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Correlation effects at the surface of an itinerant electron ferromagnet

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Abstract. The electron Green functions are calculated for a semi-infinite itinerant electron ferromagnet in the framework of the infinite-U Hubbard model close to half-filling. It is shown that the ferromagnetic state is saturated in the surface as well as in the bulk for small enough hole concentration. At the same time the empty states near the Fermi level (and the occupied ones for the case of excess electrons) are depolarized due to spin polaron effects.

1. Introduction

The problem of magnetism at transition metal surfaces [1] is interesting both in itself and in connection with general investigations of itinerant electron ferromagnets. Most spectroscopic methods such as photoemission, thermoemission and field emission are surface sensitive and their proper interpretation requires a theory of the surface electronic structure in itinerant electron ferromagnets. It is particularly necessary for the interpretation of results of such contemporary methods as one- and two-electron capture spectroscopy which investigate only the surface layer [2, 1]. Numerous band structure calculations for magnetic layers and surfaces (see e.g. [3] and also the review [1] and references therein) are an important part of such theory. But it is known from the consideration of bulk ferromagnetism in the Hubbard model that correlation effects that are beyond the local spin density functional calculations may change drastically the character of electron states, especially due to 'spin polaron' or 'non-quasiparticle' effects [4–6]. These lead, for example, to depolarization of electron states near the Fermi surface in contradiction with the usual band picture [6, 7]. Therefore the consideration of surface states in itinerant electron ferromagnets taking into account strong-correlation effects seems to be important. The present paper considers such effects in the simplest model of a saturated ferromagnetic state based on the infinite-U limit of the Hubbard model.

2. Majority-spin states

Let the ferromagnet occupy the half-space $z \geqslant 0$ with an infinite potential barrier at $z = -1$ (x, y, z are Cartesian coordinates in units of the lattice constants). We represent the

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lattice site vectors $\boldsymbol{R}$ as $(\boldsymbol{\rho}, z)$ where $z = 0, 1, 2, \ldots$ and $\boldsymbol{\rho}$ is the component of vector $\boldsymbol{R}$ in the xy-plane. We assume the transfer integrals $t_{RR'}$ to be of the form

$$t_{RR'} = \begin{cases} t_{\rho\rho'} & \text{if } z = z',\ \boldsymbol{\rho} \neq \boldsymbol{\rho}' \\ t_\perp & \text{if } \boldsymbol{\rho} = \boldsymbol{\rho}',\ |z - z'| = 1 \\ 0 & \text{otherwise.} \end{cases} \tag{1}$$

We start with the Hubbard Hamiltonian

$$H = - \sum_{\substack{RR'\sigma \\ (z,z' \geq 0)}} t_{RR'} c^\dagger_{R\sigma} c_{R'\sigma} + U \sum_{\substack{R \\ (z \geq 0)}} n_{R\uparrow} n_{R\downarrow} \tag{2}$$

where $c^\dagger_{R\sigma}$ creates an electron of spin σ on site $\boldsymbol{R}$ and $n_{R\sigma} = c^\dagger_{R\sigma} c_{R\sigma}$ in the limit $U = \infty$. We assume initially that the average number of electrons per site is $n < 1$ and the 'hole' concentration $c \equiv 1 - n$ is small. So the saturated ferromagnetic state is stable in the bulk case according to Nagaoka's theorem and numerous following considerations ([8] and references therein). The Hamiltonian (2) may be rewritten in the form [5, 6]

$$H = - \sum_{\substack{RR'\sigma \\ (z,z' \geq 0)}} P t_{RR'} c^\dagger_{R\sigma} c_{R'\sigma} P = \sum_{\substack{RR'\sigma \\ (z,z' \geq 0)}} t_{RR'} X^{0\sigma}_R X^{\sigma 0}_{R'} \tag{3}$$

where P is the projection operator on the state without doubly occupied sites and $X^{0\sigma}_R = |\boldsymbol{R}0\rangle\langle\boldsymbol{R}\sigma|$ are the Hubbard X-operators, $|\boldsymbol{R}0\rangle$ ($|\boldsymbol{R}\sigma\rangle$) being the states of site $\boldsymbol{R}$ without electrons (with one electron with spin projection $\sigma = \pm$).

To consider the electron states one should calculate the retarded anti-commutator Green functions

$$G^\sigma_{RR'}(E) = \langle\langle X^{\sigma 0}_R | X^{0\sigma}_{R'} \rangle\rangle_E \tag{4}$$

with the Hamiltonian (3). Since

$$c^\dagger_{R\sigma} = X^{\sigma 0}_R + \sigma X^{2,-\sigma}_R$$

these Green functions are equivalent to the usual one-electron (more exactly hole) ones in the infinite-U limit when operators $X^{2,-\sigma}_R$ creating a doubly occupied site are eliminated by the projection operator. Similar calculations for the bulk case have been carried out in [5]. We restrict ourselves to the case of zero temperature and consider the saturated ferromagnetic ground state $|\varphi_0\rangle$ so $X^{+-}_R |\varphi_0\rangle = 0$ for any $\boldsymbol{R}$. Then for up-spin electrons ($\sigma = +$) the equations of motion for the Green functions are formally the same as in the non-magnetic case [5]. Carrying out the Fourier transformation in the xy-plane

$$G^\sigma_{RR'}(E) = \int \frac{\mathrm{d}^2 k_\parallel}{(2\pi)^2} G^\sigma_{zz'}(E, k_\parallel) \exp(\mathrm{i}k_\parallel \cdot (\boldsymbol{\rho} - \boldsymbol{\rho}')) \tag{5}$$

(the integral being over the Brillouin zone of the surface plane lattice) and putting $z' = 0$ (which corresponds to considering surface states) one obtains the equations

$$(E - \varepsilon_\parallel(k_\parallel)) G^+_{z0}(k_\parallel, E) - t_\perp (G^+_{z-1,0}(k_\parallel, E) + G^+_{z+1,0}(k_\parallel, E)) = 0 \qquad \text{for } z \geq 1 \tag{6a}$$

$$(E - \varepsilon_\parallel(k_\parallel)) G^+_{00}(k_\parallel, E) - t_\perp G^+_{10}(k_\parallel, E) = 1 \tag{6b}$$

where

$$\varepsilon_{\parallel}(\boldsymbol{k}_{\parallel}) = \sum_{\boldsymbol{\rho}'} t_{\boldsymbol{\rho}\boldsymbol{\rho}'} \exp(\mathrm{i}\boldsymbol{k}_{\parallel} \cdot (\boldsymbol{\rho} - \boldsymbol{\rho}')).$$

The equations (6) may be formally extended into the negative-z region by making the formal assumption that $G_{-z0} = G_{z0}$. So one gets

$$(E - \varepsilon_{\parallel}(\boldsymbol{k}_{\parallel}))G^{+}_{z0}(\boldsymbol{k}_{\parallel}, E) - t_{\perp}(G^{+}_{z-1,0}(\boldsymbol{k}_{\parallel}, E) + G^{+}_{z+1,0}(\boldsymbol{k}_{\parallel}, E))$$
$$= \delta_{z0}[1 - t_{\perp} G_{10}(\boldsymbol{k}_{\parallel}, E)]. \tag{7}$$

These equations may be easily solved by Fourier transformation:

$$G^{+}_{z0}(\boldsymbol{k}_{\parallel}, E) = \int_{-\pi}^{\pi} \frac{\mathrm{d}k_z}{2\pi} G^{+}(\boldsymbol{k}, E) \exp(\mathrm{i}k_z z) \qquad (\boldsymbol{k} = (\boldsymbol{k}_{\parallel}, k_z)). \tag{8}$$

As a result we obtain for the 'bulk' and 'surface' Green functions

$$G^{+}(\boldsymbol{k}, E) = \frac{2\alpha}{(\beta + \alpha)(\beta - 2t_{\perp} \cos k_z)} \tag{9a}$$

$$G^{+}_{\mathrm{s}}(\boldsymbol{k}_{\parallel}, E) \equiv G^{+}_{00}(\boldsymbol{k}_{\parallel}, E) = \frac{\beta - \alpha}{2t_{\perp}^2} = \int_{-\pi}^{\pi} \frac{\mathrm{d}k_z}{2\pi} \frac{2\sin^2 k_z}{E - \varepsilon(\boldsymbol{k})} \tag{9b}$$

where

$$\beta = E - \varepsilon_{\parallel}(\boldsymbol{k}_{\parallel}) \qquad \alpha = \sqrt{\beta^2 - 4t_{\perp}^2}$$

(the branch with $\mathrm{Im}\,\alpha > 0$ at $\mathrm{Im}\,E > 0$ is chosen) and

$$\varepsilon(\boldsymbol{k}) = \varepsilon_{\parallel}(\boldsymbol{k}_{\parallel}) + 2t_{\perp} \cos k_z$$

is the bulk electron spectrum. So for the surface density of states

$$N^{\sigma}_{\mathrm{s}}(E) = \int \frac{\mathrm{d}^2 k_{\parallel}}{(2\pi)^2} \left(-\frac{1}{\pi} \mathrm{Im}\, G^{\sigma}_{\mathrm{s}}(\boldsymbol{k}_{\parallel}, E) \right) \tag{10}$$

for $\sigma = +$ we obtain the usual expression

$$N^{+}_{\mathrm{s}}(E) = \int \frac{\mathrm{d}^3 \boldsymbol{k}}{(2\pi)^3} \delta(E - \varepsilon(\boldsymbol{k})) 2\sin^2 k_z \tag{11}$$

with the integral extending over the Brillouin zone of the bulk metal. The multiplier $2\sin^2 k_z$ is simply the square of the wave function of the surface problem

$$\psi_{k_z}(z) = \sqrt{2} \sin k_z z \tag{12}$$

(with δ-function normalization) in the zeroth layer.

3. Minority-spin states

Now let us calculate the Green function for the 'wrong' spin projection $\sigma = -$. The corresponding states do not exist in the Hartree–Fock approximation in the $U = \infty$ limit and have a purely correlational nature, (being states of 'spin polaron' or 'non-quasiparticle' type [4–6]). It is convenient to exploit the multiplication rules for X-operators

$$X_R^{0-} = X_R^{0+} X_R^{+-} \tag{13}$$

and introduce the Green function

$$F_{R_1R_2,R'}(E) = \langle\langle X_{R_1}^{0+} X_{R_2}^{+-} | X_{R'}^{-0} \rangle\rangle_E \tag{14}$$

so that

$$G_{RR'}^{-}(E) = F_{RR,R'}(E) \tag{15}$$

(cf [5, 6]). In this way we 'decompose' the hole with spin down into the hole with spin up and a magnon. Since the charcteristic magnon frequency $\bar{\omega}$ is of order of $c|t|$ [5] the magnon cannot move in the lowest order in c. In this order the equation of motion for the function F is very simple [5, 6]

$$EF_{R_1R_2,R'}(E) - \sum_{R_3} t_{R_1R_3} F_{R_3R_2,R'}(E) = \delta_{R_2R'} \langle X_{R_1}^{0+} X_{R'}^{+0} \rangle. \tag{16}$$

The $\bar{R}_2$-dependence of F may be exhibited explicitly by writing

$$F_{R_1R_2,R'} = \delta_{R_2R'} \mathcal{F}_{R_1R'}(E) \tag{17}$$

and

$$G_{RR'}^{-}(E) = \delta_{RR'} \mathcal{F}_{RR}(E). \tag{18}$$

So in the lowest-order approximation in c the function $G_{RR'}^{-}(E)$ is a local one, i.e. the holes with spin down are localized. Nevertheless they are essential for calculations of the total density of states.

Carrying out the Fourier transformations similar to (5) and (8) we can obtain for the function $\mathcal{F}$

$$\mathcal{F}_{00}(E, k_\perp) = \int_{-\pi}^{\pi} \frac{dk_z}{2\pi} \mathcal{F}(E, k) \tag{19}$$

$$\mathcal{F}(E, k) = \frac{n(k)}{E - \varepsilon(k)} - \frac{t_\perp}{E - \varepsilon(k)} \frac{\alpha(E, k_\parallel)}{\beta(E, k_\parallel) + \alpha(E, k_\parallel)} \int_{-\pi}^{\pi} \frac{dp_z}{2\pi} \frac{n(k_\parallel, p_z) \cos p_z}{E - \varepsilon(k_\parallel, p_z)} \tag{20}$$

where

$$n(k) = \sum_R \langle X_R^{0+} X_0^{0+} \rangle \exp(i k_\parallel \cdot \rho + i k_z z). \tag{21}$$

This average may be calculated from the Green function $G_{RR'}^{+}(E)$ and so

$$n(k) = \int_{-\infty}^{\infty} dE f(E) \left(-\frac{1}{\pi} \operatorname{Im} G^+(E, k) \right) \tag{22}$$

where $f(E)$ is the Fermi distribution function. It is easy to obtain from (9*a*)

$$n(k) = 2 \sin^2 k_z f_k + n_2(k) \tag{23}$$

where $f_k = f(\varepsilon(k))$, and

$$n_2(k) = \int_{-\pi}^{\pi} \frac{dp_z}{2\pi} f_{k\parallel p_z} 2 \sin^2 p_z \cos p_z \frac{\mathcal{P}}{\cos k_z - \cos p_z} \tag{24}$$

where $\mathcal{P}$ is the symbol for principal value. Calculating

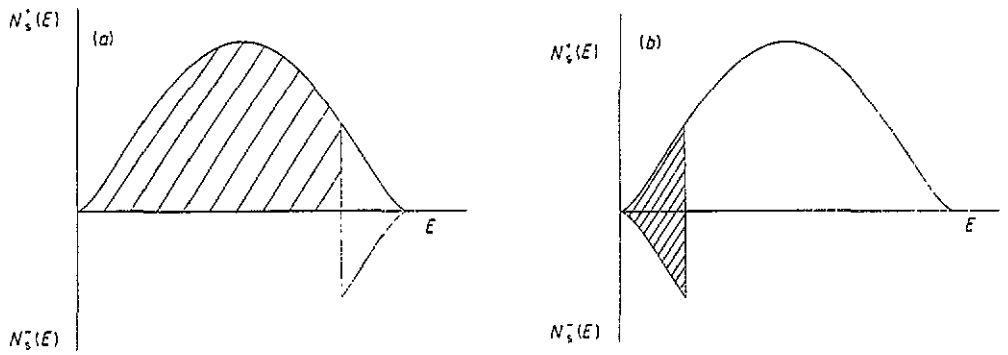

Figure 1. (*a*) The density of states in the lower Hubbard subband for $n < 1$. The occupied states are shaded. (*b*) The density of states in the upper Hubbard subband for $n > 1$. The occupied states are shaded.

$$G_s^-(E) = \int \frac{d^2k_\parallel}{(2\pi)^2} \mathcal{F}_{00}(E, k_\parallel) = \int \frac{d^3k}{(2\pi)^3} \mathcal{F}(E, k) \tag{25}$$

one obtains

$$G_s^-(E) = \int \frac{d^3k}{(2\pi)^3} \frac{n(k)}{E - \varepsilon(k)} - t_\perp \int \frac{d^3k}{(2\pi)^3} \frac{G_s^+(E, k_\parallel) n(k) \cos k_z}{E - \varepsilon(k)}. \tag{26}$$

Substituting (23), (24), (26) into (10) one finds the surface density of states of holes with spin down

$$N_s^-(E) = \int \frac{d^3k}{(2\pi)^3} \delta(E - \varepsilon(k)) \left(2f_k \sin^2 k_z + \int_{-\pi}^{\pi} \frac{dp_z}{2\pi} n_2(k_\parallel, p_z) \cos p_z \frac{\mathcal{P}}{\cos p_z - \cos k_z} \right) \sin^2 k_z. \tag{27}$$

When calculating the integral on the right-hand side of (27) it is convenient to exploit the identity

$$0 = \mathrm{Re} \int_{-\pi}^{\pi} \frac{dp_z}{2\pi} \cos p_z \frac{1}{\cos p_z - z_1} \frac{1}{\cos p_z - z_2} = \int_{-\pi}^{\pi} \frac{dp_z}{2\pi} \cos p_z \times \left(\frac{\mathcal{P}}{\cos p_z - z_1} \frac{\mathcal{P}}{\cos p_z - z_2} - \pi^2 \delta(\cos p_z - z_1) \delta(\cos p_z - z_2) \right) \tag{28}$$

for $\mathrm{Im}\, z_1, \mathrm{Im}\, z_2 \to +0$ and $-1 < \mathrm{Re}\, z_1, \mathrm{Re}\, z_2 < 1$. So $\mathcal{P}$-terms in (24) and (27) may be simply replaced by δ-functions multiplied by π when calculating $N_s^-(E)$. After simple calculations we have a very simple result

$$N_s^-(E) = N_s^+(E) f(E) \tag{29}$$

which is formally the same as for the bulk case [5]. The schematic picture of density of states for electrons (not for holes!) is shown in figure 1(*a*). The discontinuity of $N_s^-(E)$ should be smoothed by the magnon frequency, so $N_s^-(E)$ tends continuously to zero as $E \to E_F$ (cf [4, 5]). So the ferromagnetic state on the surface remains saturated because

there are no occupied electron states with $\sigma = -$. Note that the number of holes on the surface

$$c_s = \int_{-\infty}^{\infty} dE\, f(N) N_s^+(E) \tag{30}$$

varies as $c^{5/3}$ for small bulk concentration c since $N_s(E) \sim |E - E_c|^{3/2}$ near the band edge, E_c. Therefore the saturation average spin on the surface $\bar{S}_s = (1 - c_s)/2$ is larger than $\bar{S} = (1 - c)/2$ in the bulk for small c. From (29) the sum rule $\langle X_R^{00} \rangle = \langle X_R^{0-} X_R^{-0} \rangle = \langle X_R^{0+} X_R^{0+} \rangle$ holds since $f^2(E) = f(E)$ and

$$\int_{-\infty}^{\infty} dE\, f(E) N_s^-(E) = \int_{-\infty}^{\infty} dE\, f(E) N_s^+(E) = c_s. \tag{31}$$

If one considers the case where $n > 1$ and introduces the 'doubly occupied' states $|2\rangle$ instead of hole ones one obtains similar results. The difference is that the states in the lower Hubbard subband are occupied only for $\sigma = +$ and for the upper Hubbard subband the picture is as shown in figure 1(*b*).

Thus if one considers the energy scale $|\Delta E| \gg \bar{\omega}$ the empty states near the Fermi level at $n < 1$ and the occupied ones at $n > 1$ are depolarized on the surface ($N_s^+ \simeq N_s^-$) as well as in the bulk. So the predictions [6] of strong deviations of the results for spectroscopy of spin-polarized electrons from that of band structure calculations (i.e. the Hartree–Fock picture) appear to be valid even when surface effects are taken into account.

In the present work the dispersion of the magnon spectrum has been neglected. To investigate the possibility of unsaturated magnetism at the surface this must be included.

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