Midgap Surface States as a Novel Signature for $d_{x_a^2-x_b^2}$-Wave Superconductivity

Chia-Ren Hu

*Department of Physics, Texas A&M University, College Station, Texas 77843-4242**
and Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5932
and Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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It is shown that a sizable areal density of midgap states exists on a {110} surface of a $d_{x_a^2-x_b^2}$-wave superconductor, which can either have vacuum or an insulator at the surface, or be separated from vacuum or an insulator by a clean, size-quantized, normal metal overlayer. These "midgap" states have many observable consequences—some of which are briefly discussed here—which can be used as a clear signature to distinguish between d-wave and anisotropic s-wave superconductors.

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Recently there has been much interest in whether the order parameter in cuprate high-T_c superconductors is d wave or s wave in nature. This is a fundamental question, since it can provide an important clue to the mechanism question. Many theoretical model studies [1] have indicated that the superconducting condensate of cuprate high-T_c superconductors might have a d-wave symmetry. More precisely, it is the $d_{x_a^2-x_b^2}$ wave [2] defined relative to the a and b axes of the CuO_2 planes. Such a pairing gives rise to an anisotropic energy gap, which drops to zero on some nodal lines of an essentially cylindrical Fermi surface, implying that there are quasiparticles with energies arbitrarily close to the Fermi energy (called zero energy from now on). This is very different from an s-wave superconductor, which has a finite energy gap at all directions of the Fermi surface. This difference leads to very different predictions for the low temperature (T) thermodynamic and transport properties—power law T dependence for the former system versus exponential dependence for the latter. Experimentally, many measurements of such quantities on high-T_c materials indeed give power-law-like dependences, which can be interpreted as supporting the d-wave theories [3], but such an interpretation is not unambiguous: (i) This difference depends only on the vanishing energy gap of a d-wave superconductor for some directions of the Fermi surface, and not on the *sign* of the $d_{x_a^2-x_b^2}$-wave "gap-function" or "pair-potential" order parameter $\Delta(\mathbf{k}) \propto k_a^2 - k_b^2$ which varies with the relative momentum $\mathbf{k}$. Thus in principle the measured results can also be interpreted in terms of an anisotropic s-wave pairing, as is advocated by the Anderson school [4]. (ii) The expected high sensitivity to the amount of impurity scattering in a d-wave superconductor also makes interpretations of the measured results difficult. Recently, Shen *et al.* [5] have measured the angle-resolved photoemission spectrum of a single-crystal high-T_c superconductor, which allows them to look at each $\mathbf{k}$ direction of the Fermi surface individually. The result does indicate an anisotropic energy gap of the same symmetry as $|k_a^2 - k_b^2|$, but this method also does not determine the sign of the order parameter. Recently it was suggested [6] that multiple Andreev scattering in superconductor-normal metal-superconductor junctions can be used as a test for anisotropic electron pairing, but it also invokes only the $\mathbf{k}$ dependence of the energy gap. Thus these two experiments cannot distinguish between a genuine d-wave order parameter and a "pseudo-d-wave" one either. Only an experiment reported very recently [7] is designed to observe directly the sign of the order parameter in high-T_c superconductors. The preliminary results reported show some complications, but taken as a whole strongly support a d-wave interpretation.

In this Letter we would like to discuss another possible way to observe a direct consequence of the sign of a d-wave superconducting order parameter. We shall show that a $d_{x_a^2-x_b^2}$-wave order parameter can give a sizable areal density of "midgap" surface states (i.e., surface states with essentially zero energy relative to the Fermi surface) under suitable arrangements, some of which are discussed in this paper. Such midgap states would not occur in similar conditions if the superconductor is s wave, whether isotropic or anisotropic. These midgap states have many observable consequences, some of which are discussed qualitatively in this paper.

A simple situation which can lead to such a sizable area density of midgap surface states is a $d_{x_a^2-x_b^2}$-wave superconductor (S) with a {110} surface, which can be either a free surface, or coated with a clean, size-quantized, normal metal overlayer (N) of a thickness d much shorter than its mean free path ℓ. Choosing a coordinate system (x, y, z) such that $x > 0$ is the region occupied by the superconductor (thus the x axis must be along the [110] crystal direction or its equivalent), and the z axis is still along the [001] crystal direction, which is now parallel to the surface, then $k_a^2 - k_b^2 = \mp 2k_x k_y$, and the $d_{x_a^2-x_b^2}$-wave order parameter becomes also the d_{xy} wave.

Let the normal metal layer be present. (The limit $d \to 0$ gives the results for the case of no normal metal overlayer.) Then the surface states discussed here may

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be viewed as bound states formed by a particle alternately experiencing the usual specular reflections at the free surface and the Andreev reflections [8] at the N-S interface. The latter is caused by an off-diagonal pair potential, so it changes an electron of momentum $\mathbf{k}$ into a hole of momentum $-\mathbf{k}$, and vice versa, whereas the former only changes the sign of k_x, without changing the nature of the particle. Having the two types of reflections in an alternate sequence implies that the pair potential sensed by the particle at the consecutive Andreev reflections will be alternate in sign if the superconductor is d_{xy} wave, but of the same sign if the superconductor is s wave or $d_{x^2-y^2}$ wave [i.e., $d_{x_a^2-x_b^2}$ wave but the surface is $\{100\}$]. Thus if one is to treat the effect of the free surface by an image method, the proper way to extend the off-diagonal pair potential to the region $x' \equiv x + d < 0$ is by the prescription: $\Delta((k_x, k_y, k_z), (-x', y, z)) = \Delta((-k_x, k_y, k_z), (x', y, z))$, which for a d_{xy} superconductor is equal to $-\Delta((k_x, k_y, k_z), (x', y, z))$, giving a pair potential that is odd in x', much like the situation encountered in dealing with a dimerization soliton in polyacetylene [9]. It is this symmetry condition which gives rise to the midgap states, not the precise functional form of the pair potential, so we know for sure that the proximity effect will not affect our conclusion about the existence of the midgap states, their area density, and their lack of dispersion in spite of their transverse momentum (in the WKBJ approximation [10]; see later). (A more mathematical proof will be given later.) For the same reason, the area density of midgap states obtained in this analysis will be independent of d. Thus it is actually the same for the case of no normal metal overlayer.

For the simplest model calculation to illustrate the qualitative new physics involved, let the free surface of the N layer and its interface with the S region be both infinitely large and perfectly flat, and let $\ell = \infty$. We also neglect all parameter discontinuities at the N-S interface, except that of the superconducting order parameter Δ, about which we neglect the proximity effect, and assume that Δ depends on the center-of-mass coordinates $\mathbf{r} \equiv (x, y, z)$ of the pairs as simply a Heaviside step function $\Theta(x)$. A non-s-wave superconducting order parameter also depends on a relative-coordinate vector $\mathbf{s}$ of the pairs, or, after a Fourier transform, on the relative wave vector $\mathbf{k}$, which, in weak-coupling treatment, is fixed on the Fermi surface, so only its direction $\hat{\mathbf{k}} \equiv \mathbf{k}/|\mathbf{k}|$ is a variable. Thus our assumption is

$$\Delta(\hat{\mathbf{k}}, \mathbf{r}) = \Delta_0(\hat{\mathbf{k}})\Theta(x). \tag{1}$$

The elementary excitations of an inhomogeneous superconductor obey the time-independent Bogoliubov-de Gennes equations [11]:

$$\epsilon_n u_n(\mathbf{x_1}) = \hat{h}_0 u_n(\mathbf{x_1}) + \int \Delta(\mathbf{s}, \mathbf{r}) v_n(\mathbf{x_2}) d\mathbf{x_2}, \tag{2a}$$

$$\epsilon_n v_n(\mathbf{x_1}) = -\hat{h}_0 v_n(\mathbf{x_1}) + \int \Delta(\mathbf{s}, \mathbf{r}) u_n(\mathbf{x_2}) d\mathbf{x_2}, \tag{2b}$$

where $\mathbf{s} \equiv (\mathbf{x_1} - \mathbf{x_2})$, $\mathbf{r} \equiv (\mathbf{x_1} + \mathbf{x_2})/2$, and $\hat{h}_0 \equiv -\nabla^2_{\mathbf{x_1}}/2m - \mu$ in the absence of an external magnetic field and any other force fields, with μ the chemical potential. (We have put $\hbar = 1$.) With an N-S interface at $x = 0$, and in the WKBJ approximation [10], these equations have special solutions of the form

$$\begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix} = e^{i\mathbf{k}_F\cdot\mathbf{r}} \begin{pmatrix} \tilde{u}_n(\mathbf{r}) \\ \tilde{v}_n(\mathbf{r}) \end{pmatrix}, \tag{3}$$

where $\mathbf{k}_F \equiv (k_{x0}, k_y, k_z)$ is a vector on the Fermi surface, and $(\tilde{u}_n(\mathbf{r}), \tilde{v}_n(\mathbf{r}))$ obey the Andreev equations [8]:

$$\epsilon_n \tilde{u}_n(\mathbf{r}) = -im^{-1}\mathbf{k}_F \cdot \nabla\tilde{u}_n(\mathbf{r}) + \Delta(\hat{\mathbf{k}}_F, \mathbf{r})\, \tilde{v}_n(\mathbf{r}), \tag{4a}$$

$$\epsilon_n \tilde{v}_n(\mathbf{r}) = im^{-1}\mathbf{k}_F \cdot \nabla\tilde{v}_n(\mathbf{r}) + \Delta(\hat{\mathbf{k}}_F, \mathbf{r})\, \tilde{u}_n(\mathbf{r}). \tag{4b}$$

For $\Delta(\hat{\mathbf{k}}, \mathbf{r})$ given by Eq. (1), these equations can be solved exactly, giving for states bound to the normal metal overlayer [i.e., states with $|\epsilon_n(\mathbf{k}_F)| < |\Delta_0(\hat{\mathbf{k}}_F)|$]

$$(\tilde{u}_n^>, \tilde{v}_n^>) = e^{-\gamma x}(\hat{u}_n, \hat{v}_n) \quad (\text{for } x > 0), \tag{5a}$$

$$(\tilde{u}_n^<, \tilde{v}_n^<) = (e^{ik_1 x}\hat{u}_n, e^{-ik_1 x}\hat{v}_n) \quad (\text{for } x < 0), \tag{5b}$$

where

$$\hat{u}_n = \Delta_0/D, \quad \hat{v}_n = \left[-i\,\mathrm{sgn}(k_{x0})\sqrt{\Delta_0^2 - \epsilon_n^2} + \epsilon_n\right]/D, \tag{6}$$

with

$$D \equiv \left[|i\,\mathrm{sgn}(k_{x0})\sqrt{\Delta_0^2 - \epsilon_n^2} - \epsilon_n|^2 + \Delta_0^2\right]^{1/2} \tag{7}$$

and

$$\epsilon_n = \sqrt{-(k_{x0}\gamma/m)^2 + \Delta_0^2} = k_{x0}k_1/m. \tag{8}$$

Since $\hat{u}_n$ and $\hat{v}_n$ depend on the sign of k_{x0} directly as well as indirectly via Δ_0, we shall label them with another subscript $+$ or $-$.

To consider the effect of the free boundary at $x = -d$, we first make a superposition of the above special solutions for the two signs of k_{x0}. This gives

$$\begin{pmatrix} u_n^> \\ v_n^> \end{pmatrix} = e^{i\mathbf{k}_\perp\cdot\mathbf{r}_\perp} e^{-\gamma x}\left[Ae^{ik_{x0}x}\begin{pmatrix} \hat{u}_{n+} \\ \hat{v}_{n+} \end{pmatrix} + Be^{-ik_{x0}x}\begin{pmatrix} \hat{u}_{n-} \\ \hat{v}_{n-} \end{pmatrix}\right] \quad (\text{for } x > 0), \tag{9a}$$

$$\begin{pmatrix} u_n^< \\ v_n^< \end{pmatrix} = e^{i\mathbf{k}_\perp\cdot\mathbf{r}_\perp}\left[Ae^{ik_{k0}x}\begin{pmatrix} e^{ik_1 x}\hat{u}_{n+} \\ e^{-ik_1 x}\hat{v}_{n+} \end{pmatrix} + Be^{-ik_{x0}x}\begin{pmatrix} e^{-ik_1 x}\hat{u}_{n-} \\ e^{ik_1 x}\hat{v}_{n-} \end{pmatrix}\right] \quad (\text{for } x < 0), \tag{9b}$$

where $\mathbf{k}_\perp \equiv (0, k_y, k_z)$. Requiring Eq. (9b) to vanish at $x = -d$, we obtain, for the bound states, the following eigencondition:

$$e^{4ik_1 d} = \left(\frac{\hat{u}_{n+}}{\hat{v}_{n+}}\right)\left(\frac{\hat{v}_{n-}}{\hat{u}_{n-}}\right). \tag{10}$$

For an s-wave or $d_{x^2-y^2}$-wave superconductor (with $\hat{\mathbf{x}} \perp$ surface), for which $\Delta_0(-k_{x0}, k_y, k_z) = \Delta_0(k_{x0}, k_y, k_z)$, Eq. (10) may be reduced to

$$e^{4ik_1 d} = \frac{\epsilon_n + i\sqrt{\Delta_0^2 - \epsilon_n^2}}{\epsilon_n - i\sqrt{\Delta_0^2 - \epsilon_n^2}}, \tag{11}$$

but for a d_{xy}-wave superconductor, for which $\Delta_0(-k_{x0}, k_y, k_z) = -\Delta_0(k_{x0}, k_y, k_z)$, Eq. (10) may be reduced to

$$e^{4ik_1 d} = -\frac{\epsilon_n + i\sqrt{\Delta_0^2 - \epsilon_n^2}}{\epsilon_n - i\sqrt{\Delta_0^2 - \epsilon_n^2}}. \tag{12}$$

Equation (11) has no zero energy solutions, but Eq. (12) has. In fact, it has one such midgap-state solution for each allowed $\mathbf{k}_\perp$ and spin. Thus the area density of these midgap states is equal to $k_F^2/2\pi$ for a spherical Fermi surface, or $2k_F/\pi c$ for a cylindrical Fermi surface, where c is the (average) distance between neighboring conducting planes (i.e., the CuO_2 planes for high-T_c superconductors). (This is an upper bound estimate, since we must exclude those $\mathbf{k}_F$ that are very nearly parallel or perpendicular to the surface.) Whereas the total number of other bound states, for which $\epsilon_n \neq 0$ is d dependent, and can be zero if d is too small, the number of these midgap bound states is independent of d, and remains the same even when $d = 0$, i.e., when the surface at $x = 0$ is a free surface. In fact, in this case, these midgap states become the only bound states within the gap. When the proximity effect is taken into account, the $\Theta(x)$ function in Eq. (1) must be replaced by a nonstep rise to unity, with or without an initial step rise from zero. Exact solutions at $\epsilon \neq 0$ are then no longer possible in general, but the zero-energy state at each $\mathbf{k}_\perp$ and spin remains to exist and to be exactly soluble (within the WKBJ approximation), *if only* the sign of the pair potential changes with the sign of k_{x0}. Going beyond the WKBJ approximation by a perturbative analysis shows that the correction to energy is at most of the order Δ_0^2/μ. (More precisely, it is of order $m\Delta_0^2/k_{x0}^2$, so it can acquire a very weak dispersion until k_{x0} is very close to zero.) First order perturbation appears to vanish, so the energy correction may even be of higher order. In any case, the effect of this small energy correction may be considered together with the effect of a small level broadening due to impurity scattering (see below). (Note that even if these states are not of exactly zero energy, they do not have partners under particle-hole inversion.)

There should be many observable consequences due to the existence of these midgap states. In the following, we briefly discuss some of them qualitatively, leaving more of a quantitative account of them for future works.

The most well-known previous example of midgap states is found at the centers of dimerization solitons in conjugated polymers such as polyacetylene [9]. An odd off-diagonal potential is responsible for generating the midgap states in that problem as well as in the present one. However, the analogy is not complete: Aside from the dimensional difference, the wave functions for the soliton midgap states in polyacetylene are even about their centers, whereas those for the midgap states found here are odd about x' (if extended into the region $x' < 0$). A closer analog of the present midgap states is probably the very-low-energy excitations in the cores of vortices in usual s-wave superconductors [12], although important differences also exist. Nevertheless, if the midgap states found here are truly-zero energy states, they would still have to be half filled for a charge neutral system at $T = 0$, just like the case in polyacetylene. Thus the $2N_0$ midgap states, half spin up and half spin down, would still have to be filled by exactly N_0 electrons. Since these states have no dispersion (neglecting for the moment the small correction to the WKBJ approximation), Coulomb interaction energy among these electrons should split the many degenerate ways to fill the states. The lowest energy state should then have a totally antisymmetric orbital wave function times a totally symmetric spin wave function. Thus all N_0 midgap electrons would be in the same spin state at $T = 0$, forming a giant moment. (This argument is analogous to Hund's rule in atomic physics.) A small energy shift which may result from going beyond the WKBJ approximation, and a small broadening of this midgap level due to impurity scattering, can both possibly invalidate this argument, and make the giant moment not appear. But if these two characteristic energies are sufficiently small, then the giant moment can be restored with a moderate external magnetic field (at sufficiently low temperatures, by splitting the level across the Fermi surface), allowing some magnetic experiments to verify the existence of these midgap states and d-wave pairing. If charges are pulled in and out of this surface by an oscillating electric potential $V(t)$ of a very low frequency ω, then this giant moment will *decrease* whenever the system is driven away from charge neutrality. That is, the observed giant moment will vary at the frequency 2ω, and it will be 180° out of phase with the 2ω component of $V^2(t)$. This observation suggests using an ac technique to observe the giant moment, which allows one to avoid the background due to the Meissner effect.

For a sample with two parallel {110} surfaces separated by only a few coherence lengths, the midgap level due to the two surfaces will be split into a bonding level and an antibonding level, and the giant moments at the two surfaces will be antiparallel and cancel. However, this coupling is exponentially small in the separation of the two surfaces, and can be overcome by a moderate external magnetic field (needed if it is larger than the characteristic field discussed in the previous paragraph). Then observing the exponential dependence of this field on the thickness of the sample is another clear evidence for the existence of these midgap states. Of course, this field is involved only if the magnetization measurement includes the contributions from both surfaces.

The midgap states should also be observable with any experimental technique which is sensitive to the energy dependence of the density of states. If a single $\hat{\mathbf{k}}$ direction is looked at, these midgap states should appear clearly as a narrow peak essentially located at the center of a finite energy gap, if only $\hat{\mathbf{k}}$ is not very near one of the gap-node directions (assuming no other bound states exist). (This peak may be split into two peaks if the {110} film sample is sufficiently thin, or if a magnetic field is applied parallel to the surface.) If a convolution of all $\hat{\mathbf{k}}$ directions is looked at, the midgap-state peak should still be observable if it is sufficiently large and narrow, because the total density of states of a d-wave superconductor due to all unbound states still drops to zero at zero energy. However, note that the total spectral weight of these midgap states is proportional to the total {110} surface (or interface) area, whereas that of the unbound states is proportional to the total volume of the sample, so their ratio is sample dependent, and can be negligibly small for some samples.

Quasiparticle tunneling might be the most direct way to observe these midgap states. In fact, a "zero bias conductance peak" (ZBCP) has often been observed in such tunneling measurements performed on many different high-T_c superconductors using various kinds of counterelectrodes (Pb, Nb, Pt, Au, etc.), which has not yet been understood [13]. One is very tempted to associate this ZBCP with the midgap states predicted to exist in this work, although essentially none of the samples studied have {110} surfaces purposely created in them (except perhaps in [14]). We think that midgap surface states can most likely also be generated more generally in a $d_{x_a^2-x_b^2}$-wave superconductor, such as at a finite internal crack normal to the [110] direction, or at the boundary of a circular or other shaped hole in the a-b plane, etc. A magnetic field parallel to the c axis may also be able to replace the free surface of the N overlayer for reversing k_{x0} (or k_y). The first two possibilities might explain why ZBCP is so frequently observed in high-T_c superconductors, and yet not in every sample. On the other hand, to cleanly confirm the existence of such midgap states and d-wave superconductivity using quasiparticle tunneling, it is still better to use samples which are epitaxially grown single-crystal films with ideally flat {110} surfaces. For comparison one might also do the same experiment on epitaxial films with ideally flat {100} surfaces, for which midgap states should not appear, if no internal boundaries are present [15].

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* Permanent address.

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