PHYSICAL REVIEW B VOLUME 53, NUMBER 8 15 FEBRUARY 1996-II

Localized low-energy excitations in strongly correlated metals

U. Muschelknautz and M. Cyrot
Centre National de la Recherche Scientifique, Laboratoire Louis Néel, 25 avenue des Martyrs,
Boîte Postale 166, 38042 Grenoble Cedex 9, France

(Received 10 July 1995)

We calculate the energy needed to create a localized hole in a strongly correlated metal. Due to the creation of an attractive potential linked to the localized hole, there is a strong relaxation of the itinerant states. Taking into account the finite extension of the potential, we show that the energy of such an excitation is much lower than the Hartree-Fock estimate. In some cases it can be one-hundredth of the Fermi energy. The existence of these excitations can lead to many physical effects particularly in the optical conductivity.

I. INTRODUCTION

The properties of a strongly correlated metal are mainly due to the low-energy excitations. These low-energy excitations are in principle Fermi liquid excitations. However, experimental results seem to prove that non-Fermi-liquid behavior can exist in metals close to the metal-nonmetal transition (Mott transition).[1] Some theoretical results show that non-Fermi-liquid excitations can exist in models of correlated systems.[2] But there is no consensus about the description of the excitations in these materials. Some theoretical approaches start from the *t*-*J* model which neglects excitations of order U, the intra-atomic Coulomb repulsion, or W, the bandwidth. U is of order of W close to the Mott transition. We want to show that some excitations, which in a simple approach are of order U or W, can in fact be of much lower energy due to a relaxation process. Although the excitations out of states close to the Fermi level are Fermi liquid excitations, non-Fermi-liquid behavior can be obtained.

To show this we start from the Wolff model.[3] Contrary to Hubbard's, this model introduces the Coulomb repulsion on a single site. If U is large, this model leads to a magnetic impurity on this particular site. We will consider the case, not considered by Wolff, where the Hartree-Fock moment extracts a bound state from the band, i.e., the potential for a spin direction is large enough to extract a bound state and the potential for the other spin direction becomes repulsive. The excited state obtained in destroying the magnetic moment by exciting the electron out of the bound state to the continuum is from a Hartree-Fock point of view of order of U. We show that this is not exact and that this excitation is in fact of much lower energy due to the relaxation of all states in the presence of the attractive potential created on that site by the hole left after the excitation.

This calculation can be considered as a first approximation to that of a localized hole in the metallic state of the Hubbard model close to the metal-nonmetal transition. Indeed, one of us has shown that the excitation which we have considered in the Wolff model would be localized in the Hubbard model due to many-body effects, i.e., the hole would remain on this site.[4,5] This is a consequence of Anderson's orthogonality theorem.[6] The possibility of having excitations of this type, i.e., a localized hole on a site in a strongly correlated system, would be important. The fact that it would not be a high-energy excitation would give many physical effects which we will discuss at the end.

The excitation of localized electrons in metals was first studied extensively by Friedel[7,8] and then, in connection with x-ray-absorption and -emission spectra, by Mahan,[9] Nozieres and de Dominicis,[10] and other authors. A newer review about this subject has been given by Othaka and Tanabe.[11] Although the main interest there was the shape of the excitation spectrum, especially the singular behavior at the threshold, the excitation energies have been calculated in some cases too.[8,12–14] The main differences between the problem that they studied and the problem analyzed here are the following: In the x-ray-excitation problem the bound state is formed by the potential of an atom and is filled by two electrons; no local magnetic moment is assumed.[8] In our problem only *one* localized electron exists in the ground state; no bound state is extracted from the bottom of the band for the opposite-spin electrons. Furthermore in the x-ray excitation the bound-state energy is *large* (several Ry) compared to the Fermi energy $[O(0.5\text{ Ry})]$ contrary to our problem where we consider the case of a bound state close to the bottom of the band. Therefore, in the x-ray-excitation experiment, relaxation effects give only a minor contribution to the excitation energy, which is dominated by the large bound-state energy, whereas in our case the relaxation energy plays the dominant role. As a consequence of these differences our method for calculating the potentials in the ground and in the excited state is totally different from that needed in the x-ray-excitation problem.

II. MODEL

We consider the two-dimensional case, i.e., our analysis can be relevant for exactly or nearly two-dimensional systems, e.g., layered systems with a weak coupling between the layers. The Hamiltonian for the Wolff model, which we consider on a two-dimensional square lattice with lattice sites i and lattice constant a, is given by

$$H=H_0+\tfrac{1}{2}\sum_{\sigma} U\delta\langle n_\sigma(i=0)\rangle n_{-\sigma}(i=0). \tag{1}$$

The first term H_0 is a single band Hamiltonian which describes the electrons in the periodic potential built by the ion potentials and the Hartree-Fock potential of the other electrons. We choose for H_0 the tight-binding Hamiltonian on a simple square lattice, i.e.,

$$H_0 = \sum_{(\mathbf{k},\sigma)\in FS} \varepsilon_0(\mathbf{k}) c_\sigma^\dagger(\mathbf{k}) c_\sigma(\mathbf{k}), \tag{2}$$

where $c_\sigma^\dagger(\mathbf{k})$ is the creation operator for an electron with momentum $\mathbf{k}$ and spin σ and

$$\varepsilon_0(\mathbf{k}) = (W/2) + (W/4)[\cos(ak_x) + \cos(ak_y)] \tag{3}$$

is the dispersion of the band with the bandwidth W. The sum runs over all states $(\mathbf{k},\sigma)$ out of the Fermi sea (FS).

In the second term $n_\sigma(i)$ is the density of electrons with spin σ at the site i, $\langle n_\sigma(i)\rangle$ is its expectation value, and

$$\delta\langle n_\sigma(i=0)\rangle := \langle n_\sigma(i=0)\rangle - \langle n_\sigma(i=0)\rangle_{\mathrm{HF}} \tag{4}$$

its deviation from the Hartree-Fock value at the site $i=0$. The Hartree-Fock value of the density is given by

$$\langle n_\sigma(i)\rangle_{\mathrm{HF}} = (1/2)\sum_\sigma \langle n_\sigma(i)\rangle. \tag{5}$$

Thus the second term in (1) adds to the Hartree-Fock-Hamiltonian H_0 at one site $i=0$ the deviation of the expectation value of the full Coulomb interaction from its Hartree-Fock value, which is $U\langle n_\sigma(i=0)\rangle_{\mathrm{HF}}$. At the site $i=0$ we thus take into account the expectation value of the *full* Coulomb interaction. We can rewrite the second term in (1) by defining the potential

$$\delta V_{-\sigma}(i) := \begin{cases} U\delta\langle n_\sigma(i=0)\rangle & \text{for } i=0 \\ 0 \quad \text{for } i\neq 0, \end{cases} \tag{6}$$

which acts on the electrons with spin $-\sigma$ on the site $i=0$ and is zero at all other sites. The Hamiltonian then reads

$$H = H_0 + \tfrac{1}{2}\sum_\sigma U\delta V_\sigma(i) n_\sigma(i=0). \tag{7}$$

As is well known, in two dimensions an attractive (repulsive) potential extracts always a bound state from the bottom (top) of the band no matter how weak it is. Therefore, if, e.g., $\delta V_\uparrow(i=0)<0$, a bound state for spin-↑ electrons is extracted from the bottom of the band. We want to study in the following the excitation of an electron out of this bound state.

III. CALCULATION OF THE EXCITATION ENERGY

We calculate the excitation energy in three steps. First we determine the local potentials in the ground state and in the excited state. From these potentials we calculate in the second step the energies of the system in the ground state and in the excited state. The difference between both energies is the relaxation energy and gives us in the third step the excitation energy.

First step

In order to calculate the local potentials we first determine the relation between an arbitrary local potential and the electron density at each lattice site caused by this potential. This has to be done numerically since analytical solutions for this problem exist only for some special potential shapes. Koster and Slater[15–17] have solved this problem for the case of a *point potential* acting on *one* site only. We generalize their method in order to treat also *extended potentials* having finite values on *several lattice sites* which turns out to be necessary in our case. (Koster and Slater have considered the case of an extended potential only with respect to the bound states, not with respect to the scattering states.)

In the following the formalism of Koster and Slater will be generalized to extended potentials. For this section it is appropriate to use the notation $\mathbf{R}_i$ instead of i for a lattice site. Let the unperturbed system of electrons in the crystal be described by a one-electron Hamiltonian H_0 like in our model (1) and the local potential act on some lattice sites with values $V(\mathbf{R}_i,\mathbf{R}_j)$. For our problem it suffices to assume only a single electron band. The perturbed wave function for an electron with energy ε is then described in terms of the complete set of Wannier functions $a_\sigma(\mathbf{r}-\mathbf{R}_i)$,

$$\psi_{\varepsilon,\sigma}(\mathbf{r}) = \sum_{\mathbf{R}_i} U_{\varepsilon,\sigma}(\mathbf{R}_i) a_\sigma(\mathbf{r}-\mathbf{R}_i). \tag{8}$$

The coefficients $U_{\varepsilon,\sigma}(\mathbf{R}_i)$ are determined by the Schrödinger equation

$$\sum_{\mathbf{R}_i} [E_0(\mathbf{R}_i,\mathbf{R}_j) + V(\mathbf{R}_i,\mathbf{R}_j)] U_{\varepsilon,\sigma}(\mathbf{R}_j) = \varepsilon U_{\varepsilon,\sigma}(\mathbf{R}_i) \tag{9}$$

with

$$E_0(\mathbf{R}_i,\mathbf{R}_j) := \int d^2r\, a_\sigma^\dagger(\mathbf{r}-\mathbf{R}_i) H_0 a_\sigma(\mathbf{r}-\mathbf{R}_j) \tag{10}$$

and

$$V(\mathbf{R}_i,\mathbf{R}_j) := \int d^2r a_\sigma^\dagger(\mathbf{r}-\mathbf{R}_i) V a_\sigma(\mathbf{R}-\mathbf{R}_j), \tag{11}$$

where we assume that the potential does not change the spin of the electrons. The dispersion of the electron band is given by the Fourier transform of the components

$$E_0(\mathbf{R}_i,\mathbf{R}_j), \text{ i.e., } \varepsilon_0(\mathbf{k}) = \Sigma_{\mathbf{R}_i} E_0(\mathbf{R}_i,\mathbf{R}_j)\exp(-i(\mathbf{R}_i-\mathbf{R}_j)).$$

In order to get a simpler form of the equations we denote in the following a vector with coefficients $x(\mathbf{R}_i)$ by $\mathbf{x}$ and a matrix with components $X(\mathbf{R}_i,\mathbf{R}_j)$ by $\mathbf{X}$. Equation (9) can then be replaced by

$$[\mathbf{E}_0 + \mathbf{V}]\mathbf{u}_{\varepsilon,\sigma} = \varepsilon \mathbf{u}_{\varepsilon,\sigma}. \tag{12}$$

From this equation we get the coefficients for the scattering states $U_{\mathbf{k},\sigma}(\mathbf{R}_i)$ with energy $\varepsilon>0$ as well as the coefficients for the bound states $U_{b,\sigma}(\mathbf{R}_i)$ with energy $\varepsilon_b<0$. These coefficients are calculated as follows.

(i) Scattering states. The wave function is assumed to be a sum of the incident wave with energy ε and momentum $\mathbf{k}$ and outgoing waves, i.e.,

$$U_{\mathbf{k},\sigma}(\mathbf{R}_j) = \exp(i\mathbf{k}\mathbf{R}_j) + \Sigma_{\mathbf{R}_l} c(\mathbf{R}_l) \Sigma_{\mathbf{k}'} \times \exp(i\mathbf{k}'(\mathbf{R}_j-\mathbf{R}_l))/[\varepsilon-\varepsilon(\mathbf{k}')].$$

The unknown coefficients $c(\mathbf{R}_i)$ have to be determined in such a way that they satisfy the difference equation (12). This leads to the equation

$$[\mathbf{1}-\mathbf{V}\mathbf{K}_\varepsilon]\mathbf{c}=\mathbf{V}\mathbf{u}_0, \tag{13}$$

where $U_0(\mathbf{R}_i)=\exp(i\mathbf{k}\mathbf{R}_i)$ and

$$K_\varepsilon(\mathbf{R}_i,\mathbf{R}_i)=\frac{1}{N}\sum_{\mathbf{k}'}\frac{e^{i\mathbf{k}'(\mathbf{R}_i-\mathbf{R}_j)}}{\varepsilon-\varepsilon(\mathbf{k}')} \tag{14}$$

is the unperturbed electron Green's function with N being the number of lattice sites. For the derivation of (13) it has been made use of the fact that for the infinite system the incident wave satisfies the Schrödinger equation (12) with the potential set equal to zero, i.e., $\mathbf{E}\mathbf{u}_0=\varepsilon\mathbf{u}_0$. Furthermore, the property $(\varepsilon\cdot\mathbf{1}-\mathbf{E})\mathbf{K}_\varepsilon=\mathbf{1}$ of the unperturbed Green's function has been applied.

(ii) Bound state. The difference equation (12) leads to the condition

$$\mathbf{u}_{b,\sigma}-\mathbf{K}_\varepsilon\mathbf{V}\mathbf{u}_{b,\sigma}=0. \tag{15}$$

From the coefficients $U_{\mathbf{k},\sigma}(\mathbf{R}_i)$ for the scattering states and $U_{b,\sigma}(\mathbf{R}_i)$ for the bound states we get the expectation value of the density of electrons with spin σ at the site $\mathbf{R}_i$ according to

$$\langle n_\sigma(\mathbf{R}_i)\rangle=|U_{b,\sigma}(\mathbf{R}_i)|^2+\sum_{\mathbf{k}\in FS}|U_{\mathbf{k},\sigma}(\mathbf{R}_i)|^2$$

$$=:\langle n_\sigma(\mathbf{R}_i)\rangle_{\text{bound}}+\langle n_\sigma(\mathbf{R}_i)\rangle_{\text{scatt}}, \tag{16}$$

where $\langle n_\sigma(\mathbf{R}_i)\rangle_{\text{bound}}$ and $\langle n_\sigma(\mathbf{R}_i)\rangle_{\text{scatt}}$ are the densities of bound and scattering electrons with spin σ at site $\mathbf{R}_i$.

Now we are in the position to calculate the potentials in the ground and in the excited state. For the rest of this paper we use again the shorthand notation i for $\mathbf{R}_i$.

(a) Ground state. We have to determine the spin-dependent potentials according to (6):

$$\delta V_{-\sigma}(i=0)=U\delta\langle n_\sigma(i=0)\rangle. \tag{17}$$

The density deviation from the Hartree-Fock value depends, corresponding to the formalism of Koster and Slater, on the potential $\delta V_\sigma(i=0)$, i.e.,

$$\delta\langle n_\sigma(i=0)\rangle=f[\delta V_\sigma(i=0)], \tag{18}$$

where the function f has to be determined numerically according to (8)–(16). We thus have a system of equations for $\delta V_\sigma(i=0)$ and $\delta\langle n_\sigma(i=0)\rangle$ which can be solved self-consistently.

The density deviations from the Hartree-Fock value at the neighbor sites $i\neq 0$ are not considered in the determination of the ground-state potential because they are very small for a point potential as we show in the results. This has the consequence that in the ground state the total number of electrons at the site $i=0$ is the same as at all other sites, i.e.,

$$\delta\langle n_\sigma(i=0)\rangle=-\delta\langle n_{-\sigma}(i=0)\rangle \tag{19}$$

$$\Rightarrow\delta V_\sigma(i=0)=-\delta V_{-\sigma}(i=0). \tag{20}$$

For special values of U and ε_F, Eq. (17) has magnetic solutions, e.g., $\delta V_\uparrow(i=0)<0$ and $\delta V_\downarrow(i=0)>0$, and a bound state for spin-↑ electrons is extracted from the bottom of the band. This is the case we are interested in.

(b) Excited state. In the following the suffix g (ex) of a quantity denotes its value in the ground (excited) state. The Friedel sum rule yields for the excited state

$$\eta_\sigma^{(\text{ex})}(\varepsilon_F)=\pi, \tag{21}$$

which is a consequence of the creation of a hole in the bound state. This will be derived in Appendix A.

If the phase shift at the Fermi level is π this means that the potential must be *extended over several lattice sites*, since a point potential leads always to phase shifts smaller than π. For simplicity we assume that the excited state is nonmagnetic, in contrary to the ground state. This is reasonable because the main contribution to the magnetic moment in the ground state stems from the bound electron at the site $i=0$ which repels the electrons with the opposite spin direction. If the bound electron is removed a magnetic moment can only be formed by the itinerant electrons. Therefore the local magnetic moment in the excited state is smaller than in the ground state. The bound electron with spin ↑ is removed from the site $i=0$ and is put into a scattering state. Therefore we have

$$\langle n_\sigma(i)\rangle^{(\text{ex})}=\langle n_\sigma(i)\rangle_{\text{scatt}}^{(\text{ex})}. \tag{22}$$

The electron density at the site $i=0$ is reduced by the weight of the bound electron at this site $\langle n_\uparrow(i=0)\rangle_{\text{bound}}^{(g)}=|U_{b,\uparrow}^{(g)}(i=0)|^2$. Since we assume a nonmagnetic excited state the potential and density values are the same for ↑ and ↓ electrons at each lattice site and we obtain for the electron density at the site $i=0$,

$$\langle n_\sigma(i=0)\rangle^{(\text{ex})}=\tfrac{1}{2}[\langle n_\uparrow(i=0)\rangle^{(g)}+\langle n_\downarrow(i=0)\rangle^{(g)}$$

$$-\langle n_\uparrow(i=0)\rangle_{\text{bound}}^{(g)}]. \tag{23}$$

The weight $\langle n_\uparrow(i=0)\rangle_{\text{bound}}^{(g)}$ is shifted onto the neighboring sites, i.e.,

$$\sum_{i\neq 0,\sigma}\langle n_\sigma(i)\rangle^{(\text{ex})}=\sum_{i\neq 0,\sigma}\langle n_\sigma(i)\rangle^{(g)}+\langle n_\uparrow(i=0)\rangle_{\text{bound}}^{(g)}. \tag{24}$$

The potential $\mathbf{V}^{(\text{ex})}$, which has finite values not only at the central site $V(0)^{(\text{ex})}$ but also at the neighboring sites $V(1)^{(\text{ex})}$, has to be chosen in that way that the Koster-Slater formalism yields the density distribution for the excited state given by (22)–(24).

Second step

A local potential $\mathbf{V}:=(\mathbf{V}_\uparrow,\mathbf{V}_\downarrow)$, which may have different values $\mathbf{V}_\sigma$ for the two spin directions, leads to an energy shift $\Delta E(\mathbf{V})$ with respect to the value E_0 of the unperturbed system. It can be calculated, according to Refs. 7 and 18 as follows: If one includes the system in a large sphere of radius R the spectrum is quasicontinuous with level spacing $d\varepsilon=\pi v/R$, where v is the velocity corresponding to the energy ε of the level. Due to the local potential all single electron energies ε are shifted by a small amount $\Delta\varepsilon$. The level shift $\Delta\varepsilon(\mathbf{V}_\sigma)$ due to the potential $\mathbf{V}_\sigma$ is related to the phase shifts $\eta_\sigma(\varepsilon)$ produced by $\mathbf{V}_\sigma$. In the degenerate case, i.e., if several levels λ with phases $\eta_{\lambda,\sigma}(\varepsilon)$ have the same energy, one finds (cf. Refs. 7 and 18)

$$\sum_{\lambda} \Delta\varepsilon(\mathbf{V}_\sigma) = -\frac{1}{\pi}\sum_{\lambda} \eta_{\lambda,\sigma}(\varepsilon)d\varepsilon =: -\frac{1}{\pi}\eta_\sigma(\varepsilon)d\varepsilon. \tag{25}$$

Summing up all energy shifts given by (25) one obtains in the limit $R\rightarrow\infty$ the total energy shift

$$\Delta E(\mathbf{V}) = -\sum_{\sigma} \frac{1}{\pi}\int_0^{\varepsilon_F} d\varepsilon\,\eta_\sigma(\varepsilon) + \sum_{\sigma} \varepsilon_{b,\sigma} + \delta E_{\mathrm{cor}}, \tag{26}$$

where $\varepsilon_{b,\sigma}$ are the energies of the bound electrons extracted out of the band. The last term δE_{cor} is the change of the electron-electron-interaction energy due to the change of the electronic wave functions caused by the local potential. As is well known the electron-electron-interaction energy has to be subtracted from the sum over all single-particle energies if one calculates the Hartree-Fock energy of the total system. In our case the change of this energy is approximately given by (cf. Appendix C)

$$\delta E_{\mathrm{cor}} = -U\sum_{\sigma} \langle n_\sigma(i=0)\rangle \delta\langle n_{-\sigma}(i=0)\rangle. \tag{27}$$

The phase shifts are determined corresponding to Ref. 8 by

$$\eta_\sigma(\varepsilon) := -\mathrm{Im}\ \ln\ \det[\mathbf{1} - \mathbf{K}_\epsilon \mathbf{V}_\sigma]. \tag{28}$$

The bound-state energies $\varepsilon = \varepsilon_{b,\sigma}$ are the solutions of

$$\det[\mathbf{1} - \mathbf{K}_\varepsilon \mathbf{V}_\sigma] = 0, \tag{29}$$

which follows from (15).

Equations (26)–(29) together with Eqs. (8)–(24) for the potentials and the electron densities yield all information in order to calculate the energy of our system in the ground and in the excited state.

(a) Energy in the ground state. We are interested in the case where $\delta V_{\uparrow}^{(g)}(i=0)$ extracts only one bound state out of the band, i.e.,

$$E^{(g)} = E_0 - \sum_{\sigma} \frac{1}{\pi}\int_0^{\varepsilon_F} d\varepsilon\,\eta_\sigma^{(g)}(\varepsilon) + \varepsilon_{b,\uparrow}^{(g)} - U\sum_{\sigma} \langle n_\sigma(i=0)\rangle^{(g)} \delta\langle n_{-\sigma}(i=0)\rangle^{(g)}. \tag{30}$$

(b) *Energy in the excited state*. The bound state is empty, i.e.,

$$E^{(\mathrm{ex})} = E_0 - \sum_{\sigma} \frac{1}{\pi}\int_0^{\varepsilon_F} d\varepsilon\,\eta_\sigma^{(\mathrm{ex})}(\varepsilon) - U\sum_{\sigma} \langle n_\sigma(i=0)\rangle^{(\mathrm{ex})} \delta\langle n_{-\sigma}(i=0)\rangle^{(\mathrm{ex})}. \tag{31}$$

Third step

The relaxation energy is given by

$$E_{\mathrm{relax}} = E^{(\mathrm{ex})} - E^{(g)} \tag{32}$$

and the excitation energy by

$$\omega_{\mathrm{ex}} = \varepsilon_F - \varepsilon_b + E_{\mathrm{relax}}. \tag{33}$$

IV. RESULTS AND DISCUSSION

All energies are written in units of the bandwidth W. Our calculations are done for $\varepsilon_F = 0.5$. This value has been chosen because the Fermi energy of the Hubbard model close to the metal-nonmetal transition, for which the present calculation is believed to be a first approximation, lies very close to 0.5. Note that it would not seriously change our result for the excitation energy if we would take for ε_F a value close to 0.5 instead of our value $\varepsilon_F = 0.5$, since the excitation energy is determined by quantities summed up to the Fermi level. Note also that our system is metallic for both values, contrary to the Hubbard model which is metallic only away from half-filling. Thus our model can give only a description of the metallic phase but not for the insulating phase.

Let us first consider the energies and the densities of the electrons on a simple two-dimensional square lattice with dispersion (3) as a function of the strength and the extension of a local attractive potential. We use the following notations for the lattice sites in the region of the potential: $i=0$ stands for the central site (0,0) of the potential, $i=1$ for $(\pm 1,0)$ and $(0,\pm 1)$, respectively, $i=1'$ for $(\pm 1,\pm 1)$ and $i=2$ for $(\pm 2,0)$ and $(0,\pm 2)$, respectively. We restrict the potential to the sites $i=0$ and $i=1$ with values $V(0)$ and $V(1)$, respectively. The value $V(0)$ determines the depths of the potential, the ratio $V(1)/V(0)$ its extension.

A *point* potential, acting only at $i=0$, can extract only *one* bound state out of the band, and the scattering phase $\eta(\varepsilon)$, determined in this case by $\tan\eta(\varepsilon) = -\pi V(0)\rho(\varepsilon)/[1 - V(0)F(\varepsilon)]$ [with the density of states (DOS) for the square lattice $\rho(\varepsilon)$ and its Hilbert transform $F(\varepsilon)$], cannot exceed the value π. However, an *extended* potential with values $V(i)\neq 0$ for *several* sites i can extract *several* bound states out of the band, as has been pointed out, e.g., by Koster and Slater.[13–15] This is shown by our numerical calculation in Fig. 1 where the bound-state energies are plotted as a function of the potential strength for a potential with $V(i)\neq 0$ for $i\in\{0,1\}$ and $V(i)=0$ otherwise. For comparison we have also plotted the bound-state energy for a point potential (dashed line). For weak potentials the bound-state energy deviates at first hardly from zero with increasing potential strength, which is a consequence of the sharp edge at the bottom of the band of the two-dimensional DOS for a simple square lattice.

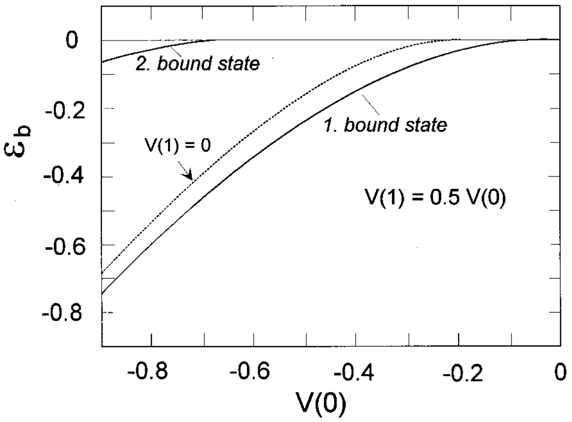

FIG. 1. Bound-state energy for extended and point (dashed line) potential as a function of $V(0)$. The second bound state for the extended potential appears at $V(0) = -0.65$.

The potential value, where the second bound state drops out of the bottom of the band, decreases for increasing extension of the potential. For $V(1)/V(0) = 0.5$ the second bound state appears at $V(0) \cong -0.65$ (cf. Fig. 1).

The phase shifts $\eta(\varepsilon)$ become larger with increasing extension of the potential as is shown in Fig. 2. They can exceed the value π also in the case where only a single bound state is present. (Note that the phase shifts for an extended potential can also exceed π because a second bound state is extracted.) At the bottom of the band the phase shifts have the value $\eta(\varepsilon=0) = \pi$ indicating that one bound state has been extracted out of the band. From Fig. 2 we expect that the relaxation energy determined essentially by integrals over all phase shifts up to the Fermi level [cf. (30)–(32)] increases rapidly, if the potential becomes more and more extended. We estimate, e.g., an increase of the relaxation energy by about a factor 3, if the value of $V(1)$ changes from 0 to $0.5V(0)$, where we have set $V(0) = -0.5$.

The electron densities for a point potential at different sites as a function of the potential strength are shown in Fig. 3. For a vanishing potential the density has the unperturbed value, which is 0.5 for the square lattice at half-filling. At the central site the density varies strongly with the potential, whereas at the neighboring sites the deviations from the unperturbed value, which are the well-known Friedel oscillations, are very small. Therefore our approximation in the determination of the ground-state potentials, where we take into account only density and potential deviations at the site $i=0$, is self-consistent. If the potential is strong attractive, nearly one electron is located at the site $i=0$, present mainly in the bound state. For very strong repulsive potentials the density vanishes, which means that the electrons are repelled from the potential site.

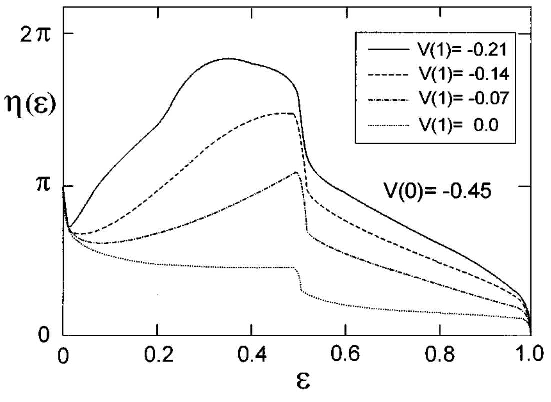

FIG. 2. Phase shifts for various potential extensions, determined by $V(1)/V(0)$, as a function of energy. (The sharp bends at the band edges and at $\varepsilon = 0.5$ are due to the shape of the DOS for the tight-binding Hamiltonian on a simple square lattice at these points.)

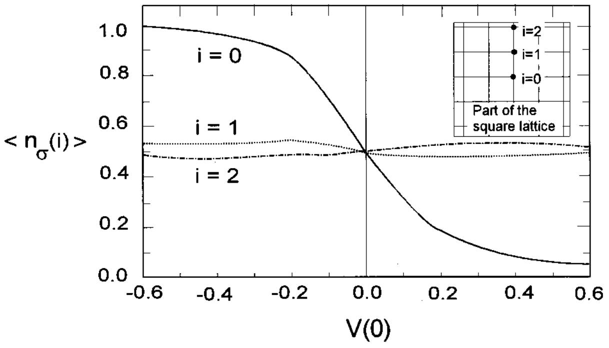

FIG. 3. Density of electrons at the sites $i=0$, $i=1$, and $i=2$ (cf. small box above) for a *point* potential, acting at the site $i=0$ only, as a function of the potential depth $V(0)$.

Figure 4(c) shows the corresponding electron densities for an extended potential with finite values at the site $i=0$ and the four nearest-neighbor sites $i=1$. The values for the potential depth have been restricted to that range, where only *one* bound state is extracted out of the band. In Figs. 4(a) and 4(b) the densities of bound and scattering electrons are plotted separately. The sum of both gives the total density in Fig. 4(c) according to (16). Now the dependence on the potential strength is not only strong at the site $i=0$ but also at the neighboring sites $i=1$. They are, however, negligible at the site $i=2$, where the densities have approximately the unperturbed value. Only for strong attractive potentials with $V(0) < -0.4$ does the density of the scattering electrons $\langle n_\sigma(i=2)\rangle_{\text{scatt}}$ and the total density $\langle n_\sigma(i=2)\rangle$ deviate a bit from the unperturbed value indicating that itinerant electrons are located in the region of the potential. The reason for this localization of itinerant electrons is that at $V(0) \cong -0.65$ a second bound state is extracted from the bottom of the band.

If the potential is repulsive, no bound electron is present, since no bound state below the band exists, and the density of scattering electrons at the central site falls off with increasing potential strength, because a very repulsive potential repels the electrons from the site $i=0$. On the other hand, if the potential is very attractive it binds one electron at site $i=0$ with the consequence that no itinerant electron can be present anymore at this site. Note that the electron density at one site cannot exceed the value 1 for a given spin direction due to the Pauli principle. For small attractive potentials the density of scattering electrons at the site $i=0$ at first increases before it falls off with increasing potential depth. The reason for this behavior is that for very weak potentials the bound state is distributed over several sites and its weight at

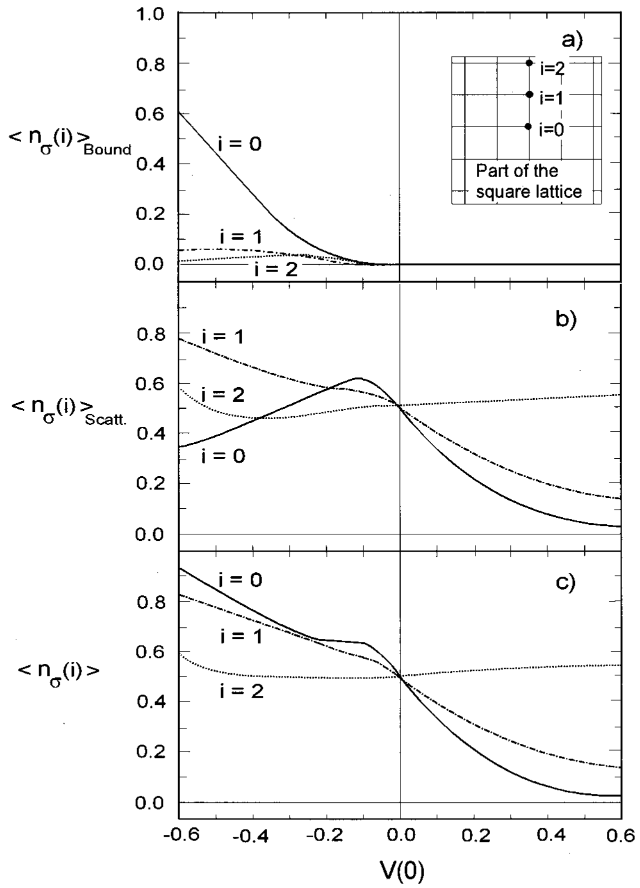

FIG. 4. Density of *bound* (a), *scattering* (b), and *all* (c) electrons at the sites $i=0$, $i=1$, and $i=2$ (cf. small box above) for an *extended* potential with $V(1)=0.5V(0)$ as a function of the potential depth $V(0)$.

the site $i=0$ is therefore very small. The electrons attracted by the potential are therefore mainly itinerant electrons with energies at the bottom of the band.

In Fig. 5 we present our results for E_{relax} and ω_{ex} as a function of the Coulomb repulsion U. The potential in the excited state, which we found to be necessarily extended over several lattice sites, we restrict on the central site $i=0$ and its four nearest neighbors $i=1$. Then we can restrict the set $\{i\}$ of sites, where we take into account the density deviations $\delta\langle n_\sigma(i)\rangle$, onto the sites $i=0$, $i=1$, and $i=1'$. Density deviations at the sites $i=2$ are already negligible [cf. Fig. 4(b)].

In the range $0.5<U<0.65$ the excitation energy (upper curve) is very small, i.e., of the order of one-hundredth of the Fermi energy: $\omega_{\mathrm{ex}}\cong O(10^{-2}\varepsilon_F)$. If one assumes W (which is the energy unit in our calculation) to be of the order of 1 eV, this excitation energy is of the order of 10 meV or 100 K, respectively, i.e., it is in the range of normal metallic excitation energies or phonon frequencies at room temperature respectively. For larger U values the excitation energy increases but nevertheless it remains significantly smaller than the Fermi energy. This behavior of ω_{ex} corresponds to a large relaxation energy E_{relax} (lower curve in Fig. 5) of the order of -0.5. For $U<0.5$ we find $\delta V_\sigma^{(g)}=0$, i.e., a nonmagnetic ground state. For $U>0.9$ the potential in the excited state extracts a second bound state from the bottom of the band. We do not consider this case here.

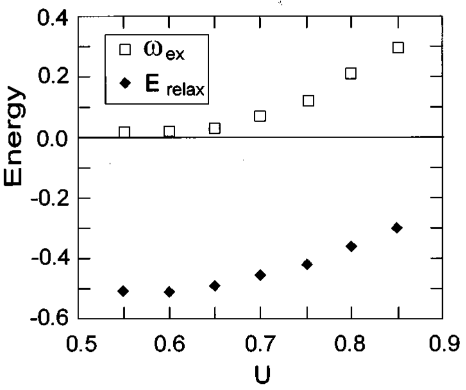

FIG. 5. Excitation (upper curve) and relaxation (lower curve) energies as a function of the intra-atomic Coulomb repulsion U for $\varepsilon_F=0.5$.

For the self-consistent determination of the electron densities and the potentials we had to do the numerical calculation (8)–(24) on a $(V(0),V(1))$ grid with finite meshes, which we have chosen as squares with length 0.025. [The curves, shown in Figs. 1, 3, and 4 are fits through the calculated values where the $V(0)$ axis is discretized in steps of 0.025.] The uncertainty of the energy values in Fig. 5 by virtue of these finite meshes we estimate to be ± 0.05.

The values of the potentials, we have found, are the following. The potential in the ground state varies between $\delta V_\sigma^{(g)}(i=0)=\pm 0.23$ and $\delta V_\sigma^{(g)}(i=0)=\pm 0.43$ for the range of U values shown in Fig. 5. This corresponds to bound-state energies between $\varepsilon_b=-0.01$ and $\varepsilon_b=-0.12$. The potential in the excited state has depths between $V^{(\mathrm{ex})}(0)=-0.64$ and $V^{(\mathrm{ex})}(0)=-0.37$ and values at the site $i=1$ near $V^{(\mathrm{ex})}(1)=-0.1$. In the excited state there are fewer electrons at the central site, compared to the value in the unperturbed case, and more electrons at the neighboring sites. The total number of electrons fulfills charge conservation, according to (22)–(24). We also checked the Friedel sum rule, which is equivalent to our requirement of charge conservation.[7,8] We have not used here this alternative to determine the potential in the excited state, because the phase shifts, whose values at the Fermi level enter in the Friedel sum rule, vary very rapidly at the Fermi energy (cf. Fig. 2). If we assume a numerical uncertainty $\Delta\varepsilon_F=\pm 0.02$ (which does not change our final result for ω_{ex} seriously), the Friedel sum rule is fulfilled within the corresponding error bars of the phase shifts.

In conclusion, we have studied the excitation of a bound electron in the Wolff model, which takes into account the intra-atomic Coulomb repulsion U on the site of the local excitation and describes the electron dynamics at the other sites within the Hartree-Fock approximation. We found that the creation of a hole in the bound state leads for a certain range of U values via a strong relaxation of all electrons to very small excitation energies of the order of one-hundredth of the Fermi energy. The large relaxation energy which we obtained stems from the fact that the electron is excited from a singly occupied state created by the magnetic moment. Our result is important for studying local excitations in strongly correlated metals. One of us has shown that, if all sites are similar, the hole created in such an excitation, which in principle can move, would be self-trapped.[5] The reason stems from the fact that the problem becomes similar to that of a particle creating a potential and moving in a Fermi liquid. This particle can, under special conditions, be self-trapped. These conditions are fulfilled in the present problem as is shown in Ref. 5. Thus, besides the Fermi liquid excitations, localized excitations could exist in strongly correlated materials. Our calculation shows that these excitations would not be of high energy of order U or W. Thus it would be important to consider them.

In that case, many effects similar to those studied by Mahan, Nozieres, and de Dominicis in the x-ray problem could occur. We mention anomalies in photoemission of electrons excited out of the lower Hubbard subband. We refer also to anomalies in the optical conductivity, which appear as an important infrared absorption and a decrease of the intensity of the Drude peak. It would also mean that the magnetic properties of the Hubbard model in that range of doping would be neither itinerant nor localized. All these consequences are under study.

ACKNOWLEDGMENTS

We would like to thank C. Lacroix for very useful discussions. This work has been supported by EEC.

APPENDIX A: PHASE SHIFTS IN THE GROUND AND IN THE EXCITED STATE

The Friedel sum rule relates the number Z of *states*, which are *created below the Fermi level* by a potential V, to the phase shifts at the Fermi level:

$$Z=\frac{1}{\pi}\sum_{\sigma}\ \eta_{\sigma}(\varepsilon_F). \tag{A1}$$

Note that Z takes into account the number Z_{scatt} of *scattering* states as well as the number Z_{bound} of localized *bound* states (cf., e.g., Refs. 7 and 8), i.e.,

$$Z=Z_{\text{scatt}}+Z_{\text{bound}}. \tag{A2}$$

The number Z of states has to be distinguished from the *screening charge* Q of V which is the number of the *occupied* states multiplied by the electron charge e. If Z_{empty} is the number of empty *bound* states it follows that

$$Q=(Z-Z_{\text{empty}})e. \tag{A3}$$

1. Ground state

The total number of electrons per site at every site, particularly at the site $i=0$, is the same as in the case of no perturbation because $\delta\langle n_{\sigma}(i=0)\rangle+\delta\langle n_{-\sigma}(i=0)\rangle=0$. Therefore the total screening charge is $Q^{(g)}=0$. Since no bound state is empty, i.e., $Z^{(g)}_{\text{empty}}=0$, we obtain from (A1) and (A3)

$$\sum_{\sigma}\ \eta^{(g)}_{\sigma}(\varepsilon_F)=0. \tag{A4}$$

2. Excited state

The total charge within the region of the potential has not changed with respect to the ground-state configuration. Therefore $Q^{(\text{ex})}=0$. The bound state in the nonmagnetic excited-state configuration is empty for both spin directions, i.e., $Z^{(\text{ex})}_{\text{empty}}=2$. We thus obtain from (A1) and (A3)

$$\eta^{(\text{ex})}_{\sigma}(\varepsilon_F)=\pi. \tag{A5}$$

APPENDIX B: UNPERTURBED GREEN'S FUNCTION AND BOUND-STATE COEFFICIENTS AND ENERGIES

The unperturbed Green's function (14) for the tight-binding Hamiltonian on a simple square lattice (cf. Refs. 15–17) reads for energies within the band $\varepsilon>0$,

$$K_{\varepsilon}(\mathbf{R}_{p,q})=\frac{1}{2\varepsilon(1)}\int_0^{\infty}dt\ e^{-i\varepsilon' t}i^{(p+q)}J_p(t)J_q(t) \tag{B1}$$

and below the band $\varepsilon<0$,

$$K_{\varepsilon}(\mathbf{R}_{p,q})=\frac{1}{2\varepsilon(1)}\int_0^{\infty}dt\ e^{-i\varepsilon' t}I_p(t)I_q(t). \tag{B2}$$

Here $\mathbf{R}_{p,q}$ is the lattice vector with coordinates (p,q) and

$$J_p(t)=\int_{-\pi}^{\pm}d\alpha\ e^{-ip\alpha+i(\sin\alpha)t}$$

$$\text{(ordinary Bessel function of order } p), \tag{B3}$$

$$I_p(t)=\frac{1}{\pi}\int_0^{\pi}d\alpha\ \cos(p\alpha)e^{t\cos\alpha}, \tag{B4}$$

$$\varepsilon'=\frac{\varepsilon-\varepsilon(0)}{2\varepsilon(1)}. \tag{B5}$$

The bound-state coefficients for a potential, extended over the sites $i\in\{0,1\}$, are related by

$$U_{b,\sigma}(1)=-\frac{C_{\varepsilon}(0,0)}{C_{\varepsilon}(0,1)}U_{b,\sigma}(0) \tag{B6}$$

and the bound-state energy is the solution of

$$\det\begin{vmatrix} C_{\varepsilon}(0,0) & C_{\varepsilon}(0,1) \\ C_{\varepsilon}(1,0) & C_{\varepsilon}(1,1) \end{vmatrix}=0 \tag{B7}$$

with

$$C_{\varepsilon}(0,0)=1-V'(0)\int_0^{\infty}dt\ e^{-\varepsilon' t}I_0(t)^2,$$

$$C_{\varepsilon}(0,1)=-4V'(1)\int_0^{\infty}dt\ e^{-\varepsilon' t}I_0(t)I_1(t), \tag{B8}$$

$$C_\varepsilon(1{,}0)=-V'(0)\int_0^\infty dt\ e^{-\varepsilon' t}I_0(t)I_1(t),$$

$$C_\varepsilon(1{,}1)=1-V'(1)\int_0^\infty dt\ e^{-\varepsilon' t}[I_0(t)^2+2I_1(t)^2+I_0(t)I_2(t)],$$

and

$$V'(i):=\frac{V(i)}{2\varepsilon(0)}. \tag{B9}$$

APPENDIX C: ENERGY CORRECTION DUE TO DOUBLE COUNTING

The total energy of our system without the local potential is, in the Hartree-Fock approximation, the sum of two terms:

$$E_{\rm HF}=\sum_{(\mu,\sigma)\in\rm FS}\varepsilon_\mu+E_{\rm cor}. \tag{C1}$$

The first term is the sum of all one-electron energies ε_μ out of the Fermi sea. The second term

$$E_{\rm cor}=-\frac{1}{2}\sum_{(\mu,\sigma)\in\rm FS}\ \sum_{(\nu,\sigma')\in\rm FS}[\langle\psi_{(\mu,\sigma)}\psi_{(\nu,\sigma')}|\nu_{\text{el-el}}\psi_{(\mu,\sigma)}\psi_{(\nu,\sigma')}\rangle\langle\psi_{(\mu,\sigma)}\psi_{(\nu,\sigma')}|\nu_{\text{el -el}}|\psi_{(\nu,\sigma')}\psi_{(\mu,\sigma)}\rangle] \tag{C2}$$

subtracts the electron-electron interaction energy which has been doubly counted in the first term. $\nu_{\text{el-el}}$ is the electron-electron interaction.

If the local potential is switched on, all electron wave functions change at the potential site according to (13) and (15). This leads to a change $\delta E_{\rm cor}$ of the term $E_{\rm cor}$. It can be calculated approximately if we take into account the change of the electron wave function (8) only at the site $i=0$, which gives the main contribution:

$$\begin{aligned}\delta E_{\rm cor}=&-\delta\Bigg\{\frac{1}{2}\sum_{(\mu,\sigma)\in\rm FS}\ \sum_{(\nu,\sigma')\in\rm FS}|U_{(\mu,\sigma)}(i=0)|^2|U_{(\nu,\sigma')}(i=0)|^2[\langle a_\sigma(i=0)a_{\sigma'}(i=0)|\nu_{\text{el -el}}|a_\sigma(i=0)a_{\sigma'}(i=0)\rangle\\&-\langle a_\sigma(i=0)a_{\sigma'}(i=0)|\nu_{\text{el -el}}|a_{\sigma'}(i=0)a_\sigma(i=0)\rangle]\Bigg\}\\=&-U\sum_\sigma\ \langle n_\sigma(i=0)\rangle\delta\langle n_{-\sigma}(i=0)\rangle.\end{aligned} \tag{C3}$$

Here the definition of the Coulomb repulsion parameter

$$U:=\langle a_\sigma(i=0)a_{-\sigma}(i=0)|\nu_{\text{el -el}}|a_\sigma(i=0)a_{-\sigma}(i=0)\rangle-\langle a_\sigma(i=0)a_{-\sigma}(i=0)|\nu_{\text{el -el}}|a_{-\sigma}(i=0)a_{-\sigma}(i=0)\rangle \tag{C4}$$

has been used. Note that the change of the one-electron energies ε_μ due to the local potential is described by the phase shifts (28).

---

[1] B. Batlogg, in *High Temperature Superconductivity: The Los Alamos Symposium—1989*, edited by K. Bedell *et al.* (Addison-Wesley, Reading, MA, 1990).

[2] Q. Si and G. Kotliar, Phys. Rev. Lett. **70**, 3143 (1993).

[3] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

[4] M. Cyrot, *Workshop on Phase Separation in Cuprate Superconductors, Erice,* edited by K. A. Mueller and G. Benedek (World Scientific, Singapore, 1992).

[5] M. Cyrot, Solid State Commun. (to be published).

[6] P. W. Anderson, Phys. Rev. Lett. **18**, 1049 (1967).

[7] J. Friedel, Philos. Mag. **43**, 153 (1952).

[8] J. Friedel, Philos. Mag. **43**, 346 (1952).

[9] G. D. Mahan, Phys. Rev. **153**, 882 (1967); **163**, 612 (1967).

[10] P. Nozieres and C. T. de Dominicis, Phys. Rev. **178**, 1097 (1969).

[11] K. Othaka and Y. Tanabe, Rev. Mod. Phys. **62**, 929 (1990).

[12] C. P. Flynn and N. O. Lopardi, Phys. Rev. B **7**, 2215 (1973).

[13] C. O. Almbladh and U. von Barth, Phys. Rev. B **13**, 3307 (1976).

[14] G. W. Bryant and G. D. Mahan, Phys. Rev. B **17**, 1744 (1978).

[15] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

[16] G. F. Koster, Phys. Rev. **95**, 1436 (1954).

[17] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

[18] B. S. DeWitt, Phys. Rev. **103**, 1565 (1956).