Josephson tunneling spectroscopy of negative-U centers

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We consider a superconductor-insulator-superconductor (SIS) junction in which the tunneling through the insulating barrier is dominated by a localized "negative-U" center. We show that the I_cR product of the junction depends sensitively on the spectrum of impurity states, and in near-resonant conditions exhibits an anomalously large I_cR product which can exceed the famous Ambegoakar-Baratoff limit by an arbitrarily large factor. The analysis is extended to problems in which there is an array of negative-U centers in the junction. We also discuss general reasons to expect significant violations of the optical conductivity sum rule in most SIS junctions and of the Ambegoakar-Baratoff result when the superconductors emerge from a non-Fermi liquid normal state.

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It has long been known that there exist localized defect states in solids that can be characterized as "negative-U centers." What this means is that the effective interactions are such that

$$U \equiv E(2)+E(0)-2E(1)<0, \tag{1}$$

where $E(n)$ is the energy of the state when occupied by n electrons; i.e., one can view these impurities as "pair binding" regions.[1] The existence of such centers has been found to explain many of the anomalous properties of various materials in which an impurity or defect with an odd number of electrons produces a diamagnetic (rather than the naively expected paramagnetic) response. In particular, this model was discussed by Anderson[2] in connection with dangling bonds in chalcogonide glasses.

An obvious question arises whether the effective attraction between electrons implied by Eq. (1) can be, in some way, harnessed to provide a mechanism for pairing in a superconductor. The trouble, of course, is that the negative-U centers with which we are familiar are highly localized, and the materials in which they occur are good insulators rather than superconductors. However, in a multicomponent system, it is possible[3] for electron itineracy to derive from one component which is proximity coupled to a set of localized negative-U centers from which the pairing arises. Indeed, superconductivity with $T_c=1.5$ K has been observed[4] in semiconducting PbTe doped with around 1% Tl, a well-known[5] negative-U center. Along these lines, two of us[6] have recently proposed that negative-U centers between the copper-oxide planes may play a role in enhancing T_c in certain cuprate high-temperature superconductors, most notably in the Hg-based materials.

In the present paper, we address less ambitious, but related issues: What is the effect of *weak* coupling between a conventional superconductor and a negative-U center? Can Josephson tunneling be used as a spectroscopic probe to *detect* the presence of negative-U centers? Manifestly, in the weak-coupling limit, the presence of a negative-U center can have little or no effect on the strength of the superconducting state, itself. However, as we will show below, the incipient pairing on the negative-U center leads to an anomalous enhancement of the I_cR product; it can exceed the famous Ambegoakar-Baratoff limit[7] by an arbitrarily large factor. By sweeping the chemical potential on the impurity site (perhaps by applying a suitable gate voltage) the impurity level can be moved closer and farther from resonance, which leads to predictable spectrocopic variations of the critical current. We also discuss the generalization of these results and their possible pertinence to recent experiments in layered superconductors.

The case of a single negative-U center. To begin, we consider a tunnel junction between two pieces of bulk superconductor through a barrier containing a single negative-U center. Specifically, we consider the model Hamiltonian

$$H=H_L+H_R+H_U+H_{tun}, \tag{2}$$

where H_L and H_R are the Hamiltonians of the left and right superconductors, which we take to be identical superconductors and well approximated by the Bougoliubov–de Gennes equations,[8] i.e.,

$$H_L=\sum_{k\sigma}(\epsilon_k-\mu)L^\dagger_{k\sigma}L_{k\sigma}+\Delta(L^\dagger_{k\sigma}L^\dagger_{-k-\sigma}+\text{H.c.}), \tag{3}$$

and the negative-U center is described by

$$H_U=-|U|c^\dagger_\uparrow c_\uparrow c^\dagger_\downarrow c_\downarrow+(\varepsilon-\mu)\sum_\sigma c^\dagger_\sigma c_\sigma. \tag{4}$$

Here, $c^\dagger_\sigma$ creates an electron on the impurity site with spin polarization σ and $R^\dagger_\sigma$ and $L^\dagger_\sigma$ create, respectively, an electron at the edge of the junction in the right and left superconductors. The tunneling Hamiltonian (which we treat as a small perturbation) is

$$H_{tun}=-\sum_\sigma [t_L L^\dagger_\sigma c_\sigma+t_R R^\dagger_\sigma c_\sigma+\text{H.c.}]. \tag{5}$$

[Of course, other interactions may be important under some circumstances, including direct tunneling through the junction (not involving the impurity) and more complicated pair tuneling and other interaction terms; under appropriate circumstances, the present model includes the most important interactions, and it is sufficient for our present purposes.]

In the absence of the tunneling term the eigenstates of the impurity are singly occupied, unoccupied, or doubly occupied (in a spin singlet). The ground state is *always* one of the latter two, so it is more convenient to express the results in terms of the single- and two-particle excitation energies ϵ_1 and ϵ_2, both positive, rather than to work directly with U and ε. For example, for $\varepsilon-\mu>0$ and $|U|<2(\varepsilon-\mu)$, the ground state has no particles in it and $\epsilon_1=\varepsilon-\mu$ and $\epsilon_2=2(\varepsilon-\mu)-|U|$. Although all of our results can be derived for the entire range of parameters, we are specifically interested in the case where ϵ_1 is large. In the single-impurity case we will use $\epsilon_1/\Delta\gg 1$ to simplify the expressions.

It is now a straightforward exercise to compute the zero temperature Josephson coupling to lowest (fourth) order in powers of H_{tun}:

$$J=\Delta\left[\frac{\pi N_F t_L t_R}{\epsilon_1}\right]^2\left[1+\frac{2\Delta}{\epsilon_2}\,\frac{\ln^2(2\epsilon_1/\Delta)}{\pi^2}\right], \tag{6}$$

where N_F is the normal-state density of states at the Fermi energy. The sign[9] of the J is such as to favor alignment of the phases (θ_L and θ_R) across the junction; i.e., the Josephson energy is $E_J=-J\cos(\theta_L-\theta_R)$. As usual, the critical current is simply $I_c=2eJ/c\hbar$.

The Josephson coupling is the sum of two terms: The first term is the contribution to the pair tunneling across the junction from processes in which first one electron and then the other passes from one side of the junction to the other. The second term comes from processes in which the second electron enters the junction before the first has left it. In this sense, one can think of the first term as being the textbook[8] result with an effective tunneling interaction $T_{LR}=t_L t_R/\epsilon_1$. However, the second term, which involves correlated pair tunneling, is a qualitatively new effect. Being proportional to Δ/ϵ_2, it diverges at the point at which the unoccupied and doubly occupied impurity states are degenerate (the impurity becomes partially occupied), i.e., a resonance condition for pair hopping. Note that, because the junction conductance is proportional to the square of the amplitude for single-particle transmission across the barrier, there is no analagous correlated pair tunneling term which contributes to $1/R$.

By itself, this expression is not terribly illuminating. However, as usual, we can express J in units of the normal-state junction conductance $1/R$, so that the highly detailed dependent factors of the tunneling matrix elements cancel, and we are left with a quantity, with units of energy, which in some sense measures how big the Josephson coupling is in natural units. R can be computed using a straightforward generalization of standard perturbative methods. It is independent of how far the impurity is from resonance (ϵ_2). In the limit of small Δ/ϵ_1, the result, the principal result of this paper, is

$$eI_cR=(\pi\Delta/2)\,[1+(2\Delta/\pi^2\epsilon_2)\ln^2(2\epsilon_1/\Delta)]. \tag{7}$$

Note that far from resonance, when the second term is absent, this result reproduces the standard Ambegoakar-Baratoff[7] relation. However, near resonance, where the unoccupied and doubly occupied states of the impurity are nearly degenerate with each other, the negative-U center gives rise to a dramatically enhanced I_cR product. When the resonance condition is too nearly satified, i.e., $\epsilon_2/\Delta<N_F t^2/\epsilon_1$, the perturbative expression is no longer useful.

Luckily, this single-impurity problem can be solved for arbitrary ϵ_2 (but still perturbatively in tunneling): integrating (projecting) out the singly occupied impurity states and the two superconductors reduces the problem to a rather simple effective Hamiltonian

$$H^{eff}=\begin{pmatrix}0 & \delta^*\\ \delta & \epsilon_2\end{pmatrix}+E_J^{(1)} \tag{8}$$

for the unoccupied and doubly occupied states in the effective proximity field

$$\delta=[\Delta N_F\log(2\epsilon_1/\Delta)/\epsilon_1]\,(t_L^2e^{i\theta_L}+t_R^2e^{i\theta_R}) \tag{9}$$

and $E_J^{(1)}$ is the contribution from the first term in Eq. (6) to the Josephson energy. The ground-state energy

$$E_J(\theta_L-\theta_R)=(\epsilon_2/2)-\sqrt{(\epsilon_2/2)^2+\delta^*\delta}+E_J^{(1)} \tag{10}$$

can now be used not only to obtain the altogether larger, $\mathcal{O}(t^2)$, contribution right at the resonance ($\epsilon_2=0$),

$$E_J^{res}=[\Delta N_F\ln(2\epsilon_1/\Delta)/\epsilon_1]\times\sqrt{t_L^4+t_R^4+2(t_Lt_R)^2\cos(\theta_L-\theta_R)}, \tag{11}$$

but also to smoothly connect with Eq. (6).[10]

In principle, when this kind of an effectively single-impurity junction is realized, the characteristic energies ϵ_2 and ϵ_1 can be varied by applying a voltage in the junction, so that the resonant condition can be tuned. In many circumstances one is faced with a collection of such impurities and so it is worth generalizing the derivation for an extended system.

Tunneling through a correlated region. The general structure of the perturbative calculation is unchanged. For the single impurity the result is determined by purely local correlations (both of the superconductors and, trivially, the impurity) and therefore a single parameter Δ/ϵ_2, controls the physics. For an extended barrier, a far more diverse roster of possibilities exists due to the interplay of disorder and coherence scales of the superconductors and in the barrier.

In the tunneling Hamiltonian we now allow for a nonuniform (though still short-ranged) hopping:

$$H_{tun}=\sum_\sigma\int d\vec r[t_L(\vec r)L_\sigma^\dagger(\vec r)c_\sigma(\vec r)+t_R(\vec r)R_\sigma^\dagger(\vec r)c_\sigma(\vec r)+\mathrm{H.c.}]. \tag{12}$$

The superconductors are still described via the Bogoliubov–de Gennes Hamiltonian or, more generally, by their anomalous (single-particle) Green functions $\mathcal{F}_{L/R}(\vec r,\tau)$.[8] The impurity region is described entirely by its (time-ordered) two-particle correlation function

$\langle T_\tau c_\downarrow(1) c_\uparrow(2) c_\uparrow^\dagger(3) c_\downarrow^\dagger(4)\rangle$, where $1,\ldots,4$ is a shorthand for space and time coordinates $(\vec{r}_1,\tau_1)$.

We now make a crucial simplifying assumption in describing the nonsuperconducting layer. We will take its single-electron Green function to be short ranged in space and time. This is certainly well justified when there is a gap or, more generally, whenever the relevant electron energy scales are large compared to Δ.

More specifically, we can always define the pair (P_2) and particle-particle propagators (P_1 and P_0) by decomposing the two-particle correlation function as

$$\begin{aligned}\langle T_\tau c_\downarrow(1) c_\uparrow(2) c_\uparrow^\dagger(3) c_\downarrow^\dagger(4)\rangle &= G(1,2)G(3,4)P_2(1,2;3,4)\\ &\quad + G(1,4)G(2,3)P_1(1,4;2,3)\\ &\quad + G(1,3)G(2,4)P_0(1,3;2,4),\end{aligned} \tag{13}$$

where $G(\vec{r}_1,\vec{r}_2,\tau_1-\tau_2) = \langle T_\tau c_\uparrow^\dagger(\vec{r}\tau) c_\uparrow(\vec{r}',\tau')\rangle$ is the imaginary-time-ordered Green function, and where $P_1 \to 0$, $P_3 \to 0$, and $P_0 \to 1$ at large distances. The pertrubative expression for the Josephson coupling involves integrals over this quanatity. We will simplify this expression by making two physically motivated assumptions. First, we will assume that the integral of G and any other less strongly peaked function f can be simplified as follows:

$$\int_0^\beta d\tau' \int d\vec{r}'\, G(\vec{r},\vec{r}',\tau') f(\vec{r}',\tau') \to \frac{1}{\epsilon} f\left(\vec{r},\frac{1}{\epsilon}\right), \tag{14}$$

where ϵ is a characteristic single-particle excitation energy (analogous to ϵ_1 above). If $f(\vec{r},0)$ is finite, we can let $f(\vec{r},1/\epsilon) \to f(\vec{r},0)$, but if f is weakly singular as $\tau \to 0$, $1/\epsilon$ plays the role of a cutoff—see below. Among other things, this permits us to substitute $P_\alpha(1,2;3,4) \to P_\alpha(1,1;4,4) \equiv \mathcal{P}_\alpha(1,4)$ in Eq. (13). Second, since we are interested in a barrier region which supports significant pairing fluctuations, we will assume that all the interesting correlation effects are reflected in the behavior of P_2 and will consequently make the simplifying approximations $P_0 = 1$ (no significant charge-density-wave fluctuations) and $P_1 = 0$ (no significant magnetic fluctuations).

With these simplifying approximations, we can bring the analog of Eq. (6), $J = J_1 + J_2$, into a somewhat more manageable form with

$$J_1 = 2\int d\vec{r}\, d\vec{r}'\, T_{LR}(\vec{r}) T_{LR}(\vec{r}') \int_0^\beta d\tau |\mathcal{F}(\vec{r}-\vec{r}',\tau)|^2, \tag{15}$$

$$J_2 = \frac{2\left|\mathcal{F}\left(\vec{0},\frac{1}{\epsilon}\right)\right|^2}{\epsilon^2} \int d\vec{r}\, d\vec{r}'\, t_L^2(\vec{r}) t_R^2(\vec{r}') \int_0^\beta d\tau\, \mathcal{P}_1(\vec{r},\vec{r}',\tau), \tag{16}$$

where $T_{LR}(\vec{r}) \equiv t_L(\vec{r}) t_R(\vec{r})/\epsilon$. Notice that the first term, as before, only depends on the parameters of the tunneling region through the typical single-particle energy ϵ and so can be viewed as a direct tunneling term but with an effective hopping matrix, $T_{LR}(\vec{r})$. More importantly, the hopping elements $t_L(\vec{r})$ and $t_R(\vec{r})$ enter J_1 and J_2 very differently, and so disorder will generally have a very different effect on the two contributions.

To make our analysis concrete, we adopt a simple model in which there are random variations of $t_L(\vec{r})$ and $t_R(\vec{r})$, but no correlations between t_L and t_R:

$$\overline{t_L(\vec{r}) t_L(\vec{r}')} = t_L^2[\alpha_L + (1-\alpha_L)\exp(-|\vec{r}-\vec{r}'|/\xi_L)] \tag{17}$$

(and similarly for t_R), but $\overline{t_L(\vec{r}) t_R(\vec{r}')} = 0$, where $\overline{t_L(\vec{r})} = t_L\sqrt{\alpha_L}$ signifies the configuration average. For simplicity, we ignore all other sources of disorder.

In terms of this model, it is possible to obtain expressions for the various contributions to the Josephson coupling in terms of various averages over the various propagators. These expressions are simple in terms of the implicitly defined intrinsic coherence lengths

$$\int d\tau d^{d-1} r\, \mathcal{P}_1(\vec{r},0,\tau) = \frac{\xi_2^{d-1}}{\epsilon_2}, \tag{18}$$

$$\int d\tau d^{d-1} r |\mathcal{F}(\vec{r},0,\tau)|^2 = \frac{\xi_0^{d-1}}{\Delta}[\Delta N_F]^2, \tag{19}$$

where, in addition,

$$\int d\tau \mathcal{F}(\vec{0},\tau) = \frac{\pi \Delta N_F}{\Delta}, \quad \mathcal{F}\left(\vec{0},\frac{1}{\epsilon}\right) = \Delta N_F \ln[\epsilon/\Delta]. \tag{20}$$

It is interesting to remark that the various expressions involving $\mathcal{F}$, which we have evaluated here in the context of BCS mean-field theory, depend on the behavior of the superconducting leads at distances *short* compared to ξ_0. Here, as we discuss below, the correlation functions intimately reflect the fact that the *normal* state of the leads is a Fermi liquid.

We do not display the complete result, here, since it is long. In the limit of weak disorder, $\alpha \to 1$, the configuration-averaged Josephson energy per unit area (area $\equiv L^{d-1}$) is readily evaluated:

$$\mathcal{J} = \frac{2\Delta(\pi N_F t_L t_R)^2}{\epsilon^2}\left(\xi_0^{d-1} + \frac{\xi_2^{d-1}\Delta}{\pi^2 \epsilon_2}\ln^2(\epsilon/\Delta)\right). \tag{21}$$

Here, the ratio of the normal contribution and correlated pair tunneling contributions to the Josephson coupling is proportional to $(\epsilon_2/\Delta)(\xi_0/\xi_2)^{d-1}$; unless the pair correlations are at quite low energy and extend over quite long distances, the anomalous (J_2) pair tunneling term will be insignificant.

Now we consider a large disorder limit $\alpha \to 0$ and for simplicity assume as well that $\xi_L, \xi_R \ll \xi_2, \xi_0$. In this case,

$$\begin{aligned}\mathcal{J} = \frac{2c_L c_R \Delta(\pi N_F t_L t_R)^2}{\epsilon^2}\Bigg[&\Upsilon_1\left(\frac{\xi_L \xi_R}{\xi_L+\xi_R}\right)^{d-1}\\ &+ \Upsilon_2 \frac{\xi_2^{d-1}\Delta}{\pi^2\epsilon_2}\ln^2(\epsilon/\Delta)\Bigg],\end{aligned} \tag{22}$$

where Υ_J are geometric factors of order 1. Here, as long as $\xi_2 \gg \xi_L$, ξ_R, there is a large enhancement of the correlated pair tunneling term. The physics of this enhancement is very simple—if ξ_2 is large, a pair can tunnel into the barrier where t_R is large, then propagate along the barrier, and finally tunnel out where t_L is large. This spatial structure amplifies the sort of resonance effects we found in the single-impurity case.

Discussion. With regards to the application of these ideas to layered superconductors, our conclusions are intriguing, but not unambiguous. Large I_cR products have recently been measured along the c axis in various layered superconductors,[11] as have dramatic shifts of optical spectral weight over large ranges of energies. The two phenomena are thought by many to be related. We find that all simple models of superconductor-insulator-superconductor (SIS) junctions (and more general models[12]) exhibit large spectral weight shifts leading to apparent sum rule violations as the system enters the superconducting state.

To see this, consider the case of a simple junction, i.e., $H_{tun} = -\Sigma_\sigma [t L_\sigma^\dagger R_\sigma + \text{H.c.}]$. Rather than computing the actual optical conductivity we use the single-band version of the optical sum rule (which relates the integrated spectral weight in a given band to the expectation value of the kinetic energy) to compute the integrated oscillator strength for the normal junction and the superconducting junction. The result is that

$$\int d\omega [\sigma_N(\omega) - \sigma_S(\omega)] = 4|t|^2 N_F^2 \Delta \ln(W/\Delta), \quad (23)$$

where σ_N and σ_S are, respectively, the frequency-dependent junction conductance with superconducting and nonsuperconducting leads. Since the f sum rule must ultimately be satisfied, presumably the correct interpretation of this result is that spectral weight is transferred over large energy ranges, beyond those described by our model, i.e., on energy scales on the order of the bandwidth, which is obviously much larger than Δ. Since this occurs even in the absence of an I_cR anomaly, we are at present unable to make a clear statement concerning the expected spectral consequences of such an anomaly. Thus, the observed apparent sum rule violations cannot be definitively linked with the presence or absence of interesting correlations in the barrier region. And, unfortunately, the experimental data on large I_cR products in the high-temperature superconductors, while very striking indeed, may potentially be hard to interpret as well, as it is intertwined with pseudogap phenomena which occur well above the superconducting transition temperature.

Perhaps yet a potentially more vexing concern has to do with the nonuniversality of the I_cR product even when tunneling through an uncorrelated insulator. The problem is that the result is strongly influenced by the short-distance and -time properties of the superconductor. In weak coupling these are inherited from the "normal" state. We have already seen one manifestation of this: the logarithm in the anomalous term is inherited from the underlying Fermi liquid (this is the same logarithm responsible for the superconducting instability). More generally, even the simple proportionality $\mathcal{F} \sim \Delta N_F$, very familiar from BCS theory (and in part responsible for the Ambegoakar-Baratoff result), between the order parameter ($\mathcal{F}$) and the mean field (Δ) need not be generic[13] either deep enough in the superconducting phase or when the normal phase is not Fermi liquid like.

In summary, we have considered a problem of tunneling through a single negative-U impurity and an extended region with incipient pairing. We find, under favorable circumstances, anomalous enhancement of the Josephson coupling due to correlated pair tunneling processes.

Note added. After submitting this paper we became aware of the related work of Hellman and Harford.[14]

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