetic impurity, superconductivity is a small perturbation within a narrower frequency range. The formation of the gap in the single-particle excitation spectrum in the superconducting state is characterized by the “mixing” of electron and hole amplitudes to form quasiparticles near the gap edge. These quasiparticles, therefore, are constructed from eigenstates of the metal that have already been strongly distorted by the impurity potential.

Equation (16.1) has important implications for spectroscopy on a superconductor, because one of the procedures for normalizing spectra taken at different lateral positions on a superconducting surface is to assume that the LDOS at a particular

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**Fig. 9.** Differential conductance (LDOS) as a function of voltage and position calculated around a nonmagnetic impurity with \( v_{\text{imp}} = 0.875 \). The LDOS is normalized by the homogeneous DOS of the normal state. The spectrum is suppressed substantially in the vicinity of the impurity. The temperature is 0.13\( \Delta_o/k_B \), which for niobium corresponds to about 2 K. (a) A coherence length appropriate for niobium, \( \xi k_F = 449 \). (b) A much shorter coherence length, \( \xi k_F = 10 \). [From Ref. 15.]
voltage much larger than $\Delta_0$ is the same. This is an attempt to correct for possible changes in the tip-surface distance on moving the tip laterally. A small change in the tip-surface distance can have a strong effect on the tunneling current. Unfortunately this procedure will prevent an experiment from seeing changes in the LDOS due to a nonmagnetic impurity, including the conductance oscillations described in Ref. 111.

We now discuss the properties of the order parameter. $\Delta(r)$ is self-consistently determined, and is shown in Fig. 8 for small $r$ to be identical in spatial structure to the normal-state spectral weight,

$$\frac{\Delta(r)}{\Delta_0} = \frac{A_0^s(r)}{2N_F} = \frac{A(r; \omega)}{A_0^s(\omega)}. \quad (16.2)$$

Because a nonmagnetic potential repulsive to electrons attracts holes, and $\Delta(r)$ depends equally on electron and hole amplitudes, one might expect a nonmagnetic potential to have little effect on the spatial dependence of the order parameter. However, the allowable maximum spectral density of holes depends on the spectral density of the electron band where the holes reside, so if most electrons in an energy range much larger than $\Delta_0$ around the chemical potential are excluded from the site, holes will be effectively excluded as well. To emphasize this point we note that the scaled anomalous spectral weight $\text{Im} F(r; r; \omega)$ is identical to the scaled $A(r; \omega)$ for the frequencies shown in Fig. 8 (and for all relevant frequencies for the self-consistency equation Eq. (11.9)). Because $\text{Im} F(r; r; \omega)$ is proportional to the product of electron and hole amplitudes, and $A(r; \omega)$ is proportional to the electron amplitude squared, the spatial structure of the electron and hole spectral weights must be similar. They are, because the normal-state spectral weight $A_0^s(r; \omega)$ is roughly frequency-independent around the Fermi energy over an energy range much greater than $\Delta_0$.

We now comment on the lack of localized states near the nonmagnetic impurity for $\xi k_F = 449$ and the small binding energy of the quasiparticle for $\xi k_F = 10$. The suppression of the order parameter near the impurity may be considered to form an attractive off-diagonal potential, which may bind quasiparticles. Localized states created by order-parameter suppression would be doubly degenerate, due to the two possible spin states (see Eq. (13.7)). If the electron part is attracted and the hole part is repelled, one might expect the effects of a nonmagnetic potential on the localized quasiparticle to cancel, because a localized quasiparticle is half hole and half electron. However, the binding energy of the localized state is an order of magnitude smaller ($\omega_{p} = (1 - 2 \times 10^{-4})\Delta_0$) than that found in Sec. 20 for a suppressed order parameter via pairing suppression. This may be explained by the well-known wavefunction reduction near the origin (quantum reflection) of a strong attractive potential on a quantum-mechanical particle. We find also that in the case of the magnetic impurity, a large enough nonmagnetic potential of either sign will suppress the binding of a quasiparticle to the impurity. We note here that the ratio of the nonmagnetic potential to the off-diagonal potential ($\delta \Delta(r)$) is much larger ($\nu_0/\Delta_0 \sim 10^4$) than the ratios of the nonmagnetic potentials to the magnetic potentials considered next.

17. Magnetic Impurity

Recently, we presented calculations of the LDOS (and thus the differential conductance in an STM experiment) in the vicinity of a magnetic impurity.14 These calculations indicated that the spatial structure of the electron amplitude of the localized state differed strongly from the hole amplitude. A further result was that the spectrum should recover to the homogeneous spectrum within a few atomic spacings. Similarly motivated calculations of the LDOS due to the $\ell = 0$ localized state have been presented since then,93 although these calculations did not address the continuum LDOS. The two models used in Ref. 93 were (1) a $\delta$-function model solved using particle-hole symmetric Green's functions, but not self-consistently, and (2) self-consistent calculations for a two-dimensional tight-binding s-wave superconductor within the BdG equations. The first method can only model the normal-state properties properly for a particle-hole symmetric band structure, such as at the Van Hove singularity in a two-dimensional tight-binding band structure. The second method must contend with numerical finite-size effects, which make it difficult to calculate the continuum states. A result obtained from the first method, which is only true for special band structures, is that the spatial structure of the electron and hole components of the quasiparticle are the same. The authors of Ref. 93 did raise the possibility of an additional nonmagnetic potential as a source of electron-hole amplitude asymmetry in the spatial structure of the localized state. We found14 and will explore that there is, for realistic band structures, electron-hole asymmetry without a nonmagnetic potential.

a. Energy and Character of Localized States

We will begin with a discussion of the energies of the localized states around a magnetic impurity and the spin character of those states. Solutions to Eq. (13.4) can be evaluated numerically. Figure 10 shows the dependence of the energies of the localized state poles for the first two angular momentum channels on the strength of the magnetic potential. Results for a short coherence length ($\xi = 10k_F^{-1}$) are shown (solid line) as well as (long dashed line) results for a long coherence length ($\xi = 449 k_F^{-1}$). The localized quasiparticle state for small $\nu$ is the spin state attracted to the classical spin, which we will label up ($\uparrow$). As the
potential strength increases, the excitation energy of each angular momentum state decreases. At some critical value \( v^{**}_s \), the localized state becomes a spin-down excitation, the energy changes abruptly, and then increases with increasing \( v_s \). This behavior can be extracted from the analytic model (Eq. (13.7)) as well.

Evident from Eq. (11.2) is that the \( \ell \)-channel electron pole involves entirely single-particle states within the spin-up band when the \( \ell \)-channel solution to Eq. (13.4), \( \Omega > 0 \). This occurs for \( v_s < v^{**}_s \). However, for \( \Omega < 0 \) (\( v_s > v^{**}_s \)), the electron pole involves entirely states within the spin-down band. The hole-like pole always involves single-particle states in the opposite spin band from the electron-like pole. The source of the quasiparticle amplitude for the various poles is indicated in Fig. 10.

Also shown in Fig. 10 are the analytic results for the pole energies for \( \alpha = 0 \) (Ref. 37) and \( \alpha = 0.704 \). The muffin-tin model is no better than the particle-hole symmetric model in predicting the localized state energies. The muffin-tin model

\[
\text{Fig. 10. Energies of the quasiparticle poles as a function of the magnetic potential strength \( v_s \) for the first two angular momentum states around the impurity. The spin-up and spin-down labels refer to the band that the excitation resides in — an excitation with negative energy (hole-like) in a spin-up band is a spin-down hole. The solid line corresponds to \( \xi_k = 10 \), the long-dashed line to \( \xi_k = 449 \), and the dot-dashed line to the result calculated with muffin-tin Green's functions and \( \alpha = 0.704 \). At a critical value of \( v_s = v^{**}_s \), the up poles cross to negative energies and the down poles cross to positive energies, indicating a change in the character of the ground state. The kink evident in the solid and long-dashed lines is real, and is due to the discontinuous (at \( T = 0 \)) change in \( \Delta(\ell) \) at \( v^{**}_s \). The unimportance of self-consistency can be gauged by the small difference between the short-coherence length result and the long-coherence length result. [From Ref. 15.]
\]
Fig. 11. Magnetization density of states integrated from below the band edge to $\epsilon$. The ground-state spin of the system corresponds to the value at zero energy (the chemical potential). The potential for (a) is below the critical potential strength $v_{\text{cr}}$, so the ground state spin is zero, whereas the potential for (b) is above $v_{\text{cr}}$, so the ground state spin is 1/2.

that lies beneath the chemical potential. This calculation is easier in the two-dimensional lattice model, so results will be presented from there. Figure 11 shows the integrated magnetization density of states,

$$ S(\epsilon) = \frac{1}{2} \int_{-\infty}^{\epsilon} d\omega \int d\mathbf{x} \text{Im}[G_\uparrow(\mathbf{x}, x; \omega) - G_\downarrow(\mathbf{x}, x; \omega)], \quad (17.1) $$

in an isotropic superconductor for (a) $v_\epsilon < v_{\text{cr}}$ and (b) $v_\epsilon > v_{\text{cr}}$. The magnetization density of states is integrated from below the band edge to an energy $\epsilon$. The spin of the ground state corresponds to the value when $\epsilon = \mu$, where $\mu$ is the chemical potential (taken here to be $\mu = 0$). The two potentials of Fig. 11(a, b) differ by about 10%, yet clearly for Fig. 11(a) the ground-state spin is zero, and for Fig. 11(b) the ground-state spin is 1/2. These values are indicated on the figure by dashed lines. The contributions to the integrated spin from around $-3.5t$ and around $4.5t$ correspond, respectively, to the bound state of the attracted spin direction and the antibound state of the repelled spin direction.

b. Differential Conductance and Local Density of States

We now focus on our results for the differential conductance near the impurity. Figures 12(a), 12(b), and 12(c) show results for $v_\epsilon = 0.52, 0.875$, and 1.75 respectively. They show the state split off from the continuum, with a larger electron-like amplitude than hole-like amplitude (12(a)), and then lower in energy with an increased electron/hole asymmetry (12(b)). Finally the larger peak becomes hole-like (12(c)). In all three cases the spectrum recovers to its bulk value within a few $k_F^{-1}$, due to the $r^{-2}$ decay of the localized state (Eq. 13.10). The asymmetry between the electron-like and hole-like peaks becomes more pronounced as $v_\epsilon$ increases. We note that the larger peak is always associated with the spin-up band, whereas the other is associated with the spin-down band. Despite the apparent differences in peak size, the spatially integrated electron spectral weight of the quasiparticle is equal to the spatially integrated hole spectral weight. The localized quasiparticle is always half electron and half hole for all potentials examined here. For $v_\epsilon < v_{\text{so}}$, the spin-up band amplitude is electron-like and the spin-down band amplitude is hole-like. At $v_{\text{so}}$ (1.32 for a free-electron model of niobium), the spin-up component becomes hole-like and the spin-down component becomes electron-like, as required by the change in the spin of the excitation.

Figure 12(d) shows the differential conductance for a markedly different coherence length, $\xi = 10k_F^{-1}$, and $v_\epsilon = 0.875$. It is evaluated for the same value of $\Delta/k_B T$ as Figs. 12(a, b, c) and looks almost identical to Fig. 12(b). Because the localized state is broadened by temperature through Eq. (2.3), this is a manifestation of the proportionality of the spectral weight to $N_t \Delta_\epsilon$ (Eq. 13.10). Figure 13 shows the spectral weight at the origin for the $\ell = 0$ state and for the $\ell = 1$ state at its first maximum for $v_\epsilon = 0.875$ as a function of $\xi^{-1}$, which is proportional to $N_t \Delta_\epsilon$. Figure 14 shows the spectral weight for $\xi = 449k_F^{-1}$ as a function of $v_\epsilon$ for the spin-up and spin-down poles at the origin for the $\ell = 0$ state and at the first maximum for the $\ell = 1$ state. It is clear that a nonmagnetic potential is not necessary to obtain an electron-hole asymmetry.

In Fig. 15 we show the asymmetry at the impurity as a function of $v_\epsilon$ for two values of $\xi$: a long coherence length appropriate for niobium and a short coherence length. From Fig. 13 it should be evident that the asymmetry is not sensitive to $\xi$. It is, however, predicted extremely well by the normal-state spin-up and spin-down band spectral weight asymmetry at the impurity (also shown in Fig. 15). We can therefore conclude that as with the nonmagnetic impurity (Fig. 9), the spatial structure of the spectral weight of the localized state around a magnetic impurity is a normal-state property. We further show in Fig. 16 for $v_\epsilon = 0.875$ the $\ell = 0$, spin-up band and spin-down band projections of the normal-state spectral weight to compare with the localized state spin-up band and spin-down band spectral weights for two values of $\xi k_F$. The normal-state and long-coherence length calculations are practically indistinguishable. The insets show $r^2 A(r)$, which removes the rapid power-law decay of the state. The localized states for all angular momenta $\ell$ will decay as the power law $r^{-2}$. For the short-coherence length calculation the effect of an exponential envelope is also visible. In the analytic result the exponential envelope should have a range $R = \pi \xi/2\sqrt{1 - (\omega_\theta/\Delta_\epsilon)^2}$, which
Fig. 12. Differential conductance (LDOS) calculated around a magnetic impurity with (a) $v_e = 0.5$, $\xi k_F = 449$; (b) $v_e = 0.875$, $\xi k_F = 449$; (c) $v_e = 1.75$, $\xi k_F = 449$; (d) $v_e = 0.875$, $\xi k_F = 10$. All are calculated with $k_B T = 0.13 \Delta_0$. In the progression from (a) to (c) the asymmetry between the two peaks increases and the higher peak moves to lower energies, eventually becoming hole-like. The LDOS is normalized by the normal-state's homogeneous density of states. [From Ref. 15.]

Fig. 12 (Continued).
Fig. 13. Spectral weight at the impurity ($r = 0$) for the first angular momentum channel, $\ell = 0$, and at the first maximum for the second angular momentum channel, $\ell = 1$, for poles in both the spin-up and spin-down bands, as a function of the inverse coherence length, showing a linear behavior. The magnetic potential strength is $\nu_s = 0.875$. [From Ref. 15.]

Fig. 14. Spectral weight at the impurity ($r = 0$) for the $\ell = 0$ channel for $\xi k_F = 449$ as a function of magnetic potential strength for poles in both the spin-up and spin-down bands. The spectral weight in the spin-up band pole of the $\ell = 0$ localized state saturates at large $\nu_s$. Also shown are the spectral weights at the first maximum for the $\ell = 1$ localized states. [From Ref. 15.]

Fig. 15. Ratio of the spectral weight in the spin-up band and in the spin-down band at the impurity ($r = 0$) as a function of magnetic potential strength. This is plotted for the normal state $\ell = 0$ projected Green’s functions (solid line) as well as for the localized states for niobium ($\xi k_F = 449$, long-dashed line), for $\xi k_F = 10$ (dot-dashed line), and for the muffin-tin model (short-dashed line). The muffin-tin model is only successful for $\nu_s < 0.5$, but that is due to a breakdown in describing the normal state. The normal-state electronic structure is a good predictor of the superconductor’s electronic structure for the entire range of $\nu_s$. [From Ref. 15.]

Corrects to better than 1% the discrepancy in Fig. 16. The power-law fall-off and exponential envelope can be seen directly from Eq. (11.10) and Eq. (13.10).

We can summarize these comments with a general equation, similar in concept to that for the nonmagnetic impurity, Eq. (16.1). That is, for a localized quasiparticle state of spin $\sigma$, the spectral weight of a localized state with angular momentum $\ell$ would be

$$A_{\ell\sigma}(r; \omega) = B A_{nr}(r; \ell) e^{-\frac{2\nu_s}{\xi k_F} \sqrt{1 - \left(\frac{\omega}{\omega_s}\right)^2}} \delta(\omega - \sigma \sigma' \omega_1),$$

(17.2)

where $B$ is a normalization factor so that the spectral weight of the state integrates to one, and $A_{nr}(r; \ell)$ is the angular-momentum $\ell$ projection of the normal-state spectral weight in the spin $\sigma$ band. We note that for small $r$ there is an approximate relationship between the superconducting state’s spectral weight and the normal state’s spectral weight in each spin band,

$$\frac{1}{2E} \int_{-E}^{E} d\omega A_{\sigma}(r; \omega) = A_{nr}(r),$$

(17.3)
Fig. 16. Spectral weights for the $\ell = 0$ localized state in the up and down bands for $v_s = 0.875$. The solid line is the normal state $\ell = 0$ projected spectral weight, the long-dashed line is the localized state in a superconductor with $\xi_{k_F} = 4.49$, and the dot-dashed line is for $\xi_{k_{F}} = 10$. The inset shows the spectral weight multiplied by $r^2$ to remove the algebraic decay. The normal-state and long-coherence length results are practically indistinguishable. The deviation shown in the short-coherence length superconductor's spectral weight is fit to within 1% by the exponential decay factor described in the text. Hence the spatial structure of the spectral weight of the superconductor's localized state is well predicted by the normal state spectral weight. [From Ref. 15.]

where $\Delta_s \ll E \ll \epsilon_F$. This, in connection with Eq. (17.2), implies a dependence on the normal-state structure of the continuum spectral weight around the magnetic impurity.

c. Recent Experimental Results

Recent experimental results on the local spectra of single atoms placed on the (110) surface of niobium\textsuperscript{113} indicate that (1) discrete states are evident within the energy gap and the LDOS associated with them is asymmetric with voltage around $V = 0$, and (2) the LDOS becomes indistinguishable from the bulk density of states within a distance greater than the Fermi wavelength but much less than the coherence length. Figure 17 shows these STM difference spectra. Three different atoms were placed on the surface: manganese (Mn), gadolinium (Gd), and silver (Ag). Niobium is an isotropic-order parameter superconductor, so the behavior of magnetic and nonmagnetic impurities should be different. The Ag

---

atom is not expected to show any magnetic behavior, whereas the $d$ electrons of Mn and the $f$ electrons of Gd may produce local moments. It is known that Mn has a local moment in bulk Nb.$^{42,43}$ Due to the differences in coordination, however, the exchange interaction of such an atom placed on the surface will not be the same, and hence it was not known whether they would produce a local moment.

The difference spectra of Fig. 17 is obtained in the following way: the tip is positioned at the given distance from the center of the impurity, and the height of the tip is adjusted until the resistance of the junction is $10^{7}$ ohms at a voltage of 10 mV. Then the tunneling spectrum taken with a similarly normalized junction far from the impurity is subtracted. As pointed out in Sec. 16, this procedure discards any uniform suppression of the local density of states over this (narrow) voltage range. A nonmagnetic impurity produces such a uniform suppression, and so the difference spectra obtained near the silver atom indicate no change from the bulk spectrum.

A quite different situation is found for the Mn and Gd atoms. Near the impurity the difference spectra indicate a suppression of the gap-edge density of states and an enhancement of the intragap density of states. It is particularly noteworthy that the spectra are extremely particle-hole asymmetric. These qualitative results are consistent with the results of Sec. 17, reported in Ref. 14 and elaborated in Ref. 15. The later theoretical work of Ref. 93 and Ref. 113 is also consistent.

An attempt was made in Ref. 113 to model the experimental results with a spherical square-well potential for the impurity and a free-electron normal-state band structure for niobium. The results of that comparison for the difference spectrum measured directly on top of the Mn atom are shown in Fig. 18. The agreement shown here is actually somewhat marginal, because the energy and height of the large hole-like peak can be fit by adjusting the range of the square-well and the strength of the spin-dependent potential. The width of the peak is determined by the temperature. The remaining feature of the spectrum is the relative height of the electron-like and hole-like peaks, which is not well fit. A more flexible model, with less trivial position-dependence of the spin-dependent potential, is able to better fit the experimental results. There are more serious problems, however, with this strategy, which are now described.

The authors of Ref. 113 argue that the Mn impurity on the Nb surface is a strong impurity, based primarily on the hole-like nature of the larger peak in the difference spectrum of Fig. 18. The actual value of the exchange integral they extract is $J = 4$ eV, which is considerably stronger than the $J = 2.7$ eV of a Mn atom in the bulk.$^{43}$ This appears unlikely, because the lower coordination number of an atom on the surface would lead to a weaker exchange interaction. The unlikely large value of $J$ is due to the assumed electronic structure of niobium in Ref. 113. Far from having a normal-state free-electron dispersion, niobium has a $d$ band at the Fermi energy that is more than half filled. These $d$-band states are most likely to interact with the $d$-state of Mn. Because this $d$ band is more than half filled, the carriers that predominantly interact with the impurity spin are holes. We reconsider the arguments of Sec. 17 in the light of a normal-state Fermi surface that is hole-like. For weak impurities, the state near the continuum is predominately hole-like near the impurity. When a quasiparticle falls into the ground state, and thus the impurity is strong, the large quasiparticle peak is electron-like. This is the opposite of the situation for an electron-like Fermi surface. Therefore, a large hole-like peak near the impurity is indicative of a weak impurity rather than a strong impurity.

In order to make further progress in a detailed comparison between theory and experiment, it appears necessary to perform a calculation based on a more appropriate model of the niobium electronic structure. Such tight-binding models are available, and work is underway in this direction.

d. Structure of the Inhomogeneous Order Parameter

We now return to the structure of $\Delta(x)$. This quantity, which is not directly observable, formed the focus of several investigations of the local structure around a magnetic impurity. The oscillation of the order parameter around a magnetic impurity was first evaluated without self-consistency.$^{62-64}$ A self-consistent
calculation of the order parameter at the impurity and very far away for weak impurity potentials was done by Schlotmann.\textsuperscript{65}

As shown in Fig. 5, for large values of \( v_s \), \( \Delta(r = 0) < 0 \). Sign changes in \( \Delta \), as seen in pair tunneling, have been suggested for magnetic impurities in the barriers of Josephson junctions.\textsuperscript{114–117} The sign change in \( \Delta(0) \) occurs at \( v_s^{\ast} \). Due to the spin and frequency symmetries of Eqs. (11.1–11.8), the anomalous spectral weight \( \text{Im} \, F(r, r, \omega) \) associated with the spin-up pole is always equal and opposite to the anomalous spectral weight associated with the spin-down pole. As the pole in the spin-up band goes from electron-like (\( \omega > 0 \)) to hole-like (\( \omega < 0 \)) and the pole in the spin-down band goes from hole-like to electron-like, the contribution to \( \Delta(0) \) changes sign abruptly at \( T = 0 \). The \( \Delta(r) \) resulting from several values of \( v_s \) and two values of the coherence length are shown in Fig. 19(a, b). The discontinuity at \( v_s^{\ast} \) is more pronounced for shorter coherence lengths because the localized state’s spectral weight is more concentrated at the impurity (Eq. (17.2)). \( \Delta(0) \) as a function of \( v_s \) is shown in Fig. 20 for two values of the coherence length. At \( T > 0 \) the transition would be smoothed somewhat.

The behavior of \( \Delta(0) \) as a function of \( v_s \) comes from the introduction at \( v_s^{\ast} \) of a quasiparticle into the ground state of the system. The spin-up quasiparticle localized near the impurity in the ground state suppresses the local order parameter. For time-reversal invariant potentials one cannot make \( \Delta(r) \) negative by inserting a single quasiparticle, because the suppression from one quasiparticle is cancelled by the lack of suppression from its unexcited Kramers doublet partner. For a spin-dependent potential, however, the anomalous spectral weight near the impurity may be almost entirely contributed by the single low-energy localized state. When a quasiparticle is present in the ground state, the ground state has spin-up \( v_s^{\ast} \) and a negative \( \Delta(r) \).\textsuperscript{14} Exciting the low-energy state for \( v_s > v_s^{\ast} \) removes the spin-up quasiparticle and therefore increases \( \Delta(0) \), whereas excitation of quasiparticles typically reduces \( \Delta(0) \) (which is the case for \( v_s < v_s^{\ast} \)). Also, exciting the low-energy state alone, such as in a tunneling experiment, reduces the total spin of the superconductor.

The behavior of \( \Delta(r) \) for large \( r \) has not been evaluated numerically. We expect the contribution of the localized state to decay with a length determined by the exponential envelope in Eq. (13.10), \( R_{\text{loc}} = \pi \xi / 2 \sqrt{1 - (\omega / \Delta_0)^2} \). The


Fig. 19. Order parameters as a function of distance from the impurity \( r \) calculated for several magnetic potential strengths for (a) \( \xi k_F = 449 \) and (b) \( \xi k_F = 10 \). In both cases there is a discontinuous change in the order parameter when \( v_s \) passes through the critical strength \( v_s^{\ast} \). [From Ref. 15.]

\textsuperscript{65} We contributions from the continuum states at a given \( \omega \) have a \( \omega \)-dependent spatial oscillation and decay as \( r^{-2} \). When these contributions are integrated from \( \Delta_0 \) to \( \omega_D \), one obtains a \( r^{-3} \sin(r/R_{\text{cont}}) \) decay, where \( R_{\text{cont}} \sim \xi \Delta_0 / \omega_D \). Because \( R_{\text{loc}} > R_{\text{cont}} \), it would be possible to have first a \( r^{-2} \exp(-r/R_{\text{loc}}) \) decay followed by an oscillatory \( r^{-3} \) decay. The oscillatory \( r^{-3} \) decay was pointed out in Ref. 65. We
emphasize that, although the order parameter appears to recover to its bulk value over a length scale much shorter than the coherence length, this is again a manifestation of the $r^{-2}$ behavior of the normal and anomalous spectral weights. When $\delta A(r)$ is multiplied by the surface area of the sphere at radius $r$, one finds that the order parameter's recovery length is on the order of the coherence length.

18. Combined Magnetic and Nonmagnetic Potentials

We now discuss the addition of a nonmagnetic potential to the magnetic potential. It has been suggested\textsuperscript{93} that introducing a $v_\circ$ with a $v_s$ will provide electron-hole asymmetry. We find that it does change the asymmetry, which we show in Fig. 21 for a particular $v_s$, but that once again this is a normal-state property. The relationship between the normal-state spectral weights and the superconducting-state spectral weights of Eq. (17.2) still holds. Introducing $v_\circ$ also alters the localized-state energies (see Eq. (13.7)), which we show in Fig. 22 for $v_s = 0.875$ and $\xi k_F = 449$. The presence of a nonmagnetic potential may affect the value of $v_\circ$\textsuperscript{93}.

We show in Fig. 23 a partial diagram of the ground state as a function of the parameters $v_s$ and $v_\circ$ for $\xi k_F = 449$. We note that the boundary between the two

Fig. 20. Order parameters at the impurity ($r = 0$) as a function of magnetic potential strength $v_s$ for two values of the coherence length. The discontinuity in the order parameter at $v_s = 0$ is much larger for the short-coherence-length superconductor. [From Ref. 15.]

Fig. 21. Ratio of the spectral weight at the impurity in the spin-up band to the spin-down band for $v_s = 0.875$ and $\xi k_F = 449$ as the nonmagnetic potential $v_\circ$ varies. In a similar result to that seen in Fig. 15, the normal-state spectral weights are good predictors of the superconducting state's spectral weight. We note that the curves are not symmetrical around $v_\circ = 0$, which results from a realistic band structure without particle-hole symmetry. [From Ref. 15.]

Fig. 22. The energy of the spin-up pole is shown as a function of nonmagnetic potential strength for $v_s = 0.875$ and $\xi k_F = 449$. The energy of the spin-down pole is just the negative of the energy of the spin-up pole. The analytic models do not perform particularly well in reproducing the pole energies, although the muffin-tin model does show a similar asymmetry around $v_\circ = 0$ to the numerical calculations. [From Ref. 15.]
strain the potential strength using the frequency-integrated spectral weight and the localized-state energy.

It seems appropriate to mention again the tendency to normalize spectra according to the LDOS measured at energies much larger than $\Delta_v$. Because the normal-state LDOS near the impurity changes substantially in the presence of magnetic or nonmagnetic impurities, an experiment performed using such a normalization procedure would yield impurity parameters of questionable validity.

![Diagram](image)

**Fig. 23.** Calculated boundary between two ground states around the magnetic impurity for $\xi k_F = 449$. For a large enough magnetic impurity strength a quasiparticle is bound in the ground state. The minimum magnetic impurity strength depends on the nonmagnetic impurity strength. For still larger magnetic impurity strengths there would be ground states with more than one bound quasiparticle. [From Ref. 15.]

ground states is not shifted much from $\xi k_F = 449$ to $\xi k_F = 10$, hence the order parameter energy is not very significant in determining this boundary.

19. **Connection to Normal-State $dl/dV$ Spectra**

The normal state may provide some guidance for attempts to extract impurity potentials in the superconducting state from STM measurements. Figure 24 shows normal-state $dl/dV$'s for various potentials. These curves should also represent the frequency-averaged spectral weight measured in the superconducting state (see Eq. (17.3)).

The enhancement or suppression of spectral weight near the origin is particularly sensitive to $v_0$. A measurement of this quantity, the energy of the localized state and the asymmetry of the electron and hole amplitudes at the impurity over-constrains $v_0$ and $v_1$, given an assumption of the shape of the potential. To extract information about the potential's detailed shape would require a fitting procedure using the differential conductance at various positions. If, for some reason, the spin-down amplitude were too small to measure, it may be possible to con-

![Diagram](image)

**Fig. 24.** Spectral weights in the normal state as functions of the distance from the impurity for several combinations of magnetic and nonmagnetic potentials (a) only a magnetic potential, and (b) a fixed magnetic potential $v_0 = 0.875$ and a varying nonmagnetic potential. By making measurements around the impurity in the normal state (or integrating the superconductor's spectrum over a frequency much larger than $\Delta_v$), information about the structure of the impurity may be obtained. [From Ref. 15.]
20. Pairing Suppression

The pairing potential, $\gamma(x)$ in Eq. (11.9), may also have spatial structure. When this parameter is changed it induces a change in the order parameter that produces an off-diagonal potential felt by the quasiparticles. We set $v_x = v_0 = 0$ so that there is no magnetic or nonmagnetic potential to compete with the order parameter change. Figure 25 shows the order parameter around a short-range suppression,

$$\gamma(x) = [1 - e^{-i(k_x x)^2}]\gamma_0,$$

(20.1)

for two values of the coherence length. The order parameter is strongly suppressed and because $\gamma(0) = 0$, $\Delta(0) = 0$. For long coherence lengths, this change in the order parameter has no effect on the local density of states (shown in Fig. 26(a)). It is possible to localize quasiparticle states, however, at shorter coherence lengths. These can produce features in the local density of states that are visible. One such case is shown in Fig. 26(b). The energy of the localized state is $\omega_n = (1 - 4 \times 10^{-3})\Delta_0$. Whereas a nonmagnetic potential changes the local density of states without significantly changing the energy gap, a pairing suppression has a very weak effect on both, especially in the long-coherence length limit.

![Graph 25. Order parameter as a function of distance $r$ from a defect with a suppressed pair potential but no single-particle potential. (From Ref. 15.)](image1)

![Graph 26. Differential conductance (LDOS), normalized by the normal-state's homogeneous DOS, and a defect with a suppressed pair potential but no single-particle potential. (a) $\xi/k_F = 449$, $\gamma = 0.13\Delta_0$ — there is no evidence of any change in the spectrum due to the order parameter suppression shown in Fig. 25. (b) $\xi/k_F = 10$, $k_BT = \Delta_0/100$ — a localized state very near the conduction enhances the continuum edge seen in tunneling near the defect. (From Ref. 15.)](image2)
As pointed out in Sec. 10, the vortex has a weak potential, on the scale of meV, extended over a long distance, of order $\xi$. The impurity, however, has a strong potential, on the order of eV, extended over a short distance, of order $A$. Localized excited states are found in both cases, but several qualitative differences should be described. Whereas even for a strong potential the impurity induces one well-localized state, and possibly a few more very weakly bound states, the vortex localizes states over a volume of order $\xi$. The quasiparticle excitation energies in a superconductor with an isotropic order parameter are shown in Fig. 27 as a function of angular momentum. Just as in an atomic system, the expectation value of the distance from the vortex core increases with increasing angular momentum. Thus the quasiparticles at greater and greater distances are more and more weakly localized. The states above 1.2 meV are in the continuum, but appear at definite energies due to the finite size of the system.

The position-dependence of quasiparticle energies implies that STM tunneling spectra taken close to the vortex core will show well-localized states within the gap. As the distance from the core increases the position of the quasiparticle states within the gap gets closer to the gap edge. Figure 28 shows the calculated differential conductance for several different distances from the vortex core, showing this characteristic feature of the intragap states.
STM measurements around a magnetic impurity are quite different. Because there is usually only one localized state the intragap energy of the state will not change with distance — but the magnitude of the LDOS will change.

VI. Impurities in Superconductors with Anisotropic Order Parameters

Several experiments, including photoemission, Josephson edge and corner tunneling devices, and tricrystal rings strongly indicate that the order parameter in high-temperature superconductors is anisotropic. These experiments also support the $d_{x^2-y^2}$ order parameter, whereas other experiments indicate the order parameter in some crystals may be $d + s$, or some other anisotropic combination.

Results for the local electronic structure of impurities in $d_{x^2-y^2}$ superconductors will be presented here. The normal-state electronic structure of the superconductor will be taken to be a one-band two-dimensional tight-binding model, based on the properties of the copper-oxygen planes in these high-temperature superconducting compounds. The nearest-neighbor and next-nearest neighbor hopping elements are chosen to be $t = 350$ meV and $t' = -56$ meV, respectively, whereas the chemical potential (which determines the doping) is $\mu = 0$.

22. ENERGY AND CHARACTER OF RESONANCES

An important distinction between isotropic and anisotropic order parameters (particularly order parameters that vanish at places on the (normal-state) Fermi surface) is that in a superconductor with an anisotropic order parameter a finite density of states remains within the energy “gap.” In the case of an order parameter that vanishes at places on the Fermi surface, there is a finite density of states down to zero energy within the energy gap. Hence any impurity-associated localized state within the gap can hybridize with the continuum of quasiparticle states within the gap. The resulting impurity feature will be a resonance, rather than the pure localized state of Sec. 17.

To illustrate this we first show in Fig. 29 the energies of the resonances in a $d_{x^2-y^2}$ superconductor for nonmagnetic potentials with strength $v_0$. These energies $\Omega$, which are identified by peaks in the DOS within our calculations, are shown along with the analytic calculations from Ref. 93 (see also Sec. 14). These analytic calculations are based on a particle-hole symmetric expression for the homogeneous Green's functions, and so are the same for $\pm v_0$.

A further problem, however, is that these analytic calculations are based on the standard method of identifying resonances: setting the real part of the T-matrix denominator zero and using the remaining imaginary part to determine the width. This method was used to derive Eq. (14.5), which applies to superconductors with asymmetric band structures and order parameter anisotropy. Results from Eq. (14.5), shown on Fig. 29, do agree better with the numerical results, although they still differ by 50% for $\Omega > 0.3\Delta_{\max}$. Results obtained using the exact numerical Green's functions in det $M$, and solving for $\text{Re}[\text{det } M] = 0$, do not differ qualitatively from those obtained from Eq. (14.5).

A useful comparison with the $d_{x^2-y^2}$ system is to a system where the order parameter is the absolute value of the $d_{x^2-y^2}$ order parameter. This order parameter, referred to as an $s^\ast$-wave order parameter, has the same magnitude as the $d$-wave order parameter but does not change sign. In contrast to the resonances for the $d$-wave system, resonances for nonmagnetic impurities in the $s^\ast$-wave system do not have lower energy than $\Omega = 0.77\Delta_{\max}$. Hence if the order parameter were $s^\ast$-wave, in order to produce low-energy resonances, the impurities would have to be magnetic.
23. **Differential Conductance and Local Density of States**

In order to describe the LDOS it is important to connect the LDOS calculated at points on the two-dimensional lattice,

\[
A(R_{ij}; \omega) = -\frac{1}{\pi} \sum_{\sigma} \text{Im} \ G_{\sigma}(R_{ij}, R_{ij}; \omega),
\]

(23.1)

to the LDOS of the real continuous system. Implied in our lattice description is the existence of Wannier functions at each lattice site in the superconductor. The continuous LDOS is then the product of the lattice LDOS with these Wannier functions,

\[
A(r; \omega) = \sum_{ij} A(R_{ij}; \omega) |\phi(r - R_{ij})|^2,
\]

(23.2)

where \(\phi(r)\) is the Wannier function associated with the single effective tight-binding band of a homogeneous copper-oxygen plane. If \(\phi(r)\) is well-localized to an individual copper site, only one term in the sums over \(i\) and \(j\) will contribute, greatly simplifying the result. The differential conductance can be determined from the LDOS of Eq. (23.2) via Eq. (2.3), so there is the following relationship between the differential conductance and the lattice LDOS:

\[
\frac{dI}{dV}(r, V) \propto \int_{-\infty}^{\infty} d\omega \frac{\partial n_{\text{STM}}(\omega)}{\partial \omega} \sum_{ij} A(R_{ij}; \omega) |\phi(r - R_{ij})|^2.
\]

(23.3)

The differential conductance at the impurity site for an isotropic order parameter superconductor is shown in Fig. 31(a) for several magnetic impurity strengths \(V_{ij}\). Because the band-structure filling is over half, the carriers are holes. As described in Sec. 17, when the carriers are holes, for weak impurity potentials the large peak at the impurity is hole-like. As the potential strength increases the large peak moves towards the chemical potential, and eventually to the electron-like continuum edge. Figure 31(b) shows the differential conductance at a nonmagnetic impurity site for a \(d_{x^2-y^2}\) superconductor for several potential strengths. In contrast to Fig. 31(a), only a hole-like peak is seen at smaller potentials, and for a large potential the peak is entirely electron-like. Figure 31(c) is for a magnetic impurity in the \(d_{x^2-y^2}\) superconductor, and indicates that the size of the large peak is about half the size as for a nonmagnetic impurity. An additional structure is evident on the electron-like side of the spectrum, which is due to the other intragap resonance (see Eqs. (14.4) and (14.5)). The two resonances of the nonmagnetic impurity are degenerate and correspond to the two spin directions. The two resonances of the magnetic impurity, however, in general occur at quite different energies.
We now show in Fig. 32 the differential conductance for magnetic and nonmagnetic impurities in a $d_{x^2−y^2}$ superconductor at sites along a direction from the impurity in the (10) direction, and also in the (11) direction. At the impurity site there is no evidence of the gap features, and the spectrum is dominated by an asymmetric resonance that is hole-like for $V = 2.5t$ and electron-like for $V = 10t$. The result for $V = 2.5t$ is in rough agreement with STS measurements near oxygen vacancies on the YBa$_2$Cu$_3$O$_{7−δ}$ surface, also shown. Immediately adjacent to the impurity the gap edge feature begins to recover in strength. Whereas the DOS for potentials of 2.5$t$ and 10$t$ are roughly identical (Fig. 30), the LDOS at the impurity site is entirely hole-like for 2.5$t$ and electron-like for 10$t$. Although our surface model is incomplete (e.g., it does not include the copper-oxygen chains), supporting evidence is provided by STS identification of a broad resonance at the oxygen vacancies for positive sample bias voltages around 700 meV, consistent with a potential of 2.5$t$.

We now consider the spatial structure of the LDOS at specific voltages. In Sec. 15 the spatial structure of the LDOS was explored for $s$-wave and $d_{x^2−y^2}$ superconductors with cylindrical Fermi surfaces. Figure 33 shows the LDOS for $V = 2.5t$ at (a) the hole-like peak and (b) the electron-like peak of the resonance. For this potential the LDOS peak at the impurity site is entirely hole-like. In addition, the LDOS along the diagonals away from the impurity vanishes for the electron-like peak of the resonance.

In Sec. 15 it was pointed out that the spatial structure of the LDOS depends on the relative magnitude of two functions — one depending on the normal Green’s function and one on the anomalous Green’s function. In the Born approximation the two functions have approximately the same magnitude. The situation is completely different for Fig. 33(a, b), for the two voltages shown correspond to the hole-like and electron-like LDOS of a resonance that is entirely hole-like at the impurity. As a result, the hole-like LDOS of the resonance has the spatial structure of $g(x; 0; ω)g(0; x; ω)$, whereas the electron-like LDOS has the spatial structure of $f(x; 0; ω)f(0; x; ω)$. The different spatial structure of these two functions is the origin of the different spatial structure apparent in Fig. 33(a, b). The vanishing of the electron-like resonance LDOS along the diagonals occurs because the anomalous Green’s function $f(0; x; ω)$ vanishes (by symmetry) for all energies for $x$ along diagonals. The normal Green’s function does not vanish along those diagonals, so the hole-like resonance LDOS has a pronounced density of states along the diagonals.

We note that such atomic-scale aspects of the LDOS would not be produced in a calculation that coarse-grained the electronic structure, such as the Eilenberger

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tral weight which is pulled into the intragap region, and becomes (in part) the intragap resonances. Again, these features are also evident in the Born approximation calculations (Fig. 7(b)). Figure 33(d) shows the LDOS around such an impurity in the normal state, indicating that although the enhancements along (10) or (11) directions are not present in the normal state, the structure on the smaller spatial scale is quite similar. The anisotropy of the order parameter serves to amplify or suppress the spatial features that already exist in the normal state.

24. LOCAL DISTORTION OF THE ORDER PARAMETER

a. Character of the Ground State

Figure 34(a) shows for magnetic impurities the order parameter at the impurity, and in the inset the total spin of the superconductor’s ground state. In contrast to the isotropic s-wave case, where the order parameter at the impurity changes abruptly at some critical potential strength, for d-wave the order parameter changes smoothly at all potentials, due to the finite width of the resonant state. For s-wave this transition is characterized by the binding of a quasiparticle in the ground state, producing an abrupt change in the ground-state spin of the superconductor from 0 to 1/2. For the d-wave superconductor there is instead a cloud of quasiparticles near the impurity potential. The nonquantized behavior arises because there are quasiparticle states at the chemical potential in the d-wave superconductor but not in the s-wave superconductor.

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Fig. 33. Spatial structure of the LDOS for fixed voltages. The potential is nonmagnetic with strength 2.5f. (a) $eV = -0.14\Delta_{\text{max}}$, and (b) $eV = 0.14\Delta_{\text{max}}$, corresponding to the hole-like and electron-like peaks of the resonant state, respectively. (c) $eV = 1.03\Delta_{\text{max}}$, showing a fourfold “cross” pattern, and (d) the LDOS around this impurity in the normal state.

Equations. These features are also not extractable from the Born approximation, because they require knowledge of whether the resonance is hole-like or electron-like at the impurity site. Born approximation calculations for the LDOS at low energies (Fig. 7(c)) do reproduce the rough angular structure far from the impurity. The enhancement of the LDOS along the diagonals of the square lattice is a result of a larger density of states of quasiparticles with group velocity along the diagonals at low energies.

Figure 33(c) shows the LDOS for a voltage just exceeding the order parameter maximum. Oscillations along the four directions corresponding to gap maxima are clearly present and are reductions of the LDOS. This is the origin of the spec-

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Fig. 34. Change in the order parameter at the impurity for (a) magnetic potentials and (b) nonmagnetic potentials. Inset of (a) is the ground-state spin for magnetic potentials. For the inset the order parameter has been increased by a factor of three to guarantee that all the distortion is within the considered far-field region. [From Ref. 119.]
The $d$-wave order parameter changes sign for sufficiently strong positive (electron repelling) nonmagnetic impurities (shown in Fig. 34(b)), but not for magnetic impurities or negative nonmagnetic impurities. The difference between positive and negative nonmagnetic impurities is due to the hole-like character of the Fermi surface — a nonmagnetic potential that repels electrons attracts the holes to the impurity. The positive nonmagnetic impurity attracts twice as much hole weight (due to spin degeneracy) to the impurity as the magnetic impurity, so the order parameter suppression is greater. A change in the order parameter sign may affect the presence or absence of a Josephson $\pi$-junction,\textsuperscript{144–147} should the coupling across an interface be near nonmagnetic impurities, such as in a rough junction.

### b. Presence of Other Local Order Parameter Symmetries

#### Near the Impurity

The symmetry properties of the order parameter near a localized impurity with the symmetry of the lattice are somewhat subtle. In the model used here of nearest-neighbor pairing, the order parameter is associated with the nearest-neighbor bonds between lattice sites rather than the sites themselves on the square lattice. An order parameter symmetry, however, is associated with a site; four symmetries are allowed, depending on the relative sign and magnitude of the four nearest-neighbor bonds emanating from a site. These four are:

\[
\Delta_d(R_{ij}) = \Delta(R_{ij}, R_{i,j+1}) + \Delta(R_{ij}, R_{i,j-1}) + \Delta(R_{ij}, R_{i+1,j}) + \Delta(R_{ij}, R_{i-1,j}),
\]

\[
\Delta_s(R_{ij}) = \Delta(R_{ij}, R_{i,j+1}) + \Delta(R_{ij}, R_{i,j-1}) - \Delta(R_{ij}, R_{i+1,j}) - \Delta(R_{ij}, R_{i-1,j}),
\]

\[
\Delta_p_x(R_{ij}) = \Delta(R_{ij}, R_{i,j+1}) - \Delta(R_{ij}, R_{i,j-1}),
\]

\[
\Delta_p_y(R_{ij}) = \Delta(R_{ij}, R_{i,j+1}) - \Delta(R_{ij}, R_{i,j-1}).
\]

These order parameters will be referred to as local order parameter symmetries. $p_x$ and $p_y$ symmetries are not typically considered, for they are associated with triplet pairing in a homogeneous superconductor.

In an inhomogeneous superconductor, however, these other symmetries naturally arise. Consider a bond-related order parameter $\Delta(R_{ij}, R_{i,j+1})$ that decreases as $j$ increases. This is naturally described by an induced $p_y$ component of the order parameter. The explanation of its presence in singlet pairing is that the system is not homogeneous. Consider a general form for the nearest-neighbor bond-related order parameter in an inhomogeneous superconductor,

\[
\Delta(R, R + \delta) = \sum_i F_i(R) \Delta_i(\delta),
\]

where $i$ labels the symmetry of the local order parameter component and $F_i$ is a spatially dependent order parameter amplitude (not the Gor'kov amplitude). The condition for singlet, even frequency pairing is that

\[
\Delta(R, R + \delta) = -\Delta(-R, -R - \delta),
\]

where $R$ can be measured from any site of symmetry. In the homogeneous superconductor $F_i(R)$ is spatially uniform and any site is a site of symmetry, so $\Delta_i(\delta) = \Delta_i(-\delta)$, eliminating $p_x$ and $p_y$ symmetry. In the inhomogeneous superconductor, however, the only site of symmetry is the site where the impurity is located. Thus the condition of Eq. (24.6) is satisfied for $p_x$ and $p_y$ symmetry if $F_i(R) = -F_i(-R)$. The local odd parity of $\Delta_i(\delta)$ is compensated for by an odd-parity amplitude $F_i(R)$.

When a superconducting transition occurs the system condenses with a particular symmetry of the order parameter. That symmetry creates other conditions on the amplitudes of the various local order parameter symmetries. For example, if the symmetry is $d_{x^2-y^2}$ an additional condition exists around a site of symmetry,

\[
\Delta(R_{ij}, R_{i,j+1}) = -\Delta(R_{ij}, R_{i,j+1}),
\]

Here again the site of symmetry is the impurity site. From Eq. (24.7) conditions on the spatial amplitudes of the local order parameter symmetries can be derived, such as $F_d(R_{ij}) = F_d(R_{ij})$ and $F_p_x(R_{ij}) = -F_p_x(R_{ij})$. The spatial amplitude of the local $d$-wave order parameter symmetry is $s$-like, whereas that of the local $s$-wave order parameter symmetry is $d$-like. Furthermore, $F_p_x(R_{ij}) = -F_p_x(R_{ij})$. These features derived from symmetry can be seen in Fig. 35(a–d), which shows the spatial amplitude of the local order parameter symmetries.

In some early work the $p_x$ and $p_y$ components were neglected (e.g., Ref. 69). The results of Ref. 69 are not strictly incorrect, however, for every bond is shared by two sites ($\Delta(R, R + \delta) = \Delta(R + \delta, R)$). Hence the description outlined above is overcomplete. The problem with neglecting $p_x$ and $p_y$ components in favor of $s$ and $d$ is that reconstructing the bond-related order parameter from $F_d(R)$ and $F_p(R)$ becomes a nonlocal problem. Another strategy would be to associate two bonds with each site and calculate symmetric and antisymmetric combinations of these two bonds. This method, however, loses the connection between the local order parameter components and the symmetries of the lattice. A more elegant
solution would consider the order parameter amplitudes to be defined on every other site. In particular, this procedure does not cause difficulties when one attempts to use the results obtained from this microscopic model to obtain coefficients for an effective Ginzburg-Landau model.

The presence of other local order parameter symmetries around the impurity can be considered a natural result of inhomogeneity, and particularly of gradients in the bond-related order parameter of the superconductor. Consideration of the symmetry of the inhomogeneous system around the impurity site allows one to derive detailed relationships among the spatial amplitudes of these new local order parameter symmetries.

**Fig. 35.** Change in the spatial amplitude of local order parameter symmetries as a function of position around the impurity. The potential is nonmagnetic with strength 2.5$\tau$. (a) $d$-wave, (b) $s$-wave, (c) $p_{\pm}$-wave, and (d) $p_{\times}$-wave local order parameter symmetries are shown.

**Fig. 36.** Comparison of theoretical results (dashed lines) with measurements (solid lines) from Refs. 122–124. The impurity parameters used were, from top down, $V_0 = 2t$, $n_t = 1.7\%$, $V_0 = 2.5t$, $n_t = 0.5\%$, $V_0 = 2.5t$, $n_t = 1.1\%$, and $V_0 = 2t$, $n_t = 1.4\%$. [From Ref. 119.]

25. **Planar Tunneling**

The detailed results obtained from calculations of the local properties of the electronic structure can also assist in understanding macroscopic measurements, such as planar tunneling spectra. The planar tunneling $dI/dV$ is proportional to the DOS, so the local information is lost. As a result, the strongly particle-hole asymmetric STM $dI/dV$ spectra of Fig. 32 are averaged to produce a planar $dI/dV$ spectrum that is essentially particle-hole symmetric.

We fit the (quite varied) planar tunneling results of three different experimental groups$^{122–124}$ (shown in Fig. 36). None of the curves in Fig. 36 looks like a typical clean $d$-wave superconductor’s DOS. Nevertheless all four curves are fit by adding

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impurities of essentially the same scattering strength to a $d_{x^2-y^2}$ superconductor in different concentrations and assuming slightly different voltage resolutions. The experimental drop in differential conductance due to the gap structure is only about 30%; we interpret the large residual differential conductance as due to a metallic background originating from the copper-oxygen chains.\textsuperscript{125,126} Note that these results are also consistent with magnetic impurities in an s*-wave superconductor at roughly double the concentration. We believe that these impurities are oxygen vacancies near the surface of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which are present in concentrations on the order of 1% even in nominally fully oxygenated samples.\textsuperscript{125–127}

Whereas the DOS for potentials of 2.5$t$ and 10$t$ are roughly identical, and thus the results in Fig. 36 can be fit with either potential strength, the LDOS at the impurity site is entirely hole-like for 2.5$t$ and electron-like for 10$t$. Because the measured LDOS at the oxygen vacancy is hole-like, the potential strength of the oxygen vacancy must be $2-2.5t$. This is an excellent example of the value of coordinating results from STS with results from bulk measurements. The planar tunneling measurements would not be sufficient to distinguish between two possible scattering strengths, but by probing the local properties of the individual impurity with STS it is possible to make this determination.

### VII. Brief Discussion of Recent Results for Dynamical Spins

In the previous section remarkable agreement was achieved between experimental and theoretical results on planar tunneling spectra by assuming the presence of a finite concentration of strongly scattering nonmagnetic impurities. The experimental planar tunneling spectra from Refs. 122–124 are characteristic of tunneling into the c-axis surface in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Due to the layered structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, these surfaces are quite special.

Tunneling into a surface whose normal has any component in the ab plane is quite different, and is characterized by the presence of a zero-bias anomaly. The traditional interpretation of this zero-bias anomaly is due to the presence at these surfaces of dynamical magnetic impurities. A model of noninteracting quantum spins present in the interface\textsuperscript{128,129} does generate this zero-bias anomaly.

\textsuperscript{128} J. A. Appelbaum, Phys. Rev. 154, 633 (1967).

Recently considerable interest has been generated by the observation that, in the absence of a magnetic field, and at sufficiently low temperatures, the zero-bias anomaly splits into two distinct peaks.\textsuperscript{130} This behavior is not consistent with a model based on noninteracting spins, in which a magnetic field is required for splitting the zero-bias anomaly. The anomaly is also split by a magnetic field, but if it were due to noninteracting spins the splitting would be characterized by a large $g$-factor at low fields. Furthermore, the splitting saturates at large fields. One new explanation that has been proposed of this effect is the presence of a subdominant order parameter, which splits a zero-bias anomaly arising from an Andreev surface bound state. Details of this theory can be found in Ref. 131, and it will not be discussed in detail here.

We find that the experimental observations from Ref. 130 can be incorporated into a model of dynamical magnetic impurities at the surface if the impurities interact with each other. These dynamical magnetic impurities would most likely be uncompensated copper spins, and appear to be present at all interfaces in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ except when $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is c-axis cleaved (parallel to the copper-oxygen planes). At sufficiently low temperatures the spin-spin interactions cause the spin dynamics to freeze out, and the spins behave essentially as static spins. The DOS from static spins has already been discussed in detail in Sec. 22, and is characterized by two peaks symmetric around the chemical potential. At higher temperatures when the timescale of the dynamics of the impurity spins is fast, the zero-bias anomaly is present, just as if the impurities were not interacting. As the temperature is lowered, however, the timescale of motion of the impurity spins increases and the tunneling spectra will show the splitting of the zero-bias anomaly. Within this model the presence of the anomalous $g$-factor is due to the interactions among the spins, and is not surprising in a system that resembles a spin glass.

Figure 37 indicates the differential DOS from an impurity calculated for various timescales of the impurity spin. The impurity potential is $V_s = 3t$. For a fast timescale (large $\omega_s$) there is spectral weight centered at the chemical potential. As the spin slows down, and thus $\omega_s$ decreases, the spin begins to appear approximately static and the characteristic double-peak spectrum of the static magnetic impurity reappears.

This is an area of considerable current interest, and further experimental probes of the interface region will be required to determine whether our explanation based on dynamical spins, the explanation of Ref. 131, or some other explanation is correct. Probes that are likely to be sensitive to the Andreev surface current are
For an impurity embedded in a host with an anisotropic order parameter, the anisotropy of the host produces rich spatial structure in the LDOS around the impurity. This structure includes the fourfold "cross" pattern, which should be apparent for voltages just above the gap maximum of a $d$-wave superconductor as well as the $45^\circ$ rotated cross pattern at low voltages. It also includes the variation in the relative heights of the electron-like and hole-like components of a resonant state. Resonant states in $d$-wave superconductors appear to explain the typical planar tunneling curves, and also may explain the recently observed splitting of the zero-bias anomaly on the $ab$ edges of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

The self-consistent calculations described here have been performed with a new, powerful Koster-Slater technique that allows the Gor'kov equation to be solved in principle exactly. We note that technique should be generalizable to any condensed electronic system where mean field theory is a good approximation. The order parameter will have different physical meanings and the self-consistency conditions are likely to have somewhat different forms, but the general technique itself should survive. It is extremely well suited for STM probes of condensed electronic systems, for its strength is in determining the short-length scale, low-energy properties of the system.

**Authors' Note**

We note the recent report of experimental STM spectra around single impurities near the $\text{Bi}_2\text{Sr}_x\text{CaCu}_2\text{O}_{8+x}$ surface.\(^{132}\)

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**Appendix**

The expansion of the Green’s functions of Eq. (11.10) suitable for a three-dimensional spherically symmetric situation are detailed here. The homogeneous Green’s functions depend on $\mathbf{r}$ and $\mathbf{r}'$ through $r$, $r'$, and $\cos \gamma = (\mathbf{r} \cdot \mathbf{r}')/rr'$. Then the Green’s functions can be expanded in Legendre polynomials $P_l(\cos \gamma)$.

\(^{132}\) E. W. Hudson, S. H. Pan, K. W. Ng, and J. C. Davis, to be published.
\[ g(\mathbf{r}, \mathbf{r}'; \omega) = g(r, r', \cos \gamma; \omega) = \frac{2\ell + 1}{4\pi} \sum_i g_i(r, r'; \omega)P_i(\cos \gamma) \quad (A.1) \]

and

\[ g_i(r, r'; \omega) = 2\pi \int_{-1}^{1} dx \, P_i(x) g(r, r', x; \omega). \quad (A.2) \]

Evaluating Eq. (A.2) for both the normal and anomalous Green's functions of Eq. (11.10) yields

\[ g_i(r, r'; \omega) = -\frac{\pi^3}{\sqrt{rr'}} \times \left[ i \left( 1 + \frac{\omega}{\sqrt{\omega^2 - 1}} \right) J_{\ell + 1/2}(\{1 + \sqrt{\omega^2 - 1/\xi}\}r^<) H_{\ell + 1/2}^{(1)}(\{1 + \sqrt{\omega^2 - 1/\xi}\}r^>) \\
- \left( 1 - \frac{\omega}{\sqrt{\omega^2 - 1}} \right) J_{\ell + 1/2}(\{1 - \sqrt{\omega^2 - 1/\xi}\}r^<) H_{\ell + 1/2}^{(2)}(\{1 - \sqrt{\omega^2 - 1/\xi}\}r^>) \right] \quad (A.3) \]

\[ f_i(r, r'; \omega) = -\frac{i\pi^3}{\sqrt{rr'}} \frac{1}{\sqrt{\omega^2 - 1}} \times \left[ J_{\ell + 1/2}(\{1 + \sqrt{\omega^2 - 1/\xi}\}r^<) H_{\ell + 1/2}^{(1)}(\{1 + \sqrt{\omega^2 - 1/\xi}\}r^>) \\
+ J_{\ell + 1/2}(\{1 - \sqrt{\omega^2 - 1/\xi}\}r^<) H_{\ell + 1/2}^{(2)}(\{1 - \sqrt{\omega^2 - 1/\xi}\}r^>) \right] \quad (A.4) \]

where \( J_\ell, H_\ell^{(1)}, \) and \( H_\ell^{(2)} \) are standard Bessel functions, \( r^< (r^>) \) is the smaller (larger) of \( r \) and \( r' \), \( \omega \) is in units of \( \Delta_o \) and \( r \) and \( r' \) are in units of \( k_F^{-1} \). The Green's functions are in units of \( N_r \).

The Gor'kov equation, Eq. (11.1), can now be written in a form diagonal in \( \ell \),

\[ G_i(r, r'; \omega) = g_i(r, r'; \omega) \\
+ \int_0^\infty r^3 d\rho \, g_i(r, \rho; \omega) V(\rho) G_i(\rho, r'; \omega). \quad (A.5) \]

Thus the three-dimensional integral has been reduced to a one-dimensional radial integral. Because the numerical inversion procedure depends on inverting a matrix whose rank is proportional to the number of spatial points considered, this reduction to a one-dimensional integral dramatically increases the speed of this calculation over a calculation for a three-dimensional potential that is not spherically symmetric.