Phase-dependent energy spectrum in Josephson weak links

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The quasiparticles energy spectrum in clean Josephson weak links is studied theoretically. The density of states (DOS) is calculated for various situations: *s*-wave or *d*-wave symmetry of the order parameter in the superconducting electrodes, the barrier consisting of a normal or a monodomain ferromagnetic metal. The number of peaks in DOS, corresponding to the Andreev bound states, in the anisotropic *d*-wave case can be greater than in the isotropic *s*-wave case, provided that the barrier acceptance angle is not too small. Energy levels of the bound states are explicitly obtained as a function of the barrier thickness and exchange field and in the *d*-wave case of the orientation of the crystalline axes of the electrodes. The spectra are strongly influenced by the macroscopic phase difference at the link. [S0163-1829(99)12621-3]

I. INTRODUCTION

Quasiparticle states in nonuniform superconductors have been studied since the early days of superconductivity. In conventional superconductor–normal-metal (S/N) junctions, in which the order parameter amplitude abruptly changes, the bound states discovered first by de Gennes and Saint James,[1] and studied afterwards by Arnold[2] and many other authors are a consequence of Andreev reflection.[3] The quasiparticle states in *s*-wave S/N/S junctions were studied more recently by Furusaki and Tsukada,[4] who found that the energy spectrum depends strongly on the pair potential phase difference between two superconductors, and that the Josephson current flows *via* the bound states. In high-T_c superconductors, where a growing amount of evidence points to the $d_{x^2-y^2}$ symmetry of the order parameter, the pair potential encounters a phase change between the *a*- and *b*-axis directions.[5] One particular feature related to the *d*-wave symmetry is the existence of the zero-energy states (ZES) at the surface of a *d*-wave superconductor,[6,7] closely related to the experimentally observed zero-bias conductance peaks (ZBCP) in tunneling spectroscopy measurements.[8] The origin of ZBCP in the ab-plane tunneling conductance in *d*-wave superconductors is the same as that of the π phase shift in the Josephson interference experiments.[9] However, π shift may arise in a junction with magnetic impurities in the barrier,[10] or in superconductor-ferromagnet (S/F) multilayers.[11,12] When the magnetic scattering is involved, one has a special case of Andreev reflection, since the magnetic exchange field is opposite for two spin orientations of the carriers forming a Cooper pair. In the past tunneling through S/Fi/S junctions, where Fi is a magnetic insulator, has been studied experimentally[13] and theoretically.[14,15] More recently, Andreev reflection has been studied in S/F junctions by de Jong and Beenakker,[16] and in S/F/S junctions where F is a ferromagnetic metal by Kuplevakhskii and Fal'ko.[17] Magnetic scattering effects in *s*-wave and *d*-wave S/N junctions with a Kondo-like magnetic barrier or containing a ferromagnetic scattering layer have been calculated by Zhu and Wang.[18]

In the present paper we calculate the quasiparticle density of states in Josephson weak links with a metallic barrier, which may consist of a normal metal (N) or of a ferromagnetic metal (F) with constant exchange field. We consider both *s*-wave symmetry and $d_{x^2-y^2}$-wave symmetry of the superconducting order parameter. In the latter case, we assume that the crystals in two (identical) superconducting electrodes are misoriented, their *a* axes making an angle θ.

Our main purpose is to investigate the influence of the phase difference at the junction on the quasiparticles energy spectrum. This phase difference, due to the flow of the supercurrent, or to the misorientation of the electrodes for *d*-wave pairing, in presence of the exchange energy $h \neq 0$ in F acquires an additional ''magnetic'' contribution. We study the change in the spectra induced by h, as well as the conditions for ZES in various situations mentioned above.

The paper is organized as follows. in Sec. II we present the general formalism, based on quasiclassical theory of superconductivity,[19] and calculate the quasiclassical Green's functions for S/F/S weak link, generalizing the approach of Buzdin *et al.*[20] to the case of *d*-wave junctions with ferromagnetic barrier.[21] From the obtained expressions easily follow simpler cases of *s*-wave junctions, with an isotropic order parameter, and of a normal metal barrier, with $h=0$. In Sec. III we calculate the resulting densities of states. We show how the local densities of states can be expressed in terms of energies of bound states and give the equations for the bound states, from which the condition for the formation of ZES follows. Section IV contains a discussion of the obtained results.

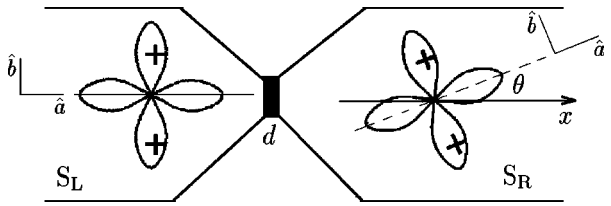

FIG. 1. Schematic illustration of the weak link. For *d*-wave pairing in S electrodes the fourfold symmetry of the pair potential is indicated.

II. QUASICLASSICAL GREEN'S FUNCTIONS

An efficient method for calculating local spectral properties of superconductors is the quasiclassical theory of superconductivity.[19] In the clean limit, and assuming that the magnetic influence on superconductivity is limited to that of the exchange field, one can use the Eilenberger quasiclassical matrix equations in the presence of the exchange energy h.[20–22]

The corresponding set of scalar equations for the quasiclassical Green's functions $g_\downarrow(\mathbf{r},\mathbf{v}_0,\omega_n)$, $f^+_{\uparrow\downarrow}(\mathbf{r},\mathbf{v}_0,\omega_n)$, and $f_{\downarrow\uparrow}(\mathbf{r},\mathbf{v}_0,\omega_n)$ is given by

$$2(w_n+ih)f_{\downarrow\uparrow}+\mathbf{v}_0\nabla f_{\downarrow\uparrow}=2g_\downarrow\Delta, \tag{2.1}$$

$$2(w_n+ih)f^+_{\uparrow\downarrow}-\mathbf{v}_0\nabla f^+_{\uparrow\downarrow}=2g_\downarrow\Delta^*, \tag{2.2}$$

$$\mathbf{v}_0\nabla g_\downarrow=\Delta^* f_{\downarrow\uparrow}-f^+_{\uparrow\downarrow}\Delta. \tag{2.3}$$

Here $\omega_n=\pi T(2n+1)$ are the Matsubara frequencies ($k_b=\hbar=1$), $\mathbf{v}_0$ is the Fermi velocity, and Δ is given by the self-consistency equation

$$\Delta(\mathbf{r},\mathbf{v}_0,\omega_n)=\pi N_0 T\int\frac{d\Omega_{\mathbf{v}_0}}{2\pi}V(\mathbf{v}_0,\mathbf{v}_0')f_{\downarrow\uparrow}(\mathbf{r},\mathbf{v}_0',\omega_n), \tag{2.4}$$

where $V(\mathbf{v}_0,\mathbf{v}_0')$ is the pairing interaction. For the opposite spin direction, the set of corresponding equations is obtained by changing $h\rightarrow -h$.[21]

We solve the above equations for a *d*-wave S/F/S junction, where S is an anisotropic superconductor with $d_{x^2-y^2}$ symmetry and $h=0$, and F is a monodomain ferromagnetic metal with constant exchange energy h and with $\Delta=0$. We assume both S and F metals clean, with same dispersion relations and with same Fermi velocity $\mathbf{v}_0$ (electron scattering on impurities in S can be neglected if $l\gg\xi_0$, where l is the electron mean free path and ξ_0 superconducting coherence length, and if $h\gg v_0/l$ in F).[20]

The barrier is assumed perpendicular to the a axis in the ab plane of the left-hand monocrystal S_L, which may be misoriented with respect to the right-hand one S_R, their a axes making an angle θ (see Fig. 1). For anisotropic pairing, the pair potential and the shape of quasiparticle spectra depend on the misorientation. For $d_{x^2-y^2}$ symmetry,[23] the pairing interaction and the pair potential in S_L are, respectively, $V(\mathbf{v}_0,\mathbf{v}_0')\propto\cos 2\varphi\cos 2\varphi'$ and $\Delta(\mathbf{v}_0)\propto\cos 2\varphi$, where φ is the angle the quasiparticle momentum makes with the a axis. Similarly, in S_R, $\Delta(\mathbf{v}_0)\propto\cos 2(\varphi-\theta)$.

Assuming a thin and short barrier of thickness $2d$ and with constant h, we find an analytical solution of Eqs. (2.1)–(2.3) taking a step-function variation of the pair potential along the x axis perpendicular to the barrier,[21]

$$\Delta(x)=\Delta^L(\phi)\Theta(-d-x)+\Delta^R(\phi)\Theta(x-d). \tag{2.5}$$

In the barrier, where $\Delta=0$, $f\neq 0$ due to the proximity effect. In the left- and right-hand superconductors, the pair potential can be taken in the form[21]

$$\Delta^{L,R}(\phi)=\Delta^{L,R}e^{\pm i\phi/2}, \tag{2.6}$$

where ϕ is an intrinsic phase difference at the contact related to the supercurrent flow,

$$\Delta^L=\Delta_0(T)\cos 2\varphi, \tag{2.7}$$

and

$$\Delta^R=\Delta_0(T)\cos 2(\varphi-\theta) \tag{2.8}$$

for *d*-wave pairing. For *s*-wave pairing $\Delta^L=\Delta^R=\Delta_0(T)$. In the following we denote $\Delta_0(0)=\Delta_0$ since we calculate density of states at $T=0$ only.[24]

We note that in principle the pair potential should be determined self-consistently. However, the self-consistent approach would greatly complicate the calculations without shedding much light on the exchange-interaction-induced states in the S/F/S case,[14,17] which is the main subject of this paper. In the S/N/S case, the validity of our model requires a weak proximity effect in S, as it may be the case at $T=0$.

Far from the barrier the Green's functions $f_{\downarrow\uparrow}$ and $g_\downarrow$ approach their respective bulk values

$$g_0^{L,R}=\frac{\omega_n}{\Omega_n^{L,R}}, \tag{2.9}$$

$$f_0^{L,R}=(f_0^{+L,R})^*=\frac{\Delta^{L,R}(\phi)}{\Omega_n^{L,R}}, \tag{2.10}$$

where

$$\Omega_n^{L,R}=\sqrt{|\Delta^{L,R}|^2+\omega_n^2}. \tag{2.11}$$

Looking for solutions of the form $g_\downarrow=g_0+g_1(x)$, $f_{\downarrow\uparrow}=f_0+f_1(x)$ in S, and using the continuity conditions at the barrier interfaces to relate them to the solution in F, one finds a position-independent normal Green's function in F, $|x|\leqslant d$,

$$g_\downarrow(\varphi,\omega_n)=-\frac{\Delta^L(\omega_n-\Omega_n^R)+\Delta^R(\omega_n+\Omega_n^L)\exp(i\phi+4d(\omega_n+ih)/v_0\cos\varphi)}{\Delta^L(\omega_n-\Omega_n^R)-\Delta^R(\omega_n+\Omega_n^L)\exp(i\phi+4d(\omega_n+ih)/v_0\cos\varphi)} \tag{2.12}$$

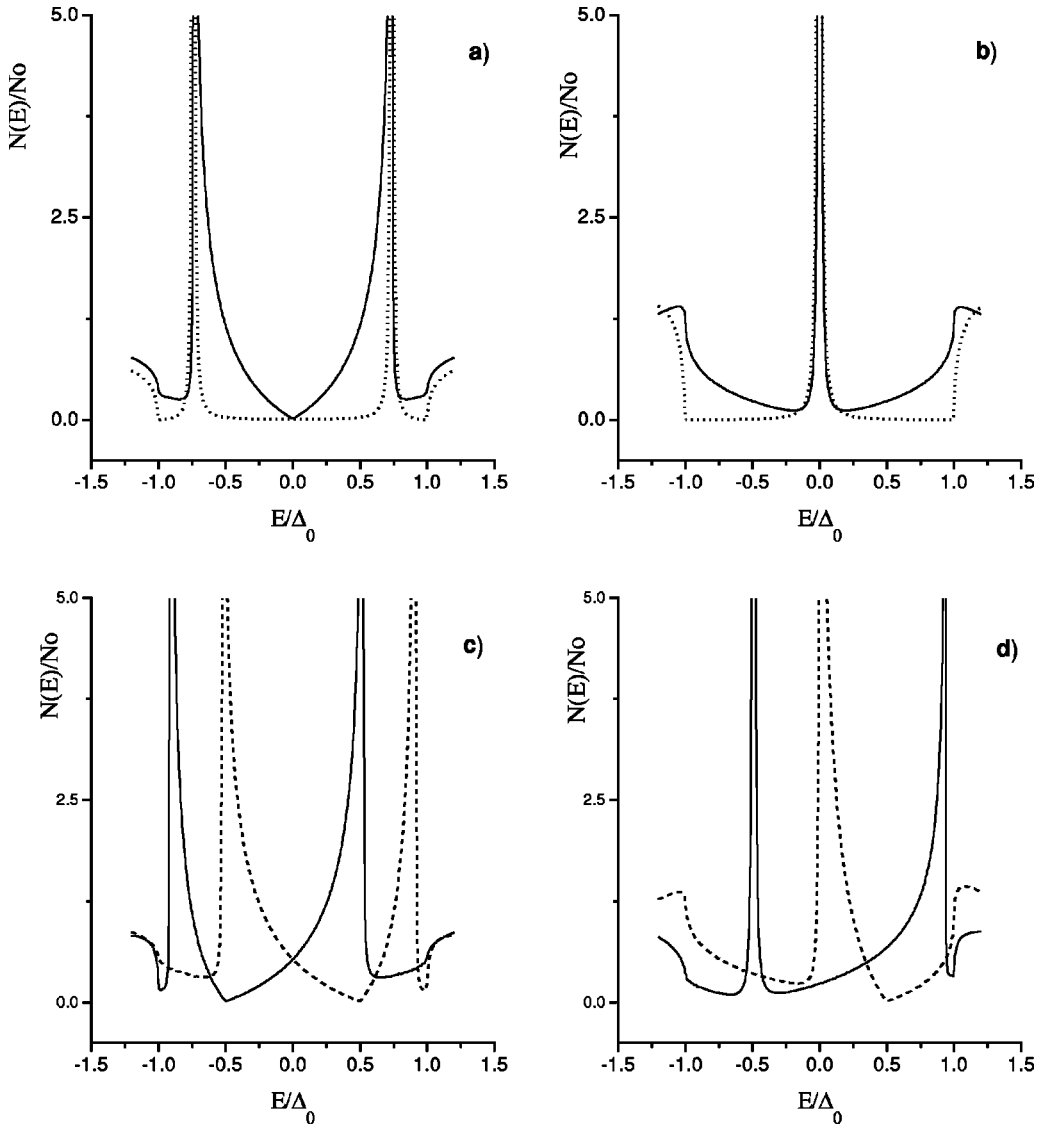

FIG. 2. DOS in the barrier of the reduced thickness $\bar{d}=1$ for S/N/S [(a),(b)] and S/F/S,$h=0.5$ [(c),(d)] junction with *s*-wave pairing in S and cylindrical Fermi surface. The ground state $\phi=0$ [(a),(c)], and nonequilibrium state with ZES, $\phi=\pi$ (b) and $\phi=\pi-1$ (d). PDOS for $\varphi=0$ (dotted curves) is shown for S/N/S junction [(a),(b)]. Spin splitting, $\sigma=\uparrow$ (solid curves) and $\sigma=\downarrow$ (dashed curves), is evident for S/F/S junction.

and $g_{\uparrow}(\varphi,\omega)$ is obtained from the above expression putting $h\rightarrow -h$.[21]

For $|x|\geqslant d$ we find

$$g_{\sigma}^{L,R}(x,\varphi,\omega_n)=g_{\sigma}(\varphi,\omega_n)e^{\alpha_n^{L,R}(d\pm x)}+\frac{\omega_n}{\Omega_n^{L,R}}(1-e^{\alpha_n^{L,R}(d\pm x)}), \tag{2.13}$$

where $\alpha_n^{L,R}=2\Omega_n^{L,R}/v_0\cos\varphi$ and $\sigma=\uparrow,\downarrow$.

From Eqs. (2.12) and (2.13) it is easy to obtain the corresponding results for a *d*-wave junction with normal metal barrier, putting $h\rightarrow 0$, and for *s*-wave junction, taking isotropic pair potential $\Delta^L=\Delta^R=\Delta_0$, with ferromagnetic ($h\neq 0$) or normal metal ($h=0$) barrier. Note that here there is no backscattering allowed, i.e., the transmission coefficient through the interface is taken equal to unity.

III. DENSITY OF STATES

The quasiparticle spectrum follows from the retarded Green's functions, obtained by the analytical continuation of $g_{\downarrow}(h)$ and $g_{\downarrow}(-h)=g_{\uparrow}(h)$. In our notation,[21] the partial density of states (PDOS), which is the angle-resolved DOS, is given by

$$N_{\sigma}(x,\varphi,E)=\lim_{\delta\rightarrow 0}\mathrm{Re}\,g_{\sigma}(x,\varphi,iw_n\rightarrow E+i\delta), \tag{3.1}$$

where φ is the angle between the direction of $\mathbf{v}_0$ and the x axis, and E is the quasiparticle energy measured from the Fermi level.

DOS is obtained by averaging PDOS over the angle φ, assuming spherical Fermi surface for the three-dimensional (3D) case (conventional superconductors), and cylindrical for the two-dimensional case (high-T_c superconductors). In the 2D case

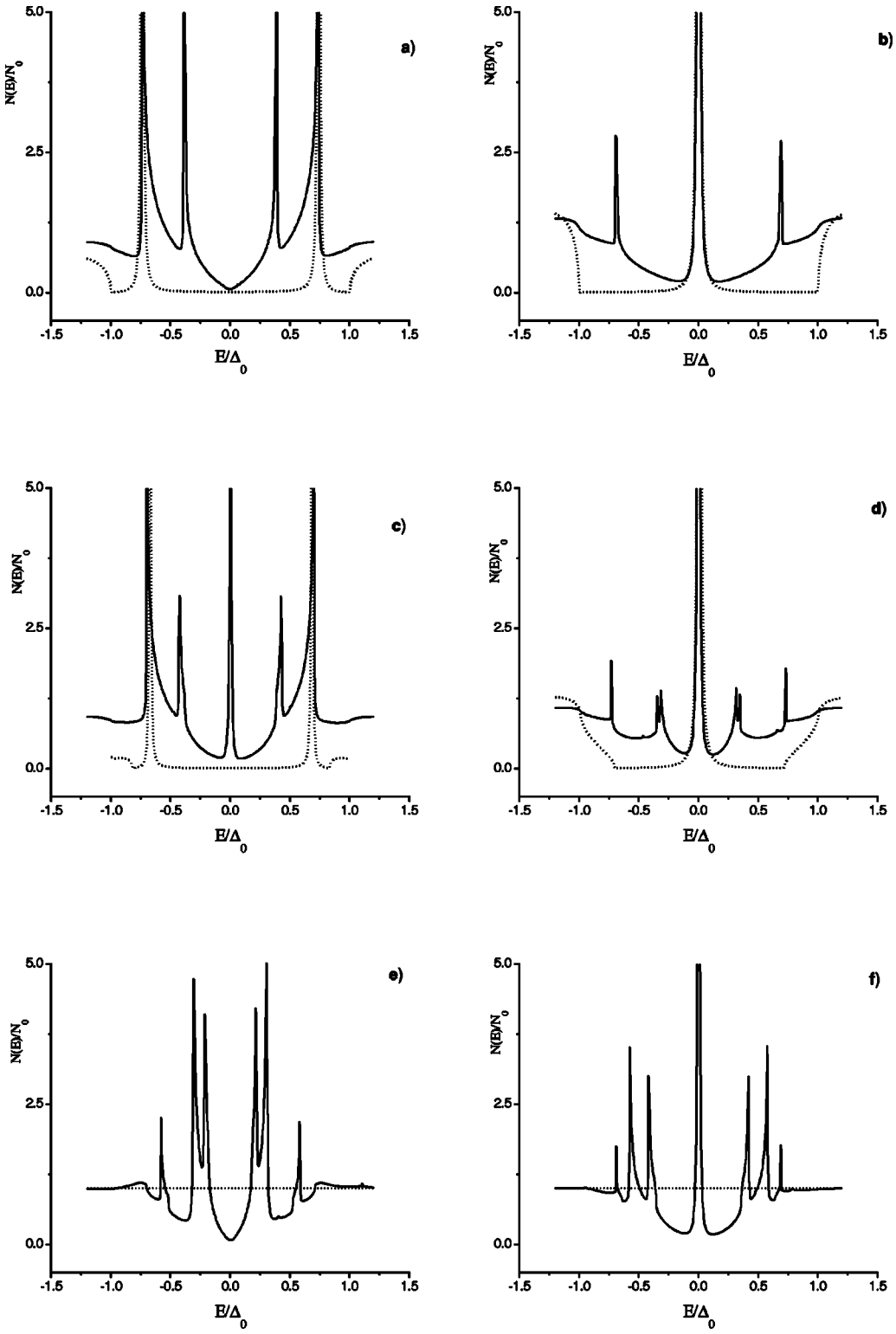

FIG. 3. DOS in the normal metal barrier of the reduced thickness $\bar{d}=1$ for S/N/S junction with d-wave pairing in S . The acceptance angle is $\varphi_c=70°$. PDOS, $\varphi=0$ (dotted curves) and DOS for cylindrical Fermi surface (solid curves), for the misorientation angle: $\theta=0$ [(a), (b)], $\theta=\pi/8$ [(c),(d)] and $\theta=\pi/4$ [(e),(f)]. The ground state, $\phi=0$ [(a),(c)], and $\phi=\pi/2$ (e), and the nonequilibrium state, $\phi=\pi$ [(b),(d)] and $\phi=0;\pi$ (f). For $\theta=\pi/2$ (a) corresponds to $\phi=\pi$, and (b) to $\phi=0$.

$$N_\sigma(x,E)/N_0=\int_{-\pi/2}^{\pi/2} d\varphi \mathcal{D}(\varphi) N_\sigma(x,\varphi,E), \qquad (3.2)$$

where $N_0=m/2\pi$, and in the 3D case

$$N_\sigma(x,E)/N_0=\int_{0}^{\pi/2} d\varphi \sin\varphi \mathcal{D}(\varphi) N_\sigma(x,\varphi,E), \qquad (3.3)$$

where $N_0=mk_F/2\pi^2$. We model the barrier with a uniform probability distribution[9] $\mathcal{D}(\varphi)=1/\int_{-\varphi_c}^{\varphi_c} d\varphi$ for the 2D case,

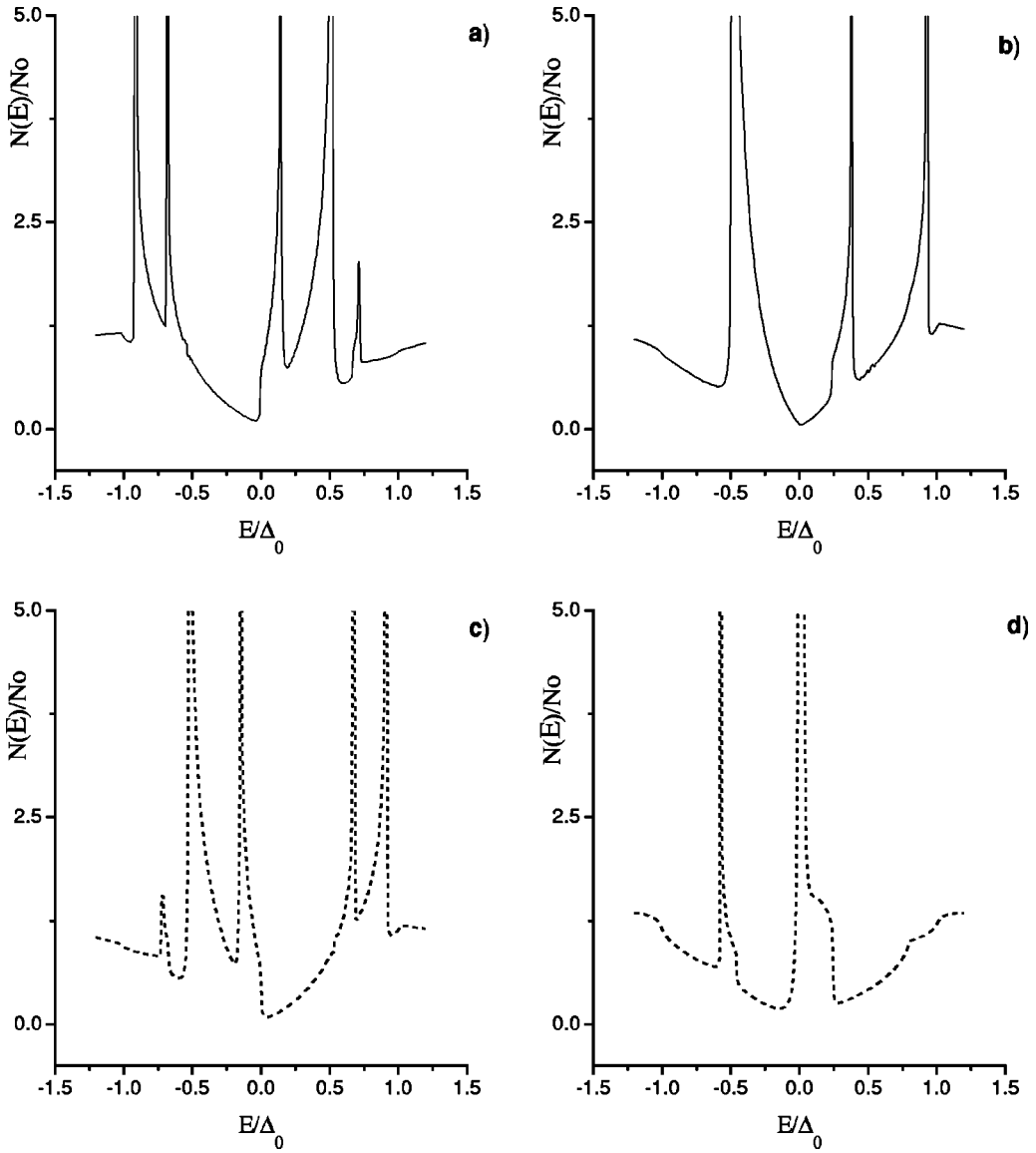

FIG. 4. DOS, for cylindrical Fermi surface, in the ferromagnetic barrier, with the reduced exchange energy $h=0.5$, and the reduced thickness $\bar{d}=1$, for S/F/S junction with d-wave pairing in S . The misorientation angle is $\theta=0$, and the acceptance angle $\varphi_c=70°$. Spin splitting: $\sigma=\uparrow$ [(a),(b)] and $\sigma=\downarrow$ [(c),(d)]. The ground state, $\phi=0$ [(a),(c)], and the nonequilibrium state with ZES, $\phi=\pi-1$ [(b),(d)].

and $\mathcal{D}(\varphi)=1/\int_0^{\varphi_c}\sin\varphi d\varphi$ for the 3D within an acceptance cone of angle $2\varphi_c$ about the interface normal, and zero outside the cone. The angle φ_c depends on the dimensions of the barrier, which we assume thin and short. We note first that for $|E|\leqslant\min(|\Delta_L|,|\Delta_R|)$ at given φ and θ, Eqs. (2.13) and (3.1) give a relation between PDOS in $S_{L,R}$ and in the barrier

$$N_\sigma^{L,R}(x,\varphi,E)=e^{\alpha^{L,R}(d\pm x)}N_\sigma(\varphi,E), \tag{3.4}$$

where $\alpha^{L,R}=2\Omega^{L,R}/v_0\cos\varphi$, $\Omega^{L,R}=\sqrt{|\Delta^{L,R}|^2-E^2}$.

The influence of the barrier is seen only in the vicinity of the interface, due to the exponential factor. Deep in S we obtain, as expected, a spin-orientation independent bulk result

$$N^{L,R}(\varphi,E)=\frac{|E|}{\Omega^{L,R}}\Theta(|E|-|\Delta^{L,R}|). \tag{3.5}$$

Since PDOS in the electrodes and in the barrier are related by Eq. (3.4), we consider in the following only (the position-independent) PDOS and DOS in the barrier $|x|\leqslant d$. The conditions for the appearance of the Andreev bound states in the quasiparticle spectra are obtained analytically, including ZES and the spin splitting. However, for the explicit evaluation of the densities of states we performed numerical calculations directly from Eqs. (2.12) and (3.1).

To find the density of states for a d-wave junction, we take anisotropic pair potentials $\Delta^{L,R}$ depending on φ and θ, Eqs. (2.7) and (2.8). For both spin directions we find that in the region $|E|>\min\{|\Delta^L|,|\Delta^R|\}$ at given φ and θ, PDOS is continuous without discrete levels. For $|E|<\min\{|\Delta^L|,|\Delta^R|\}$ PDOS in the barrier is

$$N_\downarrow(\varphi,E)=[2E(X^2\Omega^L+\Omega^R) - 2X\sin 2\gamma(\Omega^L\Omega^R+E^2)]\delta(V). \tag{3.6}$$

Here

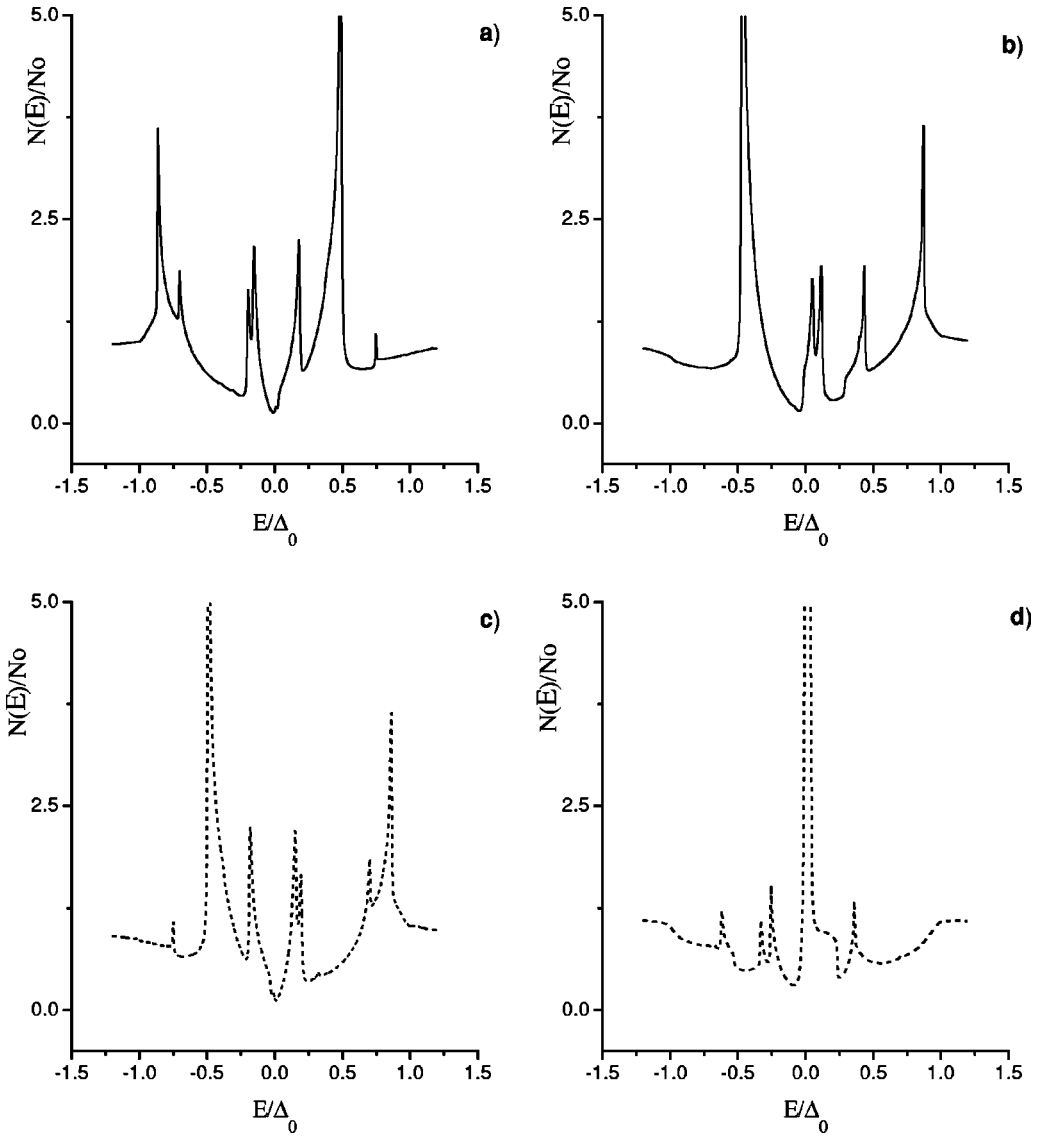

FIG. 5. Same as in Fig. 4, for $\theta=\pi/8$.

$$V=(X\Omega^L-\Omega^R)^2-E^2(1+X)^2+4X\cos^2\gamma(\Omega^L\Omega^R+E^2),$$

$$X=\Delta^R/\Delta^L=\cos 2(\varphi-\theta)/\cos 2\varphi, \tag{3.7}$$

$$\gamma=\phi/2-\bar{d}(E-h)/\cos\varphi,$$

where $\bar{d}=2d\Delta_0/v_0=(2/\pi)d/\xi_0$, $\xi_0=v_0/\pi\Delta_0$, and $N_\uparrow(h)=N_\downarrow(-h)$.

Using the formula

$$\delta[V(\varphi)]=\sum_i \frac{\delta(\varphi-\varphi_i)}{|V'(\varphi_i)|},$$

where $V'=\partial V/\partial\varphi$ and φ_i are solutions of the equation $V(\varphi_i,E)=0$, Eq. (3.6) for PDOS becomes

$$N_\downarrow(\varphi,E)=[2E(X^2\Omega^L+\Omega^R)--2X\sin 2\gamma(\Omega^L\Omega^R+E^2)]\times\sum_i \frac{\delta(\varphi-\varphi_i)}{|V'(\varphi_i)|}. \tag{3.8}$$

Therefore, bound states appear at energies E such that $V'(\varphi_i,E)=0$ and $V(\varphi_i,E)=0$ and after averaging over the angle φ, may give rise to peaks and/or divergences in DOS. In the *s*-wave case, where the pair potentaial is isotropic, the averaging over quasiparticles propagation angle φ results in an average over one-channel junctions of different lengths and PDOS for $\varphi=0$ is qualitatevely same as DOS. This is not the case for anisotropic *d*-wave pairing, where in DOS peaks corresponding to other angles can be seen as well.

This is easy to see when $\theta=0$. In this case Eq. (3.6) becomes

$$N(\varphi,E)=\Omega\sum_i \frac{\delta(\varphi-\varphi_i)\cos^2\varphi_i\cos 2\varphi_i}{D|\sin\varphi_i|}, \tag{3.9}$$

where

$$D=|4E\cos^3\varphi_i+\Omega\bar{d}(E-h)\cos 2\varphi_i| \tag{3.10}$$

and φ_i satisfies

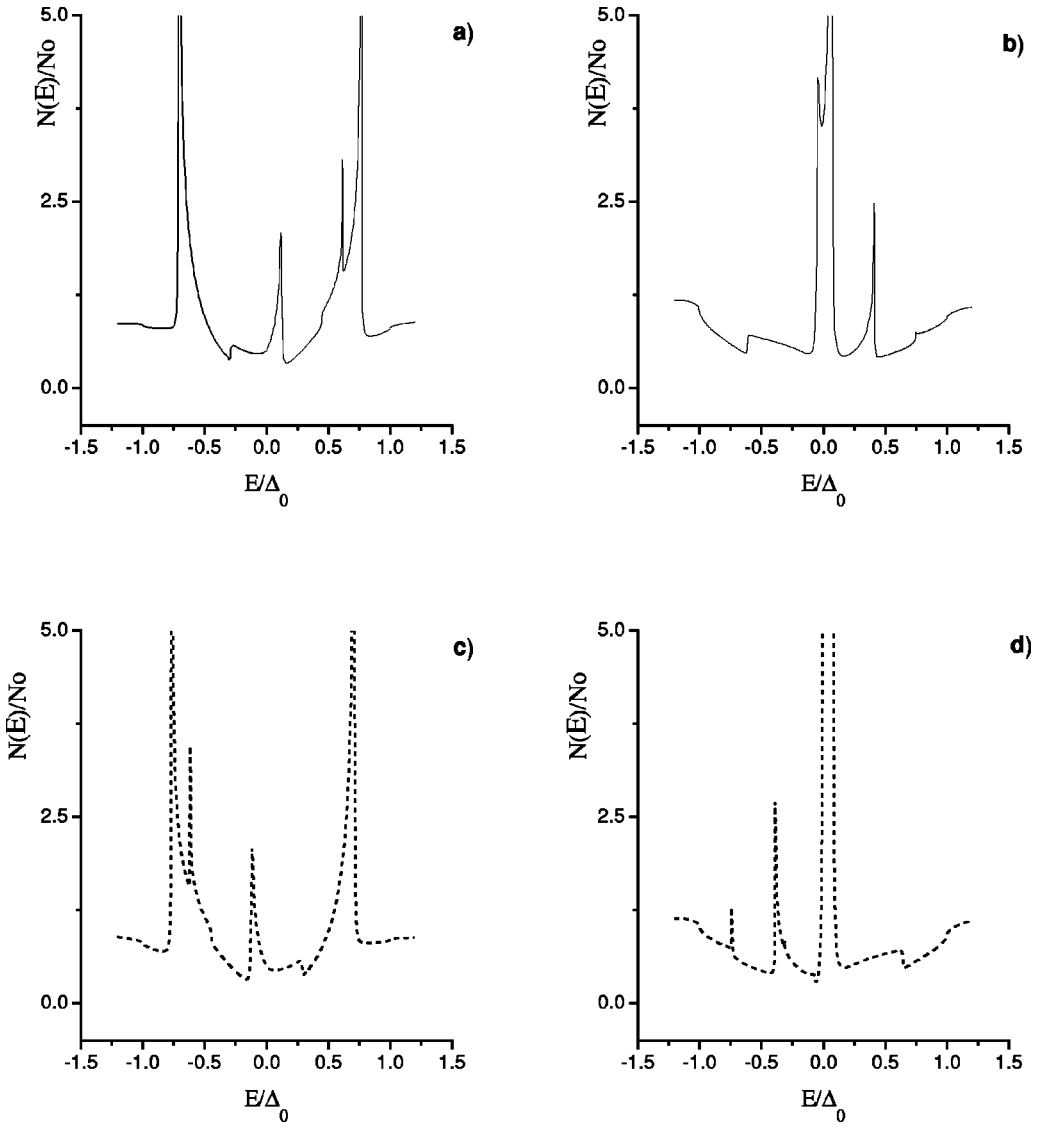

FIG. 6. DOS, for cylindrical Fermi surface, in the ferromagnetic barrier, with the reduced exchange energy $h=1.5$, and the reduced thickness $\bar{d}=1$, for S/F/S junction with d-wave pairing in S . The misorientation angle is $\theta=0$, and the acceptance angle $\varphi_c=70°$. Spin splitting: $\sigma=\uparrow$ [(a),(b)] and $\sigma=\downarrow$ [(c),(d)]. The ground state, $\phi=\pi$ [(a),(c)], and the nonequilibrium state with ZES, $\phi=\pi-3$ [(b),(d)].

$$\cos\left(\frac{\phi}{2}-\frac{\bar{d}(E-h)}{\cos\varphi_i}\right)=\pm\frac{E}{\cos 2\varphi_i}. \tag{3.11}$$

In the s-wave case this reduces to

$$N(\varphi,E)=\sum_i \frac{\delta(\varphi-\varphi_i)\cos^2\varphi_i}{|\bar{d}(E-h)\sin\varphi_i|} \tag{3.12}$$

and

$$\cos\left(\frac{\phi}{2}-\bar{d}\frac{(E-h)}{\cos\varphi_i}\right)=\pm E. \tag{3.13}$$

In the latter case, PDOS $N(\varphi_i=0,E)$ diverges at $E=E_i$ obtained from Eq. (3.13) with $\varphi_i=0$, but DOS $N(E_i)$ is finite in 3D, due to an extra factor, $\sin\varphi$ in Eq. (3.3), whereas in 2D it diverges, see Eq. (3.2).

By comparing Eqs. (3.12) and (3.9), we see that in the d-wave case one may have divergences not only for $\varphi=0$, as in the s-wave case, but also at $E=E_i$, corresponding to $\varphi=\varphi_i$, which are solutions of Eq. (3.11) with the condition $D=0$. In the general case of arbitrary θ the formation of bound states at the Fermi level, $E=0$, is of particular interest. These zero-energy states (called also midgap states) have been predicted by Hu to exist at surfaces and interfaces of $d_{x^2-y^2}$ superconductors.[7] As pointed out in the Introduction, an important consequence of these states is that they can give rise to a ZBCP in quasiparticle tunneling.

From $V(\varphi_i,E=0)=0$ it follows that the conditions for ZES are $\cos\gamma(\varphi_i,E=0)=0$ for $X>0$ and $\cos^2\gamma=1$ for $X<0$. Under above conditions, $V'(\varphi_i,E=0)=0$ as well. After the integration over the propagation angle, these resonances may lead to divergences or finite peaks in DOS at $E=0$, since the nominator in Eq. (3.8) vanishes for $\cos\gamma=0$ or $\sin\gamma=0$. Explicitly, the conditions for ZES are

$$\frac{\phi}{2}+\frac{\bar{d}h}{\cos\varphi}=\frac{(2k+1)\pi}{2} \tag{3.14}$$

for $X>0$ and

$$\frac{\phi}{2}+\frac{\bar{d}h}{\cos\varphi}=k\pi \tag{3.15}$$

for $X<0$, where k is an integer.

For $h=0$, normal metal barrier, the physical meaning of these conditions is evident, if we invoke the fundamental concept that an Andreev reflection can sense the phase or the sign of a superconducting order parameter. When the pair potentials $\Delta_L(\phi)=\Delta_L e^{-i\phi/2}$ and $\Delta_R(\phi)=\Delta_R e^{i\phi/2}$ are of different signs for the same direction φ, a ZES is formed when the transmission coefficient through the interface is unity (no back scattering). This is exactly what follows from the above conditions for $h=0$: in both cases $\phi=0$ and $X<0$, or $\phi=\pi$ and $X>0$, $\Delta_R(\phi)/\Delta_L(\phi)=Xe^{i\phi}<0$. In particular, ZES can be formed in the *s*-wave case, provided that $\phi=\pi$, similarly as in S/N superlattices.[4] In the *d*-wave case, for $h=\phi=0$ and $\theta\neq 0$, the condition for ZES is satisfied for every φ such that $X<0$.

For a transmission coefficient smaller than 1, the Andreev bound states for some φ may no longer have zero energy, but there would be still a finite area density of ZES, albeit lower than for full transparency. The difference would be only in the heights of the observed ZBCP.[7] For $h\neq 0$, we have a special case of Andreev reflection, and ZES can appear for $\phi\neq 0,\pi$ due to the ''magnetic'' phase shift, proportional to $\pm\bar{d}h$, for two spin orientations.

IV. RESULTS AND DISCUSSION

In superconducting weak links (*s*-wave or *d*-wave pairing, normal or ferromagnet metal barrier) the quasiparticle spectrum in the barrier is gapless, and strongly phase dependent. Results are illustrated in Figs. 2–6 for layered superconductors and a cylindrical Fermi surface.

For the *s*-wave case, the phase dependence is seen in Figs. 2(a) and 2(b) for a normal metal barrier, and in Figs. 2(c) and 2(d) for a ferromagnetic barrier. In the latter case the bound states for two spin orientations are no more degenerate, resulting in larger number of peaks in DOS. The peaks in DOS are at the same energies as those in PDOS for $\varphi=0$. This is shown explicitely for $h=0$, but holds for $h\neq 0$ as well. For *s*-wave pairing, ZES appear only outside the ground state. In this case, the condition for ZES, Eq. (3.14), becomes $\phi=\pi-2\bar{d}h$ for $\varphi=0$. Since $\phi_{eq}=0$ for $0\leqslant 2\bar{d}h\leqslant 1$, and $\phi_{eq}=\pi$ for $1<2\bar{d}h\leqslant 3.66$, $\phi\neq\phi_{eq}$ always.[21] Large values of $2\bar{d}h\gg 1$ correspond to the decoupling of S electrodes.[17]

In the anisotropic *d*-wave case, where the pair potential depends on the injection angle, the number of peaks in DOS can be greater than in the *s*-wave case, see Figs. 3–6. It is important to note that the shape of spectra strongly depends on the acceptance angle φ_c. For example, for $\varphi_c<64°$ the interior peaks in Fig. 3(a), corresponding to larger φ, would be absent. For given φ_c and reduced thickness $\bar{d}$, DOS strongly depends on the exchange field h in the barrier, on the misorientation angle θ, and on the phase difference ϕ.

For S/N/S junctions and $\theta=0$, where $\phi_{eq}=0$, ZES appears outside the ground state, for $\phi=\pi$ [Fig. 3(b)]. For $\theta=\pi/2$, there is a π shift of the equilibrium phase,[21] $\phi_{eq}=\pi$ and Fig. 3(a) would correspond to $\phi=\pi$ and Fig. 3(b) to $\phi=0$. For $0<\theta<\pi/2$, ZES can be formed outside the ground state, as shown in Fig. 3(d) for $\phi=\pi$ (for $\theta=\pi/8$ the equilibrium phase difference[21] is $\phi_{eq}=0$) and in Fig. 3(f) for $\phi=0,\pi$ (for $\theta=\pi/4$, $\phi_{eq}=\pi/2$). However, ZES may appear in the ground state as well, corresponding to $\varphi\neq 0$, Fig. 3(c).

The combined effect of *d*-wave symmetry and of the ferromagnetic order in the barrier in S/F/S junctions is shown in Figs. 4, 5, and 6. There is again the spin splitting of bound states, and ZES appears depending on the spin orientation. This is shown in Figs. 4(d) and 5(d) for $\phi=\pi-1$ ($\phi_{eq}=0$ for $h=0.5$ in both cases $\theta=0$ and $\theta=\pi/8$). The dependence on the misorienation is very strong, as in the S/N/S case. For example, for $\theta=\pi/2$, Figs. 4(a) and 4(c) would correspond to $\phi=\phi_{eq}=\pi$, instead to $\phi=0$ for $\theta=0$. For larger values of h, e.g., $h=1.5$, there is a π shift of the equilibrium phase difference,[21] $\phi_{eq}=\pi$ for $\theta=0$ and $\phi_{eq}=0$ for $\theta=\pi/2$. Otherwise, the results are similar, with the corresponding change in ϕ, compare Figs. 6 and 5.

For experimental verification of our results the standard method is the tunneling spectroscopy.[8,25] For nonmagnetic barriers, we found, as expected, that in *s*-wave junctions there would be no ZBCP in the equilibrium, whereas they should appear in *d*-wave junctions for $\theta\neq 0$, in accordance with many experiments. In particular, this is clearly seen in experiments with bicrystal grain-boundary junctions, fabricated with high-T_c superconductors and tunneling in the ab plane. A pronounced ZBCP was observed for *d*-wave superconductors $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $La_{1.85}Sr_{0.15}CuO_4$, whereas in *s*-wave superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ it was absent.[8]

For ferromagnetic-metal barriers there is still no measurements of DOS by tunneling spectroscopy. The fabrication of such S/F/S junctions with conventional superconductors was performed in search of the π shift. Several systems, such as V/Fe, Nb/Gd, Nb/Fe,[26] and V/Co, Nb/Co,[27] multilayers and trilayers have been prepared. For experimental checking of our results, we note that both S and F metals should be clean. The fabrication of S/F/S junctions with oxide high-T_c superconductors is much more difficult. However, ramp-type junctions with superconducting electrodes coupled in the ab plane recently were produced by heteroepithaxial growth of cuprates and manganates, such as $YBa_2Cu_3O_7$, and $La_xCu_{1-x}MnO_3$.[28]

If a spectrum with several peaks is observed experimentally in a relatively thin contact, $\bar{d}\sim 1$, this can be due to the *d*-wave symmetry in S electrodes, of an S/N/S contact with φ_c not too small, or to the presence of the ferromagnetic order in the barrier in a S/F/S contact, with *s*-wave pairing in S electrodes. A similar conclusion that the conductance of an *s*-wave junction with ferromagnetic barrier may ressemble that of a *d*-wave junction with a nonmagnetic barrier, was reached for S/N junctions.[18] To resolve between these possibilities, one should be able to prepare junctions which differ in the misorientation angle θ only. Changing θ would induce a change in DOS (and in the conductance) only in the case of *d*-wave symmetry. In contrast to the conclusion of Ref. 18, that the conductance of a *d*-wave N/F/S junction with ferromagnetic barrier may ressemble to that of an *s*-wave junction with a nonmagnetic barrier, we find that in *d*-wave S/F/S junctions the spectra are much more complicated than in the *s*-wave S/N/S case, since the number of bound states is in-

creased due to both order parameter anisotropy and spin splitting.

In conclusion, the shape of DOS strongly depends on the order parameter symmetry, on the presence of the magnetic scattering in the barrier, and on the phase difference at the junction. For both ferromagnetic and normal metal barriers we have found conditions for the formation of Andreev bound states and of peaks at Fermi energy in DOS.

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