Local spectrum of a superconductor as a probe of interactions between magnetic impurities

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Qualitative differences in the spectrum of a superconductor near magnetic impurity pairs with moments aligned parallel and antiparallel are derived. A proposal is made for a nonmagnetic scanning tunneling spectroscopy of magnetic impurity interactions based on these differences. Near parallel impurity pairs the midgap localized spin-polarized states associated with each impurity hybridize and form bonding and antibonding molecular states with different energies. For antiparallel impurity moments the states do not hybridize; they are degenerate.

The relative orientation of the moments of two magnetic impurities embedded nearby in a metallic nonmagnetic host will depend on the significance of several electronic correlation effects, such as direct exchange, double exchange, superexchange, and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. Each of these effects produces characteristic moment orientation; e.g., the RKKY interactions can align moments either parallel or antiparallel depending on the impurity separation. Reliable experimental measurements of the moment orientation as a function of impurity separation could identify the origin of magnetism in alloys of technological significance, such as the metallic ferromagnetic semiconductor GaMnAs,[1] which may eventually play a crucial role in semiconductor-based magnetoelectronics.[2] Such measurements should also clarify the interplay between metallic and magnetic behavior in layered oxides, such as the high-temperature superconductors. In this work we propose, based on theoretical calculations, a robust experimental technique for the systematic and unambiguous experimental determination of moment alignment as a function of impurity separation.

We demonstrate that in an electronic system with a gap there is a fundamental difference between the electronic states localized around parallel and antiparallel impurity moments. Around parallel impurity moments there are midgap *molecular* states (similar to bonding and antibonding states in a diatomic molecule). Around antiparallel impurity moments the states remain more *atomiclike* and are degenerate. This qualitative difference in the spectrum of an impurity pair provides a robust technique of determining the impurity-impurity interaction via *nonmagnetic* scanning tunneling spectroscopy (STS). The essential condition for practical application of this technique will be whether the splitting of the states around parallel impurity moments is large enough to be observed spectroscopically.

The gapped system we consider in detail is the superconductor $NbSe_2$, which is chosen for its extremely favorable surface properties for STS and for its quasi-two-dimensional electronic structure. STS has already been used to examine the localized states which form near isolated magnetic impurities on the surface of superconducting niobium.[3,4] We have calculated the energies and spatial structure of the electronic states near impurity pairs in $NbSe_2$ essentially exactly within mean-field theory. These calculations indicate that the size of the splitting of states around parallel impurity moments in $NbSe_2$ is measurable—they are split by a sizable percentage of the energy gap even for impurity moment separations of order 30 Å.

A nonmagnetic spectroscopy of magnetic impurity interactions is also plausible in a much wider range of materials. The localized spin-polarized states upon which the technique is based occur near magnetic impurities in most systems where there is a gap in the single-particle density of states at the chemical potential, whether or not the gap originates from superconductivity. Even when there is no true gap, if the density of states is substantially reduced at the chemical potential sharp resonances similar to the localized states will form (this has been predicted and recently observed for *d*-wave superconductors).[5–7] Resonances around parallel and antiparallel impurity pairs show similar qualitative features to localized states.

If the energy scales of moment formation and interaction are much greater than those responsible for creating the gap it is also possible to infer the impurity interaction within a material in its high-temperature metallic phase from spectroscopic measurements on the same material in a low-temperature superconducting phase. In this the STS procedure is similar to traditional ''superconducting spectroscopy,''[8] where the dependence on impurity concentration of the superconducting transition temperature T_c or the specific-heat discontinuity at T_c is used to determine the presence and rough magnitude of a single-impurity moment. However, whereas single-impurity information can often be extracted from such measurements in the dilute limit, pairwise impurity interactions are much more difficult to infer from macroscopic properties such as T_c which depend on an ensemble of local configurations.

We note that the technique described here is remarkably noninvasive compared to alternate methods. The use of a magnetic tip to probe the magnetic properties of a sample[9] may distort the natural surface orientation of moments. An alternative nonmagnetic STS technique that has been proposed, which involves a superconducting tip[10] in a Tedrow-Meservey geometry,[11] requires either an external or surface-induced magnetic field to spin-split the superconducting density of states (DOS) of the tip. Finally, the use of spin-polarized tunneling from a GaAs tip relies on a fixed orientation of the magnetic structure on the surface relative to that of the optically generated spin-polarized population in the tip.[12]

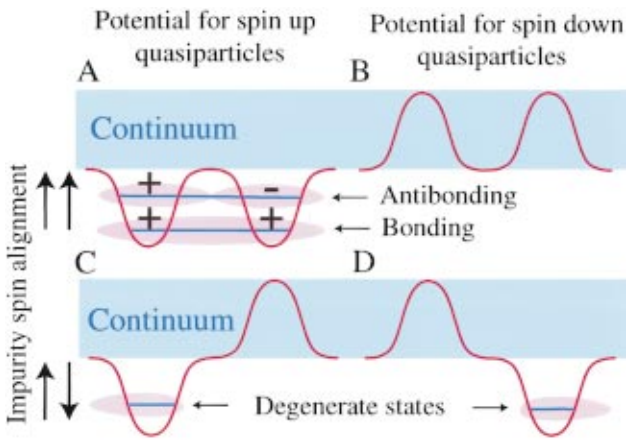

FIG. 1. (Color) Schematic of the potential for spin-up [left side, (A) and (C)] and spin-down [right-side, (B) and (D)] quasiparticles in the presence of parallel impurity spins [top row, (A) and (B)] and antiparallel impurity spins [bottom row, (C) and (D)]. For parallel impurity spins there are two localized states of spin-up quasiparticles which differ in energy, similar to the bonding and antibonding states of a diatomic molecule. There are no localized states of spin-down quasiparticles. For antiparallel impurity spins there is one spin-down quasiparticle localized state, as well as one of spin up, and the two are degenerate.

To understand the origin of the nondegeneracy of states around parallel moments and the degeneracy of states around antiparallel moments consider a heuristic picture of the two-impurity system in an isotropic-gap superconductor. For parallel alignment of the impurity moments only quasiparticles of one spin direction (assumed to be spin up) will be attracted to the impurity pair. Any localized state will thus be spin up. If the two impurities are close their two spin-up atomiclike states will hybridize and split into molecular states just as atomic levels are split into bonding and antibonding states in a diatomic molecule. Thus there will be two nondegenerate states apparent in the spectrum. This is shown schematically in the top section of Fig. 1, where the potential for spin-up quasiparticles is shown on the left [Fig. 1(A)] and for spin-down quasiparticles is shown on the right [Fig. 1(B)]. The potential for spin-down quasiparticles is everywhere repulsive, so no spin-down localized states will form.

The situation for antiparallel aligned spins, shown on the bottom of Fig. 1, is quite different. The effect of the second impurity on the state around the first is *repulsive* and so does not change the state energy much unless the impurities are very close. Furthermore the Hamiltonian has a new symmetry in this case: it is unchanged under the operation which both flips the quasiparticle spin and inverts space through the point midway between the two impurities. This operation changes the potential of Fig. 1(C) into that of Fig. 1(D). Thus instead of split states we find two degenerate atomiclike states of opposite spin, localized around each of the two impurities.

Detailed results for $NbSe_2$ are obtained by solving the following lattice-site mean-field Hamiltonian self-consistently:

$$H=-\sum_{\langle ij\rangle,\sigma} t_{ij}c^{\dagger}_{i\sigma}c_{j\sigma}+\sum_{i}\left[\Delta_i c^{\dagger}_{i\uparrow}c^{\dagger}_{i\downarrow}+\Delta^{*}_{i}c_{i\downarrow}c_{i\uparrow}\right] + V_{S1}(c^{\dagger}_{1\uparrow}c_{1\uparrow}-c^{\dagger}_{1\downarrow}c_{1\downarrow})+V_{S2}(c^{\dagger}_{2\uparrow}c_{2\uparrow}-c^{\dagger}_{2\downarrow}c_{2\downarrow}), \quad (1)$$

where $c^{\dagger}_{i\sigma}$ and $c_{i\sigma}$ create and annihilate an electron at lattice site i with spin σ. The impurities reside at lattice sites 1 and 2, the t_{ij} are the hopping matrix elements, and the Δ_i are the values of the superconducting order parameter. $NbSe_2$ has a triangular lattice, and the normal-state band structure can be

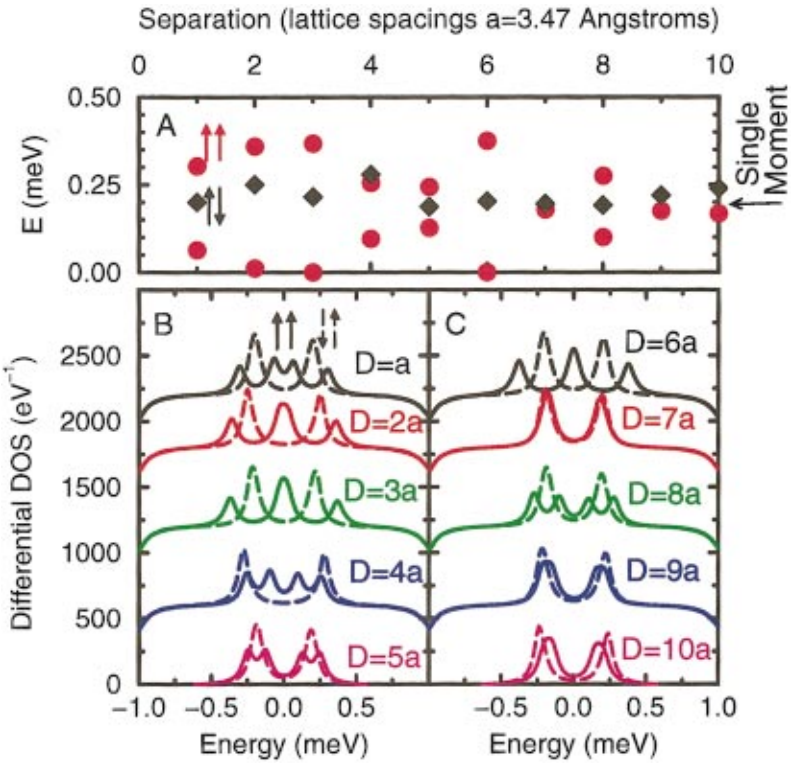

FIG. 2. (Color) (A) Energies of localized states as a function of impurity separation near parallel impurity spins (red) and antiparallel impurity spins (black). The energy is in meV and impurity separation in nearest-neighbor in-plane lattice constants (3.47 Å). (B) Differential density of states (DOS) for parallel impurity pairs (solid lines) and antiparallel impurity pairs (dashed lines) for impurity separations from one to five lattice spacings. (C) Same as (B), except for six to ten lattice spacings.

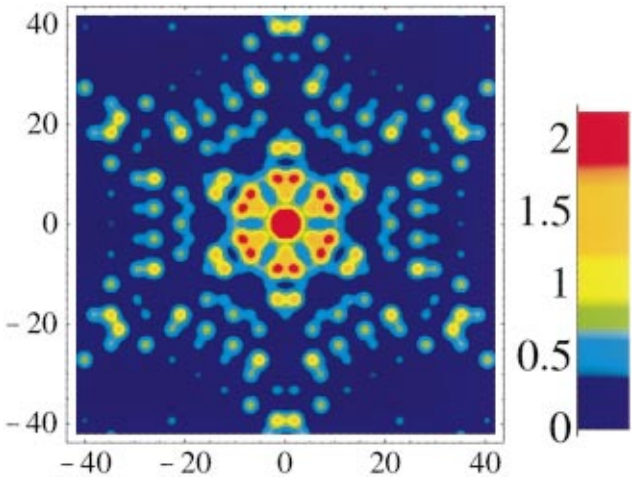

FIG. 3. (Color) Spatial structure of the holelike local density of states (LDOS) around a single impurity in the surface layer of $NbSe_2$. Nearest-neighbor in-plane separation on the triangular lattice is 3.47 Å. The units of the color scale are eV^{-1}.

modeled with an on-site energy of -0.1 eV and with nearest-neighbor and next-nearest-neighbor hopping matrix elements of -0.125 eV. These are determined from a tight-binding fit[13] to *ab initio* calculations of the electronic structure.[14] The superconducting pairing interaction is modeled with an on-site attractive potential which yields the experimental order parameter $\Delta = 1$ meV. The inhomogeneous order parameter Δ_i is determined self-consistently from the distorted electronic structure in the vicinity of the impurities. We consider equivalent parallel ($V_{S1} = V_{S2}$) or antiparallel ($V_{S1} = -V_{S2}$) impurity moments.

This model assumes the impurity spins behave as classical spins (see Refs. 3, 4, and 6). Classical spin behavior has been seen, for example, for Mn and Gd impurities on the surface of niobium.[3] The electronic structure in this model, including quasiparticle state energies and spatial structure, can be found rapidly and accurately by inverting the Gor'kov equation in a restricted real-space region including the two impurities, as described in Ref. 6. Measurements of the spatial structure of these states and of the values of the splitting

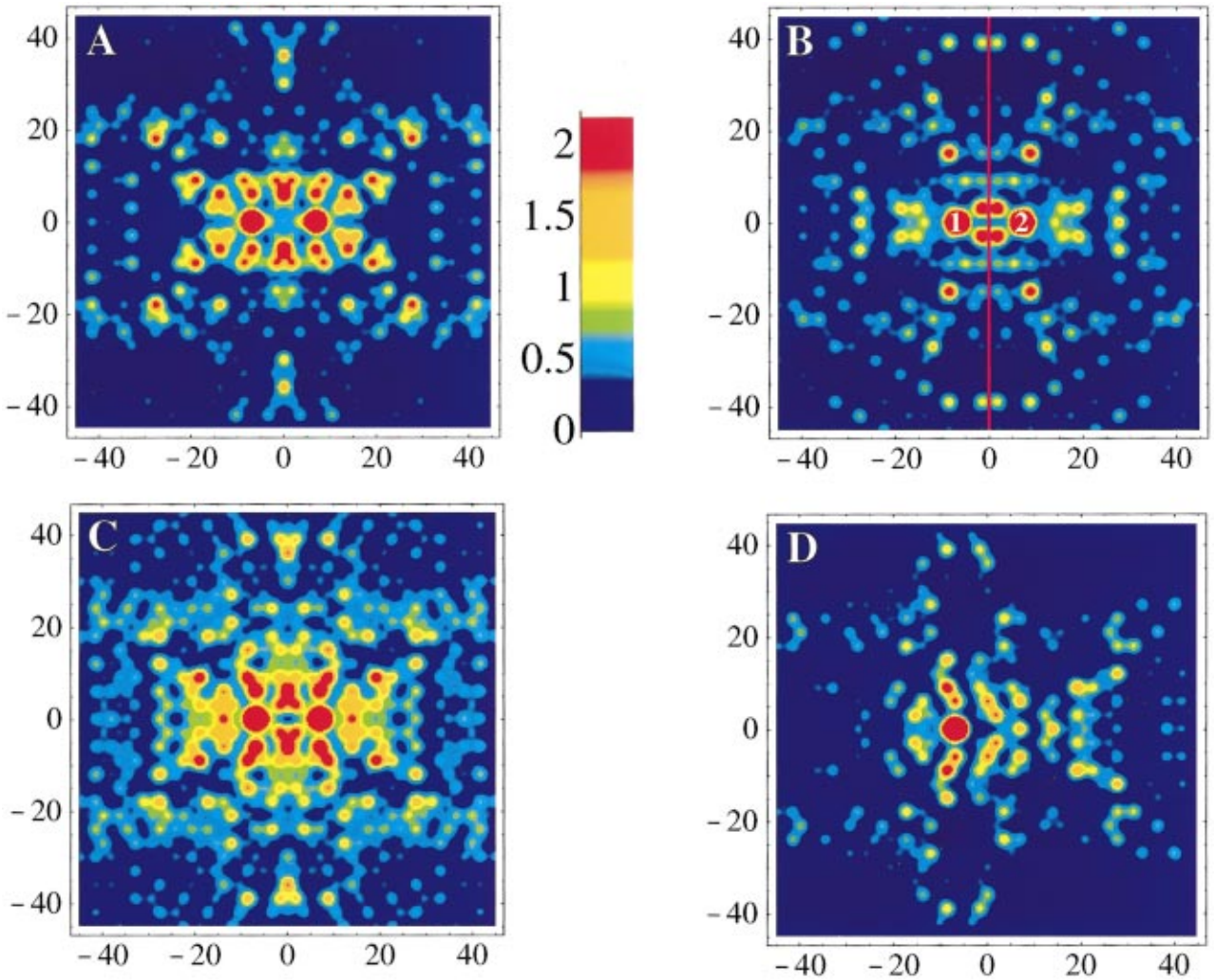

FIG. 4. (Color) LDOS around a parallel impurity pair at (A) the energy corresponding to the bonding state (-0.10 meV), and (B) the energy corresponding to the antibonding state (-0.26 meV). The impurities are at the same sites in each of (A)–(D), labeled 1 and 2 in (B). The mirror plane between the impurities is indicated by the red line in (B); there is no LDOS for the antibonding state in (B) along this plane, while there is for the bonding state (A). (C) LDOS around an antiparallel impurity pair at the energy of localized states (-0.28 meV). (D) spin-resolved LDOS at the same energy as (C) showing the predominance of LDOS around the impurity on the left. The units of the color scale are eV^{-1}.

between states can serve as a sensitive test of the model of the electronic structure of this material and of the impurity potential for a given atom.

Figure 2(A) shows the energies of the localized states in $NbSe_2$ for parallel spins (red) and antiparallel spins (black) for a sequence of impurity spacings which are multiples of the in-plane nearest-neighbor vector of the $NbSe_2$ lattice. The splitting of the bonding and antibonding states oscillates over a distance scale comparable to the Fermi wavelength of $NbSe_2$ along this direction. The splitting is proportional to the probability of a quasiparticle at one impurity propagating to the other, which is a measure of the coupling of the two atomiclike states. At large distances state energies for parallel and antiparallel moments approach the single impurity state energy, indicated on the right side of Fig. 2(A). Figure 2(B) and (C) shows the spatially integrated change in density of states due to the impurity pair for these impurity separations. The DOS of a quasiparticle of energy E in a superconductor has an electron component at energy E and a hole component at energy $-E$, so a single state will produce two peaks in the DOS unless it is closer to $E=0$ than the linewidth. That linewidth is determined by thermal broadening in the metallic probe tip, which for these plots is assumed to be $0.05\,\text{meV}=0.6\,\text{K}$. The gap in the homogeneous DOS extends from -1 meV to 1 meV in $NbSe_2$, so the variation in state energies is a substantial fraction of this gap. The clear distinction between parallel and antiparallel impurity moments in the DOS is only limited by the linewidth of the states.

A tunneling measurement of the DOS using a broad-area contact would yield the spectrum of an ensemble of impurity separations, hence STS (which measures the local DOS, or LDOS) is the ideal method for examining a single configuration of impurities. Before describing the distinct spatial differences in LDOS measurements between parallel and antiparallel alignments of impurity pairs we show the single impurity result in Fig. 3. The spatial structure of the electron and hole components of the LDOS are independently measurable by STS and can be quite different in detail. In this work we will show only the spatial structure of the hole component—similar gross structure is seen in the electronlike LDOS. Figure 3 shows the sixfold symmetric LDOS for $NbSe_2$ for $V_S=200\,\text{meV}$ at an energy of -0.19 meV. The units are angstroms and the nearest-neighbor spacing is 3.47 Å.

The details of the spatial structure can be traced directly to the normal-state electronic structure of $NbSe_2$.[6] We note that the local hopping matrix elements and the local nonmagnetic potential will differ near the impurity atoms. We find that moderate changes in these quantities do not significantly change the magnitude of the splitting of the even and odd parity states. This relative insensitivity occurs because the splitting is largely dependent on the amplitude for a quasiparticle to propagate from one impurity site to the other. Careful comparison of a measured LDOS and Fig. 3 would allow the determination of any changes in the local hopping or the nonmagnetic potential.

Plots of the LDOS for two impurities in $NbSe_2$ separated by four lattice spacings (13.88 Å) are shown in Fig. 4(A)–(D). They demonstrate via their spatial structure the qualitative differences among different types of molecular states possible around an impurity pair. Figure 4(A) is the bonding state (energy -0.10 meV) and Fig. 4(B) shows the antibonding state (-0.26 meV). The impurities are at the same sites in each of Fig. 4(A)–(D), labeled 1 and 2 in Fig. 4(B). As expected from the symmetry of these states, the antibonding state has a nodal line along the mirror plane (indicated in red) between the two impurities. No such nodal line occurs in Fig. 4(A)—in contrast the state is enhanced along the mirror plane.

The nonmagnetic STS probe cannot resolve the spin direction of the electronic states around the impurities, so around antiparallel impurity moments it detects both states. The sum of the LDOS for the two atomiclike states is symmetric around the mirror plane. Figure 4(C) is the LDOS at the energy for the two degenerate states around antiparallel impurity spins (-0.28 meV). The states are much more diffuse than the bonding state in Fig. 4(A) due to the repulsive nature of one impurity. Figure 4(D) shows the spin-resolved LDOS (which is more difficult to access experimentally), showing the LDOS of holes with the spin direction attracted to the impurity on the left. The spin-resolved LDOS at the impurity on the left is two orders of magnitude greater than at the impurity on the right. Thus the individual localized states are quite atomiclike.

We have assumed throughout that the impurity moments are locked either parallel or antiparallel. If the alignment is intermediate between the two cases then the spectrum shows nondegenerate states split less than in the parallel case. If there is some flipping of moments between parallel and antiparallel alignment on a timescale longer than the time required for the quasiparticle states to realign with the moments then the spectrum would be a linear superposition of the antiparallel and parallel spectra. If this is an activated process, this energy of activation of moment flipping could be easily distinguished by examining the temperature dependence of the spectrum.

This work describes a robust technique for determining the alignment of two impurity moments in a gapped system. The details of the expected results around magnetic impurities in the quasi-two-dimensional superconductor $NbSe_2$ have been calculated. Energies and spatial structure of bonding and antibonding states around parallel moments, and of localized atomiclike states around antiparallel moments, indicate that the two cases should be distinguishable with nonmagnetic scanning tunneling spectroscopy. This technique should be broadly applicable to a wide range of correlated electronic systems.

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