Brinkman-Rice transition in layered perovskites

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We consider a one-band model effective Hamiltonian $H_{\rm eff}$ derived previously from the three-band model H for CuO_2 planes. The parameters of $H_{\rm eff}$ are given in terms of those of H by a simple prescription. Using $H_{\rm eff}$ and the slave-boson approach of Kotliar and Ruckenstein, we determine the metal-insulator boundary and the magnitude of the charge-transfer gap as a function of the parameters of H. Our results are in better agreement with experiment than those obtained applying the slave bosons directly to H. For sufficiently large values of the Cu-O repulsion U_{pd}, treated in the Hartree-Fock approximation, there is a charge-transfer instability inside the metallic phase, very near the metal-insulator boundary.

I. INTRODUCTION

Mott insulators such as Ti_2O_3 or V_2O_3 and charge-transfer insulators such as NiO, CuO, or La_2CuO_4 are oxides whose insulating behavior is due to electron-electron interactions. Recently, the framework developed by Zaanen, Sawatzky, and Allen[1] has been successfully used to classify a large number of oxides as metals, Mott insulators, or charge-transfer insulators,[2] and to understand the insulator-metal transition in the perovskites $R{\rm NiO_3}$ for different rare earths R.[3] However, even the Mott transition in the one-band Hubbard model is still not well understood from the theoretical point of view. Brinkman and Rice[4] obtained a transition at a critical value of the on-site repulsion U_c, using the variational wave function and the approximation scheme proposed by Gutzwiller.[5] However, using a criterion due to Kohn,[6] which relates the metallic behavior to the sensitivity of the ground-state energy to changes in the boundary conditions,[6,7] it has been recently shown that a large class of generalized Gutzwiller wave functions are always metallic.[8] On the other hand, the Mott transition in an infinite-dimensional Hubbard model has been recently studied with a highly accurate method[9,10] and the resulting value of U_c lies very near to the Brinkman-Rice result. These studies[9,10] also suggest the presence of a Kondo-like resonance of the Fermi energy of the metallic system, which agrees with recent experiments in d^1 transition-metal compounds.[11] Thus, although the Brinkman-Rice transition, as originally obtained,[4] is an artifact of the approximation, the result agrees with more elaborate calculations in infinite dimensions.

Another theoretical complication is that in systems with perfect nesting of the noninteracting Fermi surface, such as the Hubbard model in a square lattice, a gap is opened for any nonzero value of the interaction due to the formation of a spin-density wave (SDW). Thus, the system is always insulating and there is no Mott transition. Several models in which the band structure inhibits the formation of the SDW have been considered.[12–14] A semimetal-insulator transition was found in a Hubbard model in a honeycomb lattice,[13] and a Mott transition was obtained in a Bethe-ansatz study of a special two-dimensional (2D) Hubbard model.[14] The experimental situation[2,3,11] seems to suggest that although most Mott and charge-transfer insulators do have a SDW, the critical parameters of the transition can be determined from a study of the paramagnetic phase. This might be due to the absence of perfect nesting at the Fermi surface of real systems.

For the Hubbard model, the Brinkman-Rice transition was recovered using the saddle-point approximation of a slave-boson (SPSB) technique.[15] Similar approximations were applied by Balseiro *et al.*[16] and by Kotliar, Lee, and Read[17] to the three-band Hubbard model H Refs. (18 and 19) usually used to describe the electronic properties of CuO_2-based superconductors. Balseiro *et al.* find a metal-insulator phase diagram similar to that of Ref. 1 and that the cuprate superconductors should be classified as charge-transfer insulators,[16] in agreement with experiment. However, in order to obtain an insulating state with the treatment of Ref. 16 for large Cu intra-atomic repulsion U_d, the parameters of the three band Hubbard model [see Eqs. (1) and (2)] should satisfy $\Delta' = \epsilon'_p - \epsilon'_d > 4\sqrt{3}t_{pd} + 12t_{pd}^2/U_d$ (note the Erratum and the different definition of Δ used in Ref. 16). This condition is hard to satisfy if the values of the parameters are taken within the range of uncertainty of constrained-density-functional calculations.[20,21]

In this work we apply the SPSB technique to a previously derived one-band effective Hamiltonian $H_{\rm eff}$.[22] The main idea is that since the effective one-band models[20–22] take into account exactly the most important local correlations, it seems better to apply any approximation scheme to $H_{\rm eff}$ than directly to H. The risk of this procedure is that $H_{\rm eff}$ neglects states of local triplet character which are present in the low-lying excited eigenstates for hole-doped systems.[23,24] However, diagonalization of small systems suggest that the ground state for the undoped system and the system doped with one hole or one electron are well described by effective one-band models.[24] These are the energies which define the gap and the metal-insulator transition.

We obtain a metal-insulator phase diagram quali-

tatively similar to that obtained applying the SPSB to H (Ref. 16) or the alloy-analog approach (similar to Hubbard III) to $H_{\rm eff}$ (Ref. 22), but for realistic parameters[20,21] the comparison with the gap deduced from optical conductivity measurements[25–27] is improved with respect to the application of the SPSB technique directly to H. We also find that for sufficiently large values of the Cu-O repulsion U_{pd} [treated in the Hartree-Fock approximation; see Eq. (2)], an abrupt change in the Cu and O occupancies takes place as a function of $\Delta = \epsilon_p - \epsilon_d$ [see Eq. (1)] for a critical value of Δ inside the metallic phase but very near the metal-insulator boundary. This instability and several others were found previously in different approximate treatments of H,[18,28–35] but using a one-band effective Hamiltonian, it has been argued that for realistic parameters, the cuprates are far from charge-density-wave or charge-transfer instabilities.[21]

The derivation of the one-band model $H_{\rm eff}$ from the three-band Hubbard H (Refs. 18 and 19) is briefly reviewed in Sec. II. The slave-boson treatment of $H_{\rm eff}$ is explained in Sec. III.

Sections IV and V contain, respectively, the results and a discussion.

II. EFFECTIVE ONE-BAND HAMILTONIAN

The procedure we use to obtain an effective one-band Hamiltonian $H_{\rm eff}$ from the three-band one H was described in detail before[22] and is similar to the one used by Schüttler and Fedro.[21] It consists essentially in the following steps: (i) expressing the O orbitals in terms of Wannier functions localized at the Cu sites, (ii) exact diagonalization of the on-site Hamiltonian and sorting out of the ground state for zero, one, and two particles at the site, (iii) mapping of these states into the four states of a one-band model at one site, and (iv) calculating the intersite interactions in this basis.

The three-band Hubbard Hamiltonian can be written in the form[18,19]

$$\begin{aligned} H = {} & \epsilon_d \sum_{i\sigma} d^\dagger_{i\sigma} d_{i\sigma} + \epsilon_p \sum_{j\sigma} p^\dagger_{j\sigma} p_{j\sigma} \\ & + U_d \sum_i d^\dagger_{i\uparrow} d_{i\uparrow} d^\dagger_{i\downarrow} d_{i\downarrow} + U_p \sum_j p^\dagger_{j\uparrow} p_{j\uparrow} p^\dagger_{j\downarrow} p_{j\downarrow} \\ & + U_{pd} \sum_{i\delta\sigma\sigma'} d^\dagger_{i\sigma} d_{i\sigma} p^\dagger_{i+\delta\sigma'} p_{i+\delta\sigma'} \\ & + t_{pd} \sum_{i\delta\sigma} \left(p^\dagger_{i+\delta\sigma} d_{i\sigma} + \text{H.c.} \right). \end{aligned} \tag{1}$$

$d^\dagger_{i\sigma}$ creates a hole with spin σ on the Cu $3d_{x^2-y^2}$ orbital at site i, while $p^\dagger_{j\sigma}$ has a similar meaning for the O orbital at site j pointing towards their nearest-neighbor (NN) Cu atoms. δ labels the four-vectors $\pm a\hat{\mathbf{x}}/2$, $\pm a\hat{\mathbf{y}}/2$, and $i+\delta$ refer to the four O NN of Cu site i. The phases of half of the d and p orbitals have been changed by a factor -1 in such a way that $t_{pd} > 0$ for all directions.[35]

We treat the interatomic repulsion U_{pd} in the Hartree-Fock approximation. Thus, except for double counting terms, Eq. (1) is replaced by a form without this term and the one-particle energies replaced by

$$\begin{aligned} \epsilon'_d &= \epsilon_d + U_{pd} \sum_{\delta\sigma} \langle p^\dagger_{j\sigma} p_{j\sigma} \rangle, \\ \epsilon'_p &= \epsilon_p + 2U_{pd} \sum_{\sigma} \langle d^\dagger_{i\sigma} d_{i\sigma} \rangle, \\ t'_{pd} &= t_{pd} - U_{pd} \langle d^\dagger_{i\sigma} p_{i+\delta\sigma} \rangle. \end{aligned} \tag{2}$$

As explained in the Introduction, an homogeneous paramagnetic state is assumed. For simplicity we also take $U_p = 0$. Since the probability of double occupancy is very small for the undoped system, this approximation is not essential.

The one-band effective Hamiltonian takes the form

$$\begin{aligned} H_{\rm eff} = {} & E_1 \sum_{i\sigma} c^\dagger_{i\sigma} c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle ij \rangle \sigma} c^\dagger_{j\sigma} c_{i\sigma} \{ t_{BB} n_{i-\sigma} n_{j-\sigma} + t_{AB} [n_{i-\sigma}(1-n_{j-\sigma}) + (1-n_{i-\sigma}) n_{j-\sigma}] \\ & + t_{AA}(1-n_{i-\sigma})(1-n_{j-\sigma}) \} + C, \end{aligned} \tag{3}$$

where $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$ and

$$\begin{aligned} & C = N U_{pd} \sum_\delta \left\{ \left[\sum_\sigma \langle d^\dagger_{i\sigma} p_{i+\delta\sigma} \rangle \langle p^\dagger_{i+\delta\sigma} d_{i\sigma} \rangle - \left(\sum_\sigma \langle d^\dagger_{i\sigma} d_{i\sigma} \rangle \right) \left(\sum_\sigma \langle p^\dagger_{i+\delta\sigma} p_{i+\delta\sigma} \rangle \right) \right] \right\}, \\ & U = E_2 - 2E_1, \quad t_{AA} = -2a_0 a_1 t_1, \\ & t_{AB} = -\left[\frac{b_1}{\sqrt{2}} + a_0 a_1 (b_2 + b_0) \right] t_1, \quad t_{BB} = -\left[a_0 a_1 (2 b_0 b_2 + b_1^2) + \sqrt{2} b_1 (a_1^2 b_2 + a_0^2 b_0) \right] t_1, \end{aligned} \tag{4}$$

where

$$
\begin{aligned}
t_0 &= 1.912 t'_{pd}, \\
t_1 &= 0.280 t'_{pd}, \\
E_1 &= \left(\epsilon'_p + \epsilon'_d\right)/2 - \left[\left(\epsilon'_p - \epsilon'_d\right)^2/4 + t_0^2\right]^{1/2}, \\
a_1^2 &= 1 - a_0^2 = \frac{1}{2}\left\{1 + \frac{\epsilon'_p - \epsilon'_d}{2\left[\left(\epsilon'_p - \epsilon'_d\right)^2/4 + t_0^2\right]^{1/2}}\right\},
\end{aligned}
\tag{5}
$$

and E_2 and b_i are given by the energy and coefficients of the ground state of the following matrix:

$$
\begin{pmatrix}
2\epsilon'_p & \sqrt{2}t_0 & 0 \\
\sqrt{2}t_0 & \epsilon'_p + \epsilon'_d & \sqrt{2}t_0 \\
0 & \sqrt{2}t_0 & 2\epsilon'_d + U_d
\end{pmatrix}.
\tag{6}
$$

Finally, for $U_{pd} \neq 0$, it is necessary to express the mean values entering the self-consistency Eqs. (2) in terms of one-band operators:[22]

$$
\begin{aligned}
\langle d^\dagger_{i\sigma} d_{i\sigma}\rangle &= a_1^2\langle n_{i\sigma}(1-n_{i-\sigma})\rangle + \left(\frac{b_1^2}{2} + b_2^2\right)\langle n_{i\sigma}n_{i-\sigma}\rangle, \\
2\langle p^\dagger_{i\sigma} p_{i\sigma}\rangle &= a_0^2\langle n_{i\sigma}(1-n_{i\sigma})\rangle + \left(b_0^2 + \frac{b_1^2}{2}\right)\langle n_{i\sigma}n_{i-\sigma}\rangle, \\
\langle d^\dagger_{i\sigma} p_{i+\delta\sigma}\rangle &= 0.478\langle d^\dagger_{i\sigma}\alpha_{i\sigma}\rangle + 0.278\langle d^\dagger_{i\sigma}\alpha_{i+2\delta\sigma}\rangle,
\end{aligned}
\tag{7}
$$

$$
\begin{aligned}
\langle d^\dagger_{i\sigma}\alpha_{i\sigma}\rangle &= -a_0 a_1\langle n_{i\sigma}(1-n_{i-\sigma})\rangle - \frac{b_1}{\sqrt{2}}(b_0 - b_2)\langle n_{i\sigma}n_{i-\sigma}\rangle, \\
\langle d^\dagger_{i\sigma}\alpha_{i+2\delta\sigma}\rangle &= -a_0 a_1\langle (1-n_{i-\sigma})(1-n_{i+2\delta-\sigma})c^\dagger_{i\sigma}c_{i+2\delta\sigma}\rangle \\
&\quad + \left(a_0 b_0 + \frac{a_1 b_1}{\sqrt{2}}\right)\left(\frac{a_0 b_1}{\sqrt{2}} + a_1 b_2\right)\langle n_{i-\sigma}n_{i+2\delta-\sigma}c^\dagger_{i\sigma}c_{i+2\delta\sigma}\rangle \\
&\quad - \left[\left(a_0 b_0 + \frac{a_1 b_1}{\sqrt{2}}\right)a_1 + a_0\left(\frac{a_0 b_1}{\sqrt{2}} + a_1 b_2\right)\right]\langle n_{i-\sigma}(1-n_{i+2\delta-\sigma})c^\dagger_{i\sigma}c_{i+2\delta\sigma}\rangle.
\end{aligned}
\tag{8}
$$

α_i refers to the O Wannier function centered at the Cu site i.[22]

As an example, if one takes for the parameters of H the values[20,21] $\Delta = \epsilon_p - \epsilon_d = 4.5$ eV, $U_d = 9$ eV, $t_{pd} = 1.5$ eV, and $U_{pd} = 0$, the resulting parameters of H_{eff} are $t_{AA} = -0.33$ eV, $t_{BB} = -0.36$ eV, $t_{AB} = -0.37$ eV, and $U = 3.38$ eV. These values are close to those obtained in previous derivations of one-band effective models.[20,21] For $U_{pd} \neq 0$ the parameters of H_{eff} depend on its solution through the self-consistent Hartree-Fock equations.

III. SLAVE-BOSON APPROXIMATION

Our treatment is a simple generalization to occupation-dependent hopping of the saddle-point approximation (SPSB) applied by Kotliar and Ruckenstein to the Hubbard model.[15] The Fock space at each site i is enlarged introducing four boson states represented by the creation operators $e^\dagger_i$ (empty), $s^\dagger_{i\sigma}$ (singly occupied with spin σ), and $b^\dagger_i$ (doubly occupied). In the combined space H_{eff} reads:

$$
\begin{aligned}
H^{\text{SB}}_{\text{eff}} &= C + E_1\sum_{i\sigma} c^\dagger_{i\sigma}c_{i\sigma} + U\sum_i b^\dagger_i b_i \\
&\quad + \sum_{\langle ij\rangle\sigma} c^\dagger_{i\sigma}c_{j\sigma}\Big[t_{AA}X^\dagger_{i\sigma}X_{j\sigma} \\
&\qquad + t_{AB}\left(X^\dagger_{i\sigma}Y_{j\sigma} + Y^\dagger_{i\sigma}X_{j\sigma}\right) \\
&\qquad + t_{BB}Y^\dagger_{i\sigma}Y_{j\sigma}\Big],
\end{aligned}
\tag{9}
$$

where

$$
\begin{aligned}
X^\dagger_{i\sigma} &= (1 - e^\dagger_i e_i - s^\dagger_{i-\sigma}s_{i-\sigma})^{-1/2} \\
&\quad \times s^\dagger_{i\sigma}e_i(1 - b^\dagger_i b_i - s^\dagger_{i\sigma}s_{i\sigma})^{-1/2}, \\
Y^\dagger_{i\sigma} &= (1 - e^\dagger_i e_i - s^\dagger_{i-\sigma}s_{i-\sigma})^{-1/2} \\
&\quad \times b^\dagger_i s_{i\sigma}(1 - b^\dagger_i b_i - s^\dagger_{i\sigma}s_{i\sigma})^{-1/2},
\end{aligned}
\tag{10}
$$

and the following constraints should be satisfied:

$$
\begin{aligned}
&\sum_\sigma s^\dagger_{i\sigma}s_{i\sigma} + e^\dagger_i e_i + b^\dagger_i b_i = 1, \\
&c^\dagger_{i\sigma}c_{i\sigma} = s^\dagger_{i\sigma}s_{i\sigma} + b^\dagger_i b_i.
\end{aligned}
\tag{11}
$$

$X^\dagger_{i\sigma}, Y^\dagger_{i\sigma}$ were chosen in such a way that in the SPSB approximation, for $U = 0$ and $t_{AA} = t_{AB} = t_{BB}$, the exact result is recovered. Also, if like in the alloy-analog approach[22] $t_{AA} = t_{AB} = t_{BB} = 0$ is taken for only one spin direction, the SPSB technique reproduces the correct effective alloy problem.

In the SPSB approximation all boson fields are taken as time-independent constants. In the paramagnetic phase, eliminating the mean values of the fields e_i and $s_{i\sigma}$ by means of the constraints (11) for an occupation $n = \sum_\sigma\langle c^\dagger_{i\sigma}c_{i\sigma}\rangle$, the energy is given by the minimum with respect to $b = \langle b^\dagger_i\rangle$ of the expression

$$
E = C + Ub^2 + E_0(n, t_{\text{eff}}),
\tag{12}
$$

where E_0 is the energy of the noninteracting system with n particles per site and nearest-neighbor hopping given by

$$t_{\rm eff}(n,b) = (n/2-b^2)(n/2-n^2/4)^{-1}[t_{AA}(1+b^2-n) + 2t_{AB}b\sqrt{1+b^2-n}+t_{BB}b^2] \quad (13)$$

For a square lattice, it can be shown that, for $\mid n-1 \mid << 1$,

$$E_0(n,t) = \mid t \mid \left[-\frac{16}{\pi^2}+\frac{\pi^2(n-1)^2}{2\ln \mid 8/[\pi^2(n-1)] \mid}\right]+nE_1. \quad (14)$$

For n=1, minimization of Eq. (12) gives $b = t_{\rm eff} = 0$ for $U \geq U_c$, reflecting the insulating state. The critical value of U at the Brinkman-Rice transition is

$$U_c = \mid 8E_0(1,t_a) \mid, \quad (15)$$

where t_a is an average hopping energy:

$$t_a = (t_{AA}+t_{BB}+2t_{AB})/4. \quad (16)$$

For n=1 and $U \leq U_c$, the double occupancy is

$$b^2 = (1-U/U_c)/4. \quad (17)$$

Another quantity of interest is the magnitude of the gap in the insulating phase. It is given by the discontinuity of the chemical potential at n=1:

$$E_g = \left.\frac{\partial E}{\partial n}\right|_{1+} - \left.\frac{\partial E}{\partial n}\right|_{1-}. \quad (18)$$

For $n \to 1$, the leading terms in $\partial E/\partial n$ and $\partial E/\partial b$ are obtained deriving only the expression between the square brackets in Eq. (13), and b and E_g can be easily obtained analytically. The resulting gap is

$$E_g = \left[(U-U_c)\left(U-U_c\frac{t_{AA}+t_{BB}-2t_{AB}}{t_{AA}+t_{BB}+2t_{AB}}\right)\right]^{1/2}. \quad (19)$$

It is interesting to mention that E_g can be interpreted as the energy of an auxiliary Bose excitation, the softening of which is responsible for the transition to the metallic state.[36]

Finally, the mean values entering the second member of Eq. (8) (in the SPSB and paramagnetic phases) are given by

$$\begin{aligned}
&\langle n_{i\sigma}n_{i-\sigma}\rangle = \langle b_i^\dagger b_i\rangle = b^2,\\
&\langle n_{i\sigma}(1-n_{i-\sigma})\rangle = \langle s_{i\sigma}^\dagger s_{i\sigma}\rangle = \frac{n}{2}-b^2,\\
&\langle (1-n_{i-\sigma})(1-n_{j-\sigma})c_{i\sigma}^\dagger c_{j\sigma}\rangle = \langle X_{i\sigma}^\dagger X_{j\sigma}\rangle\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0,\\
&\langle n_{i-\sigma}n_{j-\sigma}c_{i\sigma}^\dagger c_{j\sigma}\rangle = \langle Y_{i\sigma}^\dagger Y_{j\sigma}\rangle\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0,\\
&\langle n_{i-\sigma}(1-n_{j-\sigma})c_{i\sigma}^\dagger c_{j\sigma}\rangle = \langle Y_{i\sigma}^\dagger X_{j\sigma}\rangle\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0,
\end{aligned} \quad (20)$$

where $\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle_0$ is calculated for nearest neighbors in a noninteracting system with nearest-neighbor hopping energy $t_{\rm eff}$. Using symmetry arguments, it is easy to relate this mean value to the kinetic energy of the system:

$$\langle c_{i\sigma}^\dagger c_{i+2\delta\sigma}\rangle_0 = \frac{E_0(n,t_{\rm eff})}{2zt_{\rm eff}}, \quad (21)$$

where z is the coordination number. For a square lattice and a half-filled system we have, from Eqs. (14) and (21),

$$\langle c_{i\sigma}^\dagger c_{i+2\delta\sigma}\rangle_0 = -\frac{2}{\pi^2}\frac{t_{\rm eff}}{\mid t_{\rm eff} \mid}. \quad (22)$$

IV. NUMERICAL PROCEDURE AND RESULTS

In order to solve the self-consistency conditions for $U_{pd} \neq 0$, we used a simple iterative procedure: (i) We choose the parameters of H [Eq. (1)] for which the metallic or insulating character or the charge-transfer gap is desired. (ii) We choose initial values for the expectation values entering the second member of Eqs. (2). These values are usually consistent with the solution one expects for the parameters of H chosen or are taken from a previously obtained result for similar parameters. (iii) Using Eqs. (2) and (4)–(6) we determine the parameters of $H_{\rm eff}$. (iv) $H_{\rm eff}$ is solved in the SPSB approximation explained in Sec. III. Using Eqs. (11), (17), (20), and (22) the mean values entering the first member of Eqs. (20) are calculated. (v) Using Eqs. (7) and (8) new initial expectation values are obtained and the procedure is repeated from step (ii) on, until convergence is obtained. In spite of the simplicity of the procedure, a rapid convergence was obtained. However, in regions of parameters where more than one solution is possible, we could not always find all of them.

In Fig. 1 we show the resulting metal-insulator phase diagram as a function of U_d and $\Delta = \epsilon_p - \epsilon_d$ for several values of U_{pd}. The hopping t_{pd} was taken as the unit of energy. The main effect of the increase of U_{pd} is to decrease the critical value of Δ for fixed U_d. The effect of U_{pd} in the insulating phase is to increase the charge-

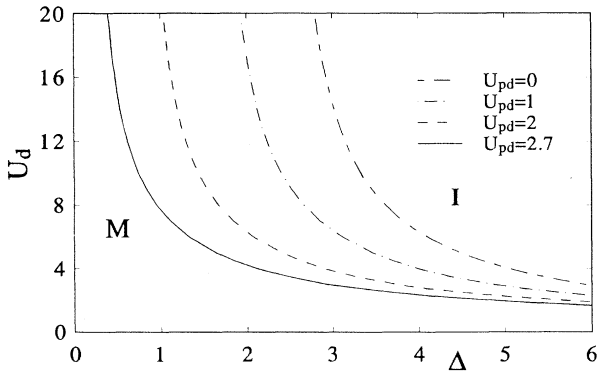

FIG. 1. Brinkman-Rice transition for the three-band Hubbard model [Eq. (1)], as a function of U_d and $\Delta = \epsilon_p - \epsilon_d$, for several values of U_{pd}. Other parameters are $U_p = 0$ and $t_{pd} = 1$.

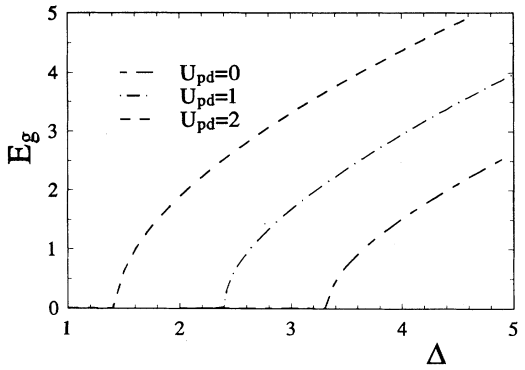

FIG. 2. Energy gap as a function of Δ for several values of U_{pd}. Other parameters are $U_d = 10, t_{pd} = 1, U_p = 0$.

transfer gap, as is clear from Fig. 2. In the Hartree-Fock approximation, increasing U_{pd} increases the effective on-site energy difference $\Delta' = \epsilon'_p - \epsilon'_d$ in the insulating phase and also the magnitude of t'_{pd} [see Eq. (2)]. The former effect, which contrary to the latter tends to increase the gap E_g, should be more important according to our results. In the metallic phase and for sufficiently low values of Δ, Δ' decreases with increasing U_{pd}.

In Fig. 3 we show the Cu on-site occupancy $n_{\mathrm{Cu}} = \langle d^\dagger_{i\uparrow} d_{i\uparrow}\rangle + \langle d^\dagger_{i\downarrow} d_{i\downarrow}\rangle$ as a function of Δ for two different values of U_{pd}. In the insulating phase $n_{\mathrm{Cu}} \approx 0.8$, in agreement with experimental observations in the undoped cuprates. As Δ is lowered n_{Cu} decreases and more rapidly after the transition to the metallic phase. In particular, for large U_{pd}, a transition from a regime for which $n_{\mathrm{Cu}} > n_{\mathrm{O}} = n - n_{\mathrm{Cu}}$ to another one for which $n_{\mathrm{Cu}} < n_{\mathrm{O}}$ takes place in a very narrow range of Δ. For $U_{pd} \geq 2.4$ and other parameters as in Fig. 3, the transition seems to be a first-order one, laying U^c_{pd} between 2.4 and 2.9. We cannot determine it accurately due to numerical difficulties. A similar transition was found previously using perturbative and variational methods,[28,29,31] $1/N$ expansion,[30,32–34] and in the strong-coupling ($t_{pd} \to 0$) limit of doped systems.[35] For these large values of U_{pd},

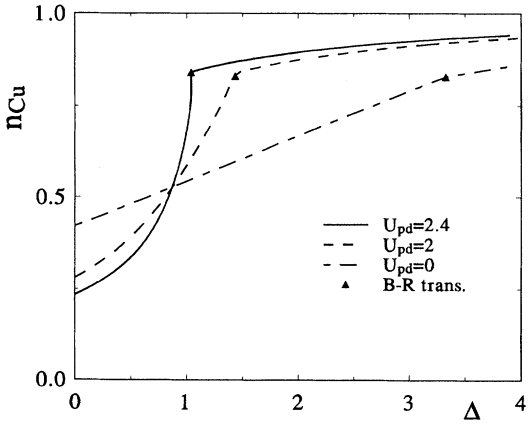

FIG. 3. On-site Cu occupancy $n_{\mathrm{Cu}} = \sum_\sigma \langle d^\dagger_{i\sigma} d_{i\sigma}\rangle$ as a function of Δ for several values of U_{pd}. Other parameters as in Fig. 2.

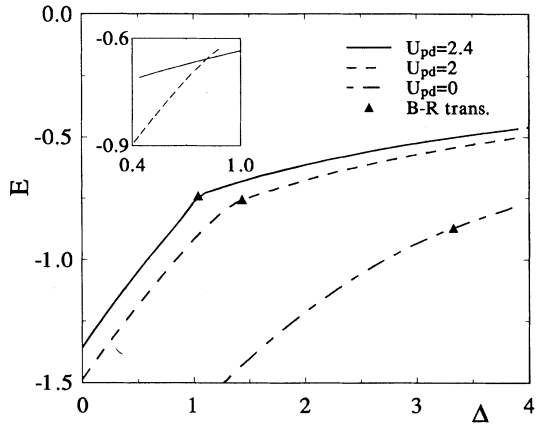

FIG. 4. Energy per Cu ion as a function of Δ for several values of U_{pd}. Other parameters as in Fig. 2. The inset shows a region of parameters where two self-consistent solutions have been found. The solid (dashed) line corresponds to the insulator (metallic) solution.

we have found two solutions of the self-consistency equations near the Brinkman-Rice transition. Their energy as a function of Δ is shown in Fig. 4. The inset corresponds to a $U_{pd} = 3$. There is a crossing between the metallic and the insulator energy solutions. The metallic solution has always lower on-site Cu occupancy than the insulator one, then this energy crossing produces a jump in the on-site Cu occupancy. This metal-insulator transition is thus of first order.

Finally, in Fig. 5 we show the mean value $\langle d^\dagger_{i\sigma} p_{i+\delta\sigma}\rangle$ as a function of Δ. For not too small values of Δ, as Δ is lowered, the magnitude of this mean value increases, particularly after the transition to the metallic state, indicating a larger degree of delocalization of the holes. The decrease in the magnitude of $\langle d^\dagger_{i\sigma} p_{i+\delta\sigma}\rangle$ with decreasing Δ for low values of Δ and large values of U_{pd} is due to the fact that the effective one-particle oxygen level ϵ'_p lies *below* the Cu one ϵ'_d [see Eqs. (2) and Fig. (3)] and the difference $\epsilon'_d - \epsilon'_p$ increases.

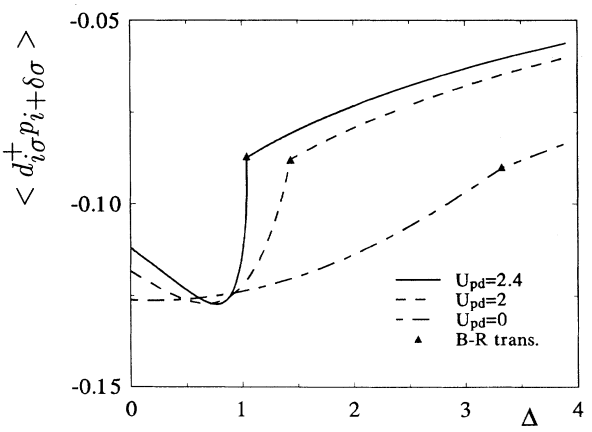

FIG. 5. Nearest-neighbor Cu-O correlation function $\langle d^\dagger_{i\sigma} p_{i+\delta\sigma}\rangle$ as a function of Δ for several values of U_{pd}. Other parameters as in Fig. 2.

V. DISCUSSION

We have obtained a metal-insulator phase diagram, energy gap, and other properties of undoped cuprate superconductors, using the saddle-point approximation of a slave-boson (SPSB) technique and an effective one-band model $H_{\rm eff}$ derived from the three-band one H. We believe that $H_{\rm eff}$ is accurate enough to describe the ground state and the gap of undoped systems.

The phase diagram is qualitatively similar to that obtained by applying the SPSB approximation directly to H (Ref. 16) or by applying the alloy-analog approach (Hubbard III) to $H_{\rm eff}$.[22] However, there are important quantitative differences. In comparison with the results of Ref. 16, the Brinkman-Rice transition is shifted to lower values of $\Delta = \epsilon_p - \epsilon_d$, improving the agreement with experiment for a range of reasonable parameters for La_2CuO_4 or other cuprates.[20,21,37] As an example, taking $U_d = 10$ eV, $U_{pd} = t_{pd} = 1$ eV, and $\Delta = 3$ eV we obtain, for the parameters of $H_{\rm eff}$, U=3.75 eV $t_{AA} = -0.20$ eV, $t_{AB} = -0.25$ eV, $t_{BB} = -0.22$ eV, and the material is an insulator with an energy gap $E_g = 1.67$ eV, in reasonable agreement with experiment.[25–27] Instead, applying the SPSB approximation directly to H one obtains that the paramagnetic system would be metallic. Another difference with the latter approach is that we have $\langle d^\dagger_{i\sigma} p_{i+\delta\sigma}\rangle \neq 0$ even in the insulating phase, since local charge fluctuations between the d orbital and the p Wannier function with the same symmetry are always allowed. In the alloy-analog approach to $H_{\rm eff}$, the metal-insulator transition is shifted to even lower values of Δ when compared with the present results.[22]

The advantage of applying the slave-boson techniques to $H_{\rm eff}$ instead of directly to H is that $H_{\rm eff}$ takes into account exactly the Cu intratomic Coulomb repulsion U_d and most of the hopping t_{pd}.[22] Thus, the errors involved in the mean-field treatment, particularly when the local constrains are replaced by average local ones,[38] are expected to be reduced.

For sufficiently large values of U_{pd}, we obtain a rapid change in the Cu and O valences as a function of Δ inside the metallic phase, near the metal-insulator transition (MIT). For U_{pd} larger than a critical value U^c_{pd} our results suggest that the change in valence is abrupt, becoming a charge-transfer instability (CTI) which coincides with the MIT. Thus, the MIT becomes first order for $U_{pd} > U^c_{pd}$. This is in agreement with Refs. 28–35. Also these studies show that the CTI is accompanied with phase separation. As explained in Ref. 32 phase separation is expected when the renormalized kinetic energy is no longer large enough to provide an upward curvature to the total energy as a function of doping. The CTI appears to be also related with superconductivity.[30,32] It is interesting to note that the critical value U^c_{pd} we obtain applying the SPSB technique to $H_{\rm eff}$ is similar to that obtained applying the $1/N$ expansion to $H_{\rm eff}$,[30,32–34] although some arguments in favor of much larger U^c_{pd} have been given.[21] This critical value might be underestimated by the Hartree-Fock approximation. Also, preliminary results applying the alloy-analog approach to $H_{\rm eff}$, as in Ref. 22, suggest that $U^c_{pd}/t_{pd} \sim 5$, nearly 2 times larger than the present result with the SPSB approximation.

A similar treatment as the one presented here can be applied to other perovskites and oxides. However, the derivation of the effective Hamiltonian depends on the particular atomic structure considered.

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