Local electronic structure of a single magnetic impurity in a superconductor

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Abstract

The electronic structure near a single classical magnetic impurity in a superconductor is determined using a fully self-consistent Koster-Slater algorithm. Localized excited states are found within the energy gap which are half electron and half hole. Within a jellium model we find the new result that the spatial structure of the positive-frequency (electron-like) spectral weight (or local density of states), can differ strongly from that of the negative frequency (hole-like) spectral weight. The effect of the impurity on the continuum states above the energy gap is calculated with good spectral resolution for the first time. This is also the first three-dimensional self-consistent calculation for a strong magnetic impurity potential.
Magnetic impurities have a dramatic effect on superconductivity. Most work on the experimental and theoretical effects of magnetic impurities have focused on bulk thermodynamic quantities, such as the reduction of the superconducting transition temperature $T_c$ with increasing magnetic impurity concentration [1]. Theoretical approaches to treat the thermodynamic effects of impurities include Born scattering (Abrikosov-Gor’kov theory) [2] and approximate solutions to all orders in the impurity potential for classical [3–5] and quantum [6] spins. A key issue addressed in Ref. 3 was the evolution of localized excited states around impurities into an impurity band, eventually leading to gapless superconductivity at high enough impurity concentrations. The effects of impurities on bulk properties have also been treated within a strong-coupling formalism, but not self-consistently or beyond the Born approximation (e.g. Ref. 7). Concern about bulk properties in the above and related work did not extend to properties very near the impurity.

Among the first properties calculated in the vicinity of an impurity were the structures of screening clouds around a charged impurity [8,9] and a magnetic impurity [9,10] 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 [11,12]. A self-consistent calculation of the order parameter at the impurity and very far away for weak impurity potentials was done by Schlottmann [13]. Interest in local properties near impurities has been revived by advances in scanning tunneling microscopy (STM) near impurities embedded in a metallic medium [14].

Motivated by the possibility of measuring the local electronic structure near an impurity in a superconductor with an STM, the differential conductivity through an STM tip was calculated near impurities for superconductors with isotropic and anisotropic gaps within the Born approximation [15]. The differential conductivity measured at a point $x$ and voltage $V$ and temperature $T$ can be related to the local density of states (LDOS) at the tip location as follows:

$$\frac{dI(x, V, T)}{dV} = \frac{1}{N_o} \int_{-\infty}^{\infty} d\omega \frac{\partial n(\omega)}{\partial \omega} \left( \frac{\text{Im} G(x, x; \omega = eV)}{\pi} \right).$$

(1)
Here $e$ is the charge of the electron, $n(\omega)$ is the Fermi occupation function at temperature $T$, $N_o$ is the density of states at the Fermi level, and $dI/dV$ is in units of the normal-metal’s differential conductivity. The local density of states is the imaginary part of the retarded Green’s function fully dressed by the interaction of the electronic system with the impurity. Within the Born approximation, then, the differential conductivity can be expressed in terms of the retarded homogeneous Green’s functions of the superconductor, $g(\mathbf{x}, \mathbf{x}'; \omega)$ and $f(\mathbf{x}, \mathbf{x}'; \omega)$ (where $f$ is the anomalous Green’s function), in the following way:

$$
\frac{dI(\mathbf{x}, V)}{dV} \propto \Im \left[ g(\mathbf{x}, \mathbf{x}; eV) + g(\mathbf{0}, \mathbf{x}; eV) - f(\mathbf{0}, \mathbf{x}; eV) - f(\mathbf{x}, \mathbf{0}; eV) \right]
$$

(2)

where the impurity is at the location $\mathbf{0}$ in the solid and the non-magnetic impurity potential is $V_0 \delta(\mathbf{x})$. For a BCS superconductor with an isotropic order parameter in a parabolic band, for $\omega$ much smaller than the Fermi energy,

$$
g(\mathbf{x}, \mathbf{x}'; \omega) = -\frac{\pi N_o}{k_F} e^{-\sqrt{\Delta^2 - \omega^2} k_{FR}} \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \left( \cos k_{FR} + \frac{\omega}{\sqrt{\Delta^2 - \omega^2}} \sin k_{FR} \right)
$$

$$
f(\mathbf{x}, \mathbf{x}'; \omega) = -\frac{\pi N_o \Delta}{k_F \sqrt{\Delta^2 - \omega^2}} e^{-\sqrt{\Delta^2 - \omega^2} k_{FR}} \sin k_{FR}
$$

(3)

where $r = |\mathbf{x} - \mathbf{x}'|$, $\Delta$ is the order parameter, and $\xi = \hbar k_F / \pi \Delta$ is the coherence length. These expressions are valid for $\omega$ above and below $\Delta$ so long as the imaginary parts of both $f$ and $g$ are multiplied by $\text{sgn}\omega$.

The Born approximation calculation would not yield any localized states around the impurity, and does not consider the effect of the change in electronic structure on the local order parameter $\Delta(\mathbf{x})$. Recent preliminary STM results indicate certain features of the local density of states near a magnetic impurity [16]: (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. A calculation beyond the Born approximation where the order parameter is self-consistently determined and the continuum spectrum is found would be useful for explaining these results.
We will present a fully self-consistent calculation of the local electronic structure near a magnetic impurity which is based on a Koster-Slater-like Green’s function technique rather than the Bogoliubov-de-Gennes (BdG) equations \[17\]. The BdG equations are Schrödinger-like equations for the electron and hole components of the quasiparticle wavefunctions. The localized states of a vortex core in a superconductor and other properties revealed by the LDOS were calculated self-consistently using the BdG equations \[18,19\]. These results were compared with a measurement of a single vortex by an STM on superconducting NbSe$_2$ \[20\]. The BdG equations were successfully used again to explain the STM observations of the vortex lattice \[21\].

Since the original application of the Green’s function algorithm to localized vibrational modes \[22\], it has been applied to numerous problems including conduction electrons in metals \[23\] and impurity states in magnets \[24\], but not to superconductors. To place this algorithm in context we will contrast it with the BdG equations. To find the quasiparticle wavefunctions, typically the inhomogeneity is placed in a sphere of radius $R$ with appropriate boundary conditions. The value of $R$ is determined by the spectral resolution necessary for accurately determining the order parameter self-consistently and the spectral width of features measurable by (for example) the STM. The typical complications resulting from approximating an infinite system by a finite-size system apply, such as discrete states above the energy gap and the heavy investment of computer time required for large values of $R$.

The Green’s function method works within a sphere whose radius is determined by the range of the inhomogeneous potential. In essence we shall invert the Dyson equation in real space. The Dyson equation for an inhomogeneity in a superconductor, the Gor’kov equations \[25\], can be written as:

$$
\int d\mathbf{x}'' [\delta(\mathbf{x} - \mathbf{x}'') - g_\sigma(\mathbf{x}, \mathbf{x}'', \omega) V(\mathbf{x}'')] G_\sigma(\mathbf{x}'', \mathbf{x}; \omega) = g_\sigma(\mathbf{x}, \mathbf{x}; \omega)
$$

where

$$
g_\sigma(\mathbf{x}, \mathbf{x}; \omega) = 
\begin{pmatrix}
g_\sigma(\mathbf{x}, \mathbf{x}; \omega) & f_\sigma(\mathbf{x}, \mathbf{x}; \omega) \\
f^*_\sigma(\mathbf{x}, \mathbf{x}; -\omega) & -g^*_\sigma(\mathbf{x}, \mathbf{x}; -\omega)
\end{pmatrix},
$$
the same relationship exists among $G_\sigma$, $G_\sigma$ and $F_\sigma$, and

$$V(x'') = \begin{pmatrix}
\sigma V_S(x'') + V_0(x'') & \delta \Delta(x'') \\
\delta \Delta(x'') & \sigma V_S(x'') - V_0(x'')
\end{pmatrix}. \tag{6}$$

$\delta \Delta(x) = \Delta(x) - \Delta_0$, where $\Delta(x)$ is the position-dependent order parameter and $\Delta_0$ is the order parameter of the homogeneous superconductor. $V_S(x)$ is a localized, spin-dependent potential, such as one originating from a classical spin. $V_0(x)$ is a localized non-magnetic potential. The quantization direction of the superconductor's spins ($\sigma = \pm 1/2$) is chosen parallel to the direction of the classical spin. For the purposes of heuristic arguments in this Letter we will assume ferromagnetic coupling between impurity spin and electron spin ($V_S < 0$). Antiferromagnetic coupling only produces the trivial change that the antiparallel spin quasiparticle is attracted to the classical spin. $g_\sigma$ is given by Eqs. (3) with $N_o$ labelling the density of states for each spin. $G_\sigma \neq G_{-\sigma}$ due to the differences in the potential in Eq. (3). The self-consistency equation is

$$\delta \Delta(x) = \gamma \sum_\sigma \int_{-\infty}^{\infty} d\omega n(\omega) \Im F_\sigma(x, x'; \omega) - \Delta_0, \tag{7}$$

where $\gamma$ is the pairing strength.

One strength of this formalism is its reliance on the short-range nature of the inhomogeneous potential. Solution of Eq. (4) requires inverting the frequency-dependent real-space matrix $M(\omega) = \delta(x-x') - g_\sigma(x, x'; \omega) V(x')$. For $x'$s where $V(x')$ is negligible, that portion of $M(\omega)$ is triangular and trivially invertible. Hence the numerical complexity of inverting $M(\omega)$ is governed by the range of $V(x)$. The radius of the sphere the system is solved in is governed by the range of the longest-range potential, which in this paper will be $\delta \Delta(x)$.

As a special case of Eq. (4), the energies of the localized states within the gap correspond to those $\omega > 0$ where $\det M(\omega) = 0$. We model the impurity with a Gaussian $V_S(x)$ of range $k_F^{-1}$. Figure 1 shows the dependence of the localized state energies for the first two angular momentum channels on the strength of the magnetic potential, $v_s = \pi N_o |\sigma \int dV(x)|$. For $V_0 = 0$, the Eqs. (4)- (7) are unchanged by the transformation $\omega \to -\omega$ and $s \to -s$ so the poles of $G_\sigma(\omega)$ must come in symmetric pairs ($\sigma = \pm 1/2$) around $\omega = 0 \tag{26}$. The
quasiparticle state for small $v_s$ corresponding to these poles consists of an electron ($\omega > 0$) in the spin band parallel to the classical spin, which we will label up ($\uparrow$), and a hole ($\omega < 0$) in the other spin band ($\downarrow$). A hole in the down band has spin up and is attracted to the classical spin. Spin is a good quantum number for the quasiparticle, which is spin up. The spatially-integrated spectral weight is one-half each for the electron and hole components (this is true for all localized quasiparticle states in this model).

For small $v_s$ an already existing quasiparticle can be bound by the classical spin. This allows for local pair-breaking excitations of energy less than $2\Delta_o$. As the potential strength increases, the excitation energy of each angular momentum state $\ell$ decreases, at some critical value ($v_{sl}^*$) vanishes, and then begins to increase. For $v_s > v_{sl}^*$ the ground state contains a spin-up quasiparticle bound to the classical spin [3]. The low-energy excitation now corresponds to removing that quasiparticle, which is a spin-down excitation. This qualitative behavior of the excitation energies can be extracted from the Shiba model [3], where the magnetic potential is modeled by a delta function at the impurity site. In Ref. 3 zeros of $M(\omega)$ are found, neglecting the component of $\text{Re}g(x,x';\omega)$ which is symmetric for $\omega \rightarrow -\omega$. These poles are shown in Figure 1.

Even in the normal state the spectral weight of the up band has a peak at the origin, while that of the down band is pushed away from the origin. In the superconductor this asymmetry is evident in the quasiparticle spectral weights. Figure 2 shows the calculated angular momentum $\ell = 0$ spectral weights in the up and down bands for two values of $v_s$, indicating that the asymmetry of the spatial structure of the spectral weights becomes more pronounced with increasing $v_s$. Also shown are $\ell = 1$ spectral weights for $v_s = 0.875$. The asymmetric localized-state spectral weights produce differential conductivities which are asymmetric as well [27]. Figure 3 shows differential conductivities for $v_s = 1.75$ at three locations — right at the impurity, $k_F^{-1}$ away, and $10k_F^{-1}$ away. By $10k_F^{-1}$ the spectrum has recovered to the homogeneous spectrum. The differential conductivity farther away can be easily recovered by constructing the self-consistent $T$-matrix $V(x')\delta(x' - x'\prime) + V(x')G(x', x'\prime; \omega)V(x''\prime)$ directly from the dressed Green’s functions. The spatial dependence of the differential conductivity
far away from the impurity is qualitatively identical to the Born result \[15\].

The asymmetric behavior of the electron-like and hole-like spectral weights due to the difference between the up band states and down band states does not emerge from the model of Ref. 3, which implies identical spatial dependences of the spectral weights for the up and down bands. As pointed out by Koster and Slater \[23\], proper treatment of the symmetric real part of \( g(0,0; \omega) \) is essential for obtaining the local electronic properties around an impurity. The proper approximation for the real symmetric part of the Green’s function is to average it over a small volume given by the range of the potential modeled by the delta function. We therefore introduce a new parameter into the Shiba model, \( \alpha \), which is the \( \omega \)-symmetric part of \( \text{Re} \langle g(0,0; \omega = 0) \rangle / \pi N_o \). The brackets indicate that \( g(0,x; \omega = 0) \) has been averaged over a small volume. For \( \alpha \neq 0 \) the ratio of the spectral weight of the up band at the impurity, \( A^\uparrow(0) \), to the spectral weight of the down band at the impurity, \( A^\downarrow(0) \), is

\[
\frac{A^\uparrow(0)}{A^\downarrow(0)} = \frac{1 + 2\alpha v_s + (1 + \alpha^2)v_s^2}{1 - 2\alpha v_s + (1 + \alpha^2)v_s^2}. \tag{8}
\]

The introduction of \( \alpha \) does not change the localized state energies qualitatively.

We now discuss the structure of \( \Delta(x) \). Figure 4 shows \( \delta \Delta(x) \)'s for two values of \( v_s \). While oscillating with wavelength \( \sim \pi k_F^{-1} \), \( \delta \Delta(x) \) falls off to a negligible potential within \( 10k_F^{-1} \). This justifies performing the numerical calculation in a sphere of that radius. A typical radial grid of 100 points provides a numerically robust solution. The self-consistent solution also depends on the value of \( N_o \Delta_o/k_F^3 \), which for niobium is \( 3.6 \times 10^{-5} \) \[28\].

As shown in Figure 4, for large values of \( v_s \), \( \Delta(x = 0) < 0 \). Sign changes in \( \Delta \), as seen in pair tunneling, have been suggested for magnetic impurities in the barriers of Josephson junctions \[29\]. Our sign change in \( \Delta(0) \) occurs (at \( T = 0 \)) precisely at \( v_s^{*0} \). The symmetry of Eqs. (4)-(7) under \( \omega \rightarrow -\omega \) and \( s \rightarrow -s \) implies that \( \text{Im} F^\uparrow(r,r,\omega) = -\text{Im} F^\downarrow(r,r,-\omega) \).

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. \( \Delta(0) \) as a function of \( v_s \) is shown in the insert of Figure 4. 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 $v_{s0}^*$ 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. Exciting the low-energy state (removing the spin-up quasiparticle) causes a pair to enter the condensate. We find that exciting the low-energy state for $v_s > v_{s0}^*$ increases $\Delta(0)$, whereas excitation of quasiparticles typically reduces $\Delta(x)$ (which is the case for $v_s < v_{s0}^*$). Also, exciting the low-energy state reduces the induced spin of the superconductor at the impurity. We note that this picture should have implications for the theory of gapless superconductivity, which is now based on the formation of impurity bands through hybridization of single-quasiparticle excited states around impurities, without consideration of the coherence of excitations with the condensate.

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FIGURES

FIG. 1. Solid lines indicate the self-consistently calculated localized excited state energies for angular momentum channels $\ell = 0$ and 1. The analytic model of Ref. 3 is shown by the dashed lines. At a critical value of $v_s = v_{s0}^*$, the character of the $\ell = 0$ state changes from spin up to spin down. The kink evident in the solid line is real, and is due to the discontinuous change (at $T = 0$) in $\Delta(x)$ at $v_{s0}^*$.

FIG. 2. Spectral weights for the $\ell = 0$ state’s up-band component (electron-like for $v_s < v_{s0}^*$) and down-band component (hole-like for $v_s < v_{s0}^*$) as a function of position for two values of the magnetic potential. Also shown are the spectral weights for the up and down bands for $\ell = 1$ for $v_s = 0.875$.

FIG. 3. Differential conductivity ($dI/dV$), relative to the normal metal at three distances (in units of $k_F^{-1}$) from the impurity for $v_s = 1.75$, showing the evolution of the spectrum from one dominated by the localized states near $r = 0$ to one dominated by the bulk spectrum at $r = 10$. The curve at $r = 0$ has been shrunk by a factor of two so that it can appear on the same scale as the other two curves. The presence of the large peak near the origin on the negative-frequency side of the spectrum indicates that the impurity is strong ($v_s > v_{s0}^*$). $dI/dV$ has been evaluated from Eq. (1) with $\beta = 7.5/\Delta_o$, which for niobium corresponds to $T \sim 2K$.

FIG. 4. Change in the local order parameter, $\delta \Delta(x)$, for two values of the magnetic potential. The change becomes negligible beyond $10k_F^{-1}$. (Insert) Order parameter at the impurity, $\Delta(0)$, as a function of $v_s$, indicating a discontinuous change at $v_{s0}^*$. 

11
Localized State Energies (units of $\Delta_0$)

Fig. 1
Fig. 2

Spectral Weight

$\Gamma_s = 0.875$

$\Gamma_s = 1.75$

Spin up
Spin down

$l=0$

$l=1$

$\Gamma_s = 0.875$

$r$ (units of $k_F^{-1}$)
\( v_s = 1.75 \)

- \( r = 0 \)
- \( r = 1 \)
- \( r = 10 \)
Fig. 4