# Quantum Interference between Impurities: Creating Novel Many-Body States in $s$-wave Superconductors

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We demonstrate that quantum interference of electronic waves that are scattered by multiple magnetic impurities in an $s$-wave superconductor gives rise to novel bound states. We predict that by varying the inter-impurity distance or the relative angle between the impurity spins, the states' quantum numbers, as well as their distinct frequency and spatial dependencies, can be altered. Finally, we show that the superconductor can be driven through multiple local crossovers in which its spin polarization, $\langle s_z \rangle$, changes between $\langle s_z \rangle = 0, 1/2$ and 1.

Over the last two years, several beautiful experiments have studied quantum interference of electronic waves that are scattered by multiple impurities [1–4]. In a groundbreaking experiment, Manoharan *et al.* [1] used a corral of magnetic impurities on the surface of a metallic host to demonstrate that quantum interference can lead to the focusing of electronic waves into a quantum image. Moreover, using scanning tunneling spectroscopy (STS), Derro *et al.* [2] were the first to observe four resonance states in the local density of states (DOS) of the one-dimensional chains in $YBa_2Cu_3O_{6+x}$. These states were interpreted as arising from quantum interference of electronic waves scattered by two magnetic impurities [5]. Quantum interference effects were also studied in optical quantum corrals by Chicanne *et al.* [3] and between impurities located on quantum dots by Holleitner *et al.* [4]. Some first theoretical work [6] has focused on impurity geometries in metallic systems similar to the one studied by Manoharan *et al.* In contrast, quantum interference in strongly correlated electron systems, such as superconductors (with the exception of $NbSe_2$ [7]), charge- and spin-density-wave systems, or even semi-conductors, have not yet been addressed. However, the study of interference effects in theses systems involving spin impurities is not only of great fundamental interest, but might also possess important applications in the field spin electronics [8] and quantum information technology [9].

In order to describe the properties of complex impurity structures such as quantum corrals, it is first necessary to understand interference effects associated with the presence of few impurities. In this Letter we therefore consider two impurities embedded in a general $s$-wave superconductor (SC). The presence of two magnetic impurities allows for a coupling of the bound states associated with a single impurity [10], and gives rise to the emergence of novel many-body states. We show that the nature of these novel states, i.e., their quantum numbers, can be altered by varying the distance between the two impurities, $\Delta r$, or the relative angle between the directions of their spin moments, $\alpha$. Moreover, we demonstrate that these changes are accompanied by local crossovers in which

the spin polarization of the superconductor changes between $\langle s_z \rangle = 0, 1/2$, and 1. We predict that the interplay between the states' quantum numbers and the inter-impurity distance determines the distinct frequency and spatial dependence of the two-impurity bound states. Finally, we discuss the implications of our work for systems with a larger number of impurities.

Starting point for our calculations is the $\hat{T}$-matrix formalism [10] which we generalized to treat the case of $N$ impurities of spin $S$ with non-magnetic and magnetic scattering potentials [5, 11]. In the following, we focus on the case $N = 2$, and, following Ref.[10], treat the impurity spins as classical, static variables, corresponding to the limit $\beta_0 = JS/2 = const.$ and $S \to \infty$. In a fully gaped s-wave SC, this approximation is well justified since no Kondo-effect occurs for sufficiently small coupling between the impurities and the delocalized electrons. Within this approach, any interaction between the impurities is only important to the extent that it determines the angle, $\alpha$, between the direction of the impurity spins. Within the Nambu-formalism and in Matsubara frequency space the electronic Greens function in the presence of $N$ impurities is given by

$$
\begin{aligned}
\hat{G}(r, r', \omega_n) \ = \ & \hat{G}_0(r, r', \omega_n) \\
& + \sum_{i,j=1}^{N} \hat{G}_0(r, r_i, \omega_n) \hat{T}(r_i, r_j, \omega_n) \hat{G}_0(r_j, r', \omega_n) \ , \quad (1)
\end{aligned}
$$

where the $\hat{T}$-matrix is obtained from the Bethe-Salpeter equation

$$
\begin{aligned}
\hat{T}(r_i, r_j, \omega_n) \ = \ & \hat{V}_{r_i} \delta_{r_i, r_j} \\
& + \hat{V}_{r_i} \sum_{l=1}^{N} \hat{G}_0(r_i, r_l, \omega_n) \hat{T}(r_l, r_j, \omega_n) \ . \quad (2)
\end{aligned}
$$

In the case of two impurities

$$
\hat{V}_{r_1} = \frac{1}{2} \left( U_1 \sigma_0 + J_1 S \sigma_3 \right) \tau_3 \ ;
$$

$$
\hat{V}_{r_2} = \frac{1}{2} \left( U_2 \sigma_0 + J_2 S \sigma_3 \cos\alpha + J_2 S \sigma_1 \sin\alpha \right) \tau_3 \ ;
$$

$$
\hat{G}_0^{-1}(\mathbf{k}, i\omega_n) = \left[ i\omega_n \tau_0 - \epsilon_\mathbf{k} \tau_3 \right] \sigma_0 + \Delta_\mathbf{k} \tau_2 \sigma_2 \ . \quad (3)
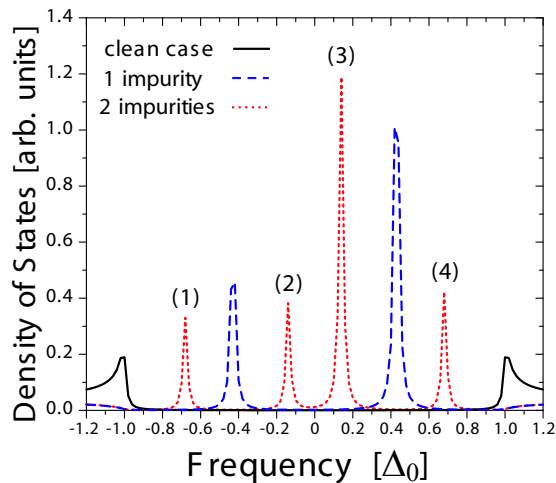$$

FIG. 1: DOS for the clean case (solid line), a single impurity (dashed line), and two impurities (dotted line) for $\beta_0 = 300$ meV. For (b) and (c) the DOS is shown at the impurity site.
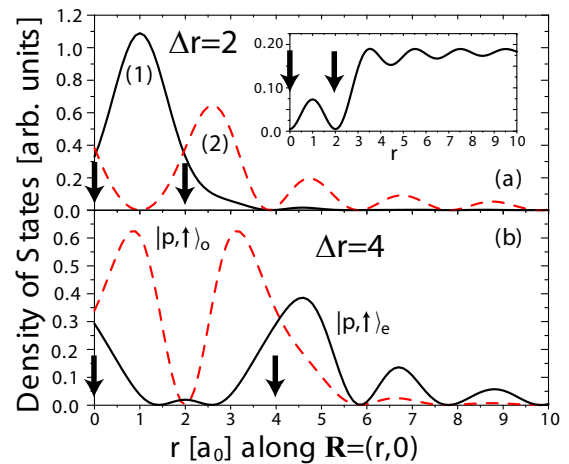


FIG. 2: (a) Spatial dependence of peak (1) and (2) in the DOS along the $\hat{x}$-axis ($\mathbf{R} = (r, 0)$) for two magnetic impurities located at $r = 0$ and $r = 2$ with parallel spins. Inset: Spatial dependence of the DOS at $\omega = \pm\Delta_0$. (b) Same as (a) but with impurities located at $r = 0$ and $r = 4$.

Here, $\hat{V}_{r_1,r_2}$ is the scattering matrix for the impurities located at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. Without loss of generality, we take the spin of impurity 1 to be parallel to the $\hat{z}$-axis, while that of impurity 2 is rotated from the $\hat{z}$-axis into the $zx$-plane by an angle $\alpha$. $\hat{G}_0(\mathbf{k}, i\omega_n)$ is the Greens function of the unperturbed (clean) system in momentum space, and $\sigma_i$, $\tau_i$ are the Pauli-matrices in spin and Nambu-space, respectively. $U_i$ and $J_i$ are the potential and magnetic scattering strengths of the impurities. We consider a two-dimensional (2D) electronic system whose normal state dispersion is given by $\epsilon_{\mathbf{k}} = k^2/2m - \mu$ ($\hbar = 1$), where $\mu = k_F^2/2m$ is the chemical potential, and $k_F = \pi/2$ is the Fermi wave-vector (we set the lattice constant $a_0 = 1$). The results and conclusions presented below are qualitatively robust against changes in the form of $\epsilon_{\mathbf{k}}$, the dimensionality of the $s$-wave SC, or the size of the momentum-independent SC gap, $\Delta_0$. For definiteness we set $\mu = 370$ meV and $m^{-1}/\Delta_0 = 15$, but quantitatively similar results are obtained for $m^{-1}/\Delta_0 = 30$. The DOS, $N(\mathbf{r}, \omega)$, presented below is obtained from a numerical computation of Eqs.(1)-(3) with $N(\mathbf{r}, \omega) = A_{11} + A_{22}$ and $A_{ii}(\mathbf{r}, \omega) = -\mathrm{Im}\, \hat{G}_{ii}(\mathbf{r}, \omega + i\delta)/\pi$.

For a single magnetic impurity in an s-wave SC, the $\hat{T}$-matrix possesses poles at frequencies $\omega_{res}^{(1,2)}$, reflecting the presence of two bound states. The spectroscopic evidence for these bound states are two peaks in the DOS, as shown in Fig. 1, where we present the DOS obtained from Eqs.(1)-(3) at the impurity site; for comparison, we also plot the DOS of the clean system. These results are in general agreement with those of STS experiments [12], which provides further support for the validity of the $\hat{T}$-matrix approach. Assuming for definiteness that the impurity spin $\mathbf{S} \| \hat{z}$ and $J > 0$, we find that the bound state at $\omega_{res}^{(1)} < 0$ ($\omega_{res}^{(2)} > 0$), which we denoted by $|p, \downarrow\rangle$ ($|h, \uparrow\rangle$), is particle-like (hole-like) with spin along the $-z$-

direction ($+z$-direction).

We next consider two magnetic impurities with parallel spins, $U_i = 0$ and $J_i = J$. For $\Delta r = \infty$, the two sets of bound states given by $|p, \downarrow, i\rangle$ and $|h, \uparrow, i\rangle$ ($i = 1, 2$) are degenerate. However, for $\Delta r < \infty$, the probability that an electron scattered by one of the impurities is also scattered by the second one is non-zero. Hence, quantum interference of electronic waves that are scattered by both impurities leads to the formation of novel even and odd (or bonding and anti-bonding) states, $|p, \downarrow\rangle_{e,o} = (|p, \downarrow, 1\rangle \pm |p, \downarrow, 2\rangle)/\sqrt{2}$, and similarly for the hole-like states. This picture is confirmed by the numerically computed DOS shown in Fig. 1 for two impurities located at $\mathbf{r}_1 = (0, 0)$ and $\mathbf{r}_2 = (2, 0)$, and $\beta_0 = 300$ meV (the DOS shown is that on one of the impurity sites). As expected, the DOS exhibits four mid-gap peaks with peak $(1), (2)$ corresponding to the particle-like states $|p, \downarrow\rangle_{e,o}$ and peak $(3), (4)$ to the hole-like states $|h, \uparrow\rangle_{e,o}$.

To determine which peaks in the DOS correspond to the even and odd states, we plot in Fig. 2a the spatial dependence of the particle-like states (1) and (2) along the $\hat{x}$-axis with $\mathbf{R} = (r, 0)$ (the location of the impurities at $r = 0$ and $r = 2$ are indicated by arrows). Since the DOS of the odd states vanishes by symmetry at the midpoint between the two impurities, i.e., at $r = 1$, peak (2) and (1) correspond to the odd and even particle-like states, respectively. Note that their spatial dependence is remarkably different: while the odd state exhibits oscillations well beyond the two impurity region, the even state is primarily confined to the region between the two impurities. This qualitative difference is associated with the $(k_F r)$-oscillations of the $|p, \downarrow, i\rangle$-states. Since $k_F = \pi/2$ and $\Delta r = 2$, the wave-functions of $|p, \downarrow, 1\rangle$ and $|p, \downarrow, 2\rangle$ are shifted by a phase $\Delta\phi = k_F \Delta r = \pi$ outside the two-
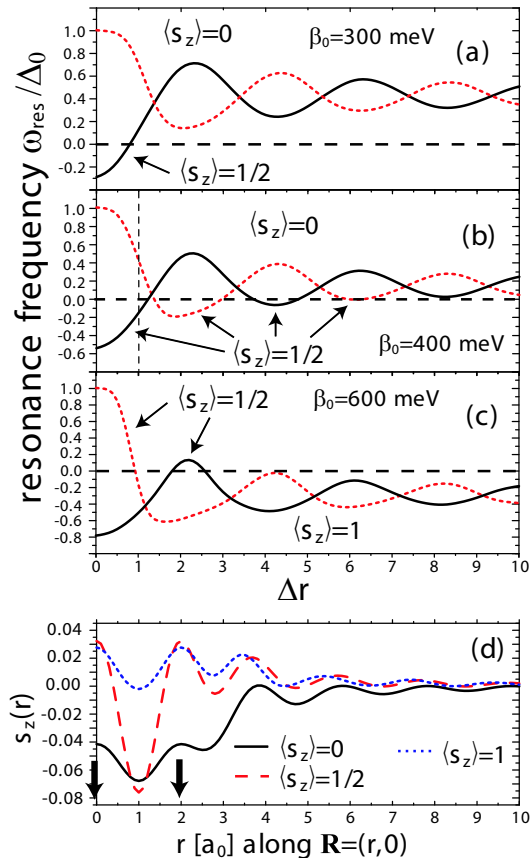
FIG. 3: $\omega_{res}$ for the even (solid line) and odd state (dotted line) as a function of $\Delta r$ for parallel impurity spins and (a) $\beta_0 = 300$ meV; (b) $\beta_0 = 400$ meV; and (c) $\beta_0 = 600$ meV. The ranges of $\Delta r$ with $\langle s_z \rangle = 1/2$ are indicated by arrows. (d) Local spin polarizations, $s_z(r)$, along the $\hat{x}$-axis, for $\alpha = 0$.

impurity region ($r > 2$ in Fig. 2a) and their spatial oscillations are consequently out-of-phase. Thus, $|p, \downarrow, 1\rangle$ and $|p, \downarrow, 2\rangle$ interfere destructively for $|p, \downarrow\rangle_e$, and only weak spatial oscillations are observable in the DOS for $r > 2$. In contrast, $|p, \downarrow\rangle_o$ shows constructive interference of $|p, \downarrow, i\rangle$ ($i = 1, 2$) and its spatial oscillations are enhanced for $r > 2$. By changing the inter-impurity distance to $\Delta r = 4$, with $\Delta \phi = 2\pi$, the interference pattern between the even and odd states is exchanged, and $|p, \downarrow\rangle_e$ ($|p, \downarrow\rangle_o$) now exhibits strong (weak) oscillations beyond the two impurity region, $r > 4$, as shown in Fig. 2b.

In Fig. 3 we present the bound state energies of the states $|p, \downarrow\rangle_{e,o}$ as a function of $\Delta r$ for $\alpha = 0$ (the frequencies of the $|h, \uparrow\rangle_{e,o}$-states are obtained via $\omega_{res} \to -\omega_{res}$). The amplitude of the oscillations in $\omega_{res}$ decays as $\Delta r^{-d/2} e^{\Delta r / \xi}$ in d-dimensions, but since $\xi > v_F / \Delta_0 \approx 20$, the exponential decay is barely perceivable in Fig. 3. The oscillations' spatial period, $1/k_F$, directly reflects that of the $(k_F r)$-oscillations in the wave-functions of $|p, \downarrow\rangle_{e,o}$, in contrast, to the $(2k_F r)$-oscillations of the DOS. For cer-

tain $\Delta r$, the splitting between the even and odd states vanishes and the two sets of bound states are decoupled. This decoupling arises whenever the bound state wavefunctions of one impurity possess a node at the position of the other impurity. The same type of oscillations were obtained in Ref.[7] for the case of NbSe$_2$.

At small $\Delta r$, the bound state energy of $|p, \downarrow\rangle_e$ crosses zero, and the state becomes hole-like, $|h, \downarrow\rangle_e$ (at the same time, the state $|h, \uparrow\rangle_e$ transforms into $|p, \uparrow\rangle_e$). We find that this zero-crossing of $\omega_{res}$ is accompanied by a crossover in the spin-polarization of the superconducting system which at $T = 0$ is given by

$$\langle s_z \rangle = \frac{1}{2} \int d^2 r \int_{-\infty}^{0} d\omega \left[ A_{11}(\mathbf{r}, \omega) - A_{22}(\mathbf{r}, \omega) \right] . \quad (4)$$

This crossover is similar to the one predicted to occur when the scattering strength, $\beta_0$, of a single magnetic impurity in an s-wave SC exceeds a critical value, $\beta_c$ [11, 13] (for the band parameters chosen, we obtain $\beta_c \approx 460$ meV). At this point, the impurity breaks a Cooper-pair and forms a bound state with one of its electrons. Specifically, for $\mathbf{S} \| \hat{z}$ and $J > 0$, the spin polarization changes from $\langle s_z \rangle = 0$ for $\beta < \beta_c$, to $\langle s_z \rangle = 1/2$ for $\beta > \beta_c$. Similarly, for $\beta_0 > \beta_c/2$, the system undergoes a crossover at $\Delta r_c$, and for $\Delta r < \Delta r_c$ one electron of the broken-up Cooper-pair forms a single bound state with both impurities. For $\Delta r \to 0$, the DOS reduces to that of a single magnetic impurity with scattering strength $2\beta_0$. Accordingly, $|p, \uparrow\rangle_o$ moves towards the particle-hole continuum and vanishes for $\Delta r \equiv 0$. Finally, a comparison of Fig. 2 and Fig. 3a shows that, as expected, the spatially more confined bound state possesses a larger $|\omega_{res}|$ than the spatially more extended one.

As $\beta_0$ approaches $\beta_c$ from below, the number of crossovers increases, as shown in Fig. 3b for $\beta_0 = 400\,\text{meV} \approx 0.87\beta_c$. Due to the oscillatory behavior of $\omega_{res}$, the bound state energy of the $\downarrow$-state crosses zero for several value of $\Delta r_c$. As a result, the spin-polarization oscillates between $\langle s_z \rangle = 0$ and $1/2$ and the electronic system can be tuned through multiple crossovers by varying $\Delta r$. The same tuning could also be achieved by keeping $\Delta r$ constant and altering $k_F$ through changes in the doping level using recently developed field-effect transistor geometries [14].

For $\beta_0 \geq \beta_c$ the superconductor exhibits a different crossover in which its spin polarization changes from $\langle s_z \rangle = 1$ to $\langle s_z \rangle = 1/2$. For $\Delta r = \infty$, each impurity breaks one cooper pair and the spin polarization of the superconducting system is $\langle s_z \rangle = 1$. As $\Delta r$ decreases, one of the bound state energies crosses zero at least once, as shown in Fig. 3c where we present $\omega_{res}$ for the $\downarrow$-states and $\beta_0 = 600\,\text{meV} > \beta_c$. Accordingly, $\langle s_z \rangle$ changes from 1 to 1/2. Since for $\Delta r \to 0$, the odd bound state vanishes by symmetry, the spin polarization reaches $\langle s_z \rangle = 1/2$ for any value of $\beta_0 \geq \beta_c$.
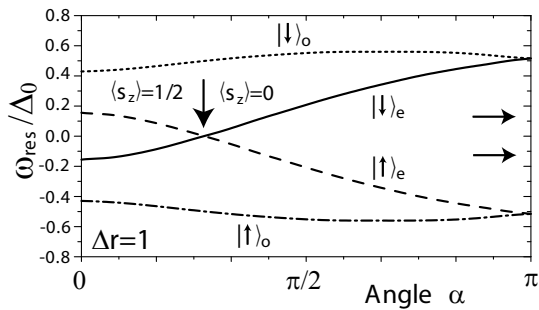
FIG. 4: $\omega_{res}$ as a function of the angle, $\alpha$, between the direction of the impurity spins for $\Delta r = 1$ and $\beta_0 = 400$ meV.

Changes in $\langle s_z \rangle$ are also reflected in the spatially resolved spin polarization, $s_z(r) = \int_{-\Delta}^{0} d\omega (A_{11} - A_{22})$, which due to the limited frequency integration is experimentally more easily accessible. In Fig. 3d, we plot $s_z(r)$ along $\mathbf{R} = (r, 0)$ for two impurities located at $r = 0$ and $r = 2$ and $\langle s_z \rangle = 0, 1/2$, and 1, corresponding to $\beta_0 = 300, 400$ and $800$ meV, respectively. For $\langle s_z \rangle = 0$, the spin polarization near the impurities is negative, as expected for $\mathbf{S} \| \hat{z}$ and $J > 0$. For $\langle s_z \rangle = 1/2$, *both* impurities form a single bound state with an electron in the $| \downarrow \rangle_o$-state (see Figs. 3b). Thus, $s_z(r)$ is substantially increased at the impurity sites, but remains practically unchanged at $r = 1$. In contrast, for $\langle s_z \rangle = 1$, the electron from the second broken Cooper-pair joining the two-impurity bound state is in the $| \downarrow \rangle_e$-state, and consequently, $s_z(r)$ increases primarily around $r = 1$. Note, that for two impurities separated by $\Delta r = 4$, the first electron to join the two-impurity bound state is in the $| \downarrow \rangle_e$-state, while the second one is in the $| \downarrow \rangle_o$-state, with corresponding changes in $s_z(r)$.

The superconducting system can also be tuned through a crossover by changing the angle, $\alpha$, between the two impurity spins, as shown in Fig. 4, where we plot $\omega_{res}$ for all four bound states as a function of $\alpha$ (the impurities are located at $\mathbf{r}_1 = (0, 0)$ and $\mathbf{r}_2 = (1, 0)$). Since we choose $\beta_0 = 400$ meV $> \beta_c/2$ we have $\langle s_z \rangle = 1/2$ for $\alpha = 0$, corresponding to the vertical dashed line in Fig. 3b. As $\alpha$ increases from zero, the frequencies of the even bound states move towards $\omega = 0$ which they cross zero at $\alpha \approx 0.27\pi$. Simultaneously the spin polarization changes from $\langle s_z \rangle = 1/2$ to $\langle s_z \rangle = 0$. The frequency separation between the even and odd states of a given spin direction decreases with increasing $\alpha$ and vanishes at $\alpha = \pi$. This is expected since for antiparallel impurity spins ($\alpha = \pi$), the bound states for impurity 1 ($|p, \downarrow, 1\rangle$ and $|h, \uparrow, 1\rangle$) and impurity 2 ($|p, \uparrow, 2\rangle$ and $|h, \downarrow, 2\rangle$) possess different quantum numbers; thus they cannot be coupled and remain degenerate. However, since the bound states of one impurity are subjected to the repulsive potential of the second impurity, their resonance frequencies are larger than those of a single impurity with the same $\beta_0$

(indicated by the arrows on the right). This repulsion leads to the disappearance of all bound states for $\Delta r \to 0$.

Finally, a non-zero $U$ transfers spectral weight between the particle- and hole-like states and increases $\beta_c$, but does not affect our above conclusions. Moreover, a self-consistent approach that allows for a gap suppression near the magnetic impurity does not change the qualitative features of the DOS discussed above [11], in agreement with experiment [12].

The results presented above suggest that a superconducting system with $N$ impurities and $\beta_0 > \beta_c/N$ can be tuned through multiple crossovers with spin polarizations ranging from $\langle s_z \rangle = 0$ to $N/2$, depending on $\beta_0$, the inter-impurity distances, and the angles between the spin moments. Work is currently under way to study these crossovers in more complex impurity geometries, such as quantum corrals, as well as the extensions to other host materials, such as unconventional SC, charge-density-wave systems, or semi-conductors [15].

In summary, we show that quantum interference of electronic waves scattered by two magnetic impurities in an s-wave SC gives rise to novel bound states. We predict that by varying the inter-impurity distance or the angle between the impurity spins, the states' quantum numbers can be altered, and the SC can be driven through multiple local crossovers in which its spin polarization changes between $\langle s_z \rangle = 0, 1/2$ and 1.

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