Transfer-integral expansion for the d-p model of the CuO_2 plane: A single hole in the antiferromagnetic state

Mitsuo Kataoka
Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980, Japan
(Received 28 March 1994)

The motion of a hole doped into the antiferromagnetic CuO_2 plane is studied by means of a perturbation theory on the basis of the d-p model. The existing perturbation theories are improved by calculating the perturbation corrections up to the third order of the transfer integrals and also by taking account of various spin-exchanged states explicitly. The calculated results show that the third-order perturbation correlation cannot change the qualitative properties of the hole motion and that the spin-exchanged states play a vital role in determining the band structure of the hole motion. The obtained lowest band of the hole is split off far away from upper excited bands and corresponds to spin-singlet states which consist of antiparallel spins of neighboring Cu d and O p orbits. The bottom of the lowest band appears at the same position in the reciprocal space as that obtained on the basis of the t-J model. Nevertheless, its bandwidth is much larger than that predicted by the t-J model, revealing quite different processes of the hole motion between the d-p and t-J models. The simplification of the d-p model by assuming an infinite Coulomb interaction U_d on Cu sites gives rise to a large quantitative change in the band structure for a set of realistic parameter values. This result is argued in connection with slave-boson theories of the d-p model.

I. INTRODUCTION

Since the discovery of the cuprate oxides with high superconducting transition temperatures T_c, many theoretical works on the CuO_2 plane have been accumulated. This is because the CuO_2 plane is the common frame of the high-T_c cuprates and is considered to be responsible for the electronic properties of those cuprates.[1] To understand the electronic state in the CuO_2 plane, Emery[2] has proposed the d-p model, where Cu $3d$ and two O $2p$ orbits are taken into account, and the strong Coulomb interactions between electrons play an essential role in determining the electronic state. This many-body system has been investigated by use of various sophisticated methods, such as exact diagonalization of the Hamiltonian for small clusters, perturbation theory, effective t-J Hamiltonian, slave-boson technique, and equation of motion for Green's function.[1] These theories succeeded in revealing various aspects of the many-electron system. However, applicabilities of these theories to a realistic d-p system still remain to be further investigated.

Among these methods, the t-J model was studied most frequently. This model was first proposed for an effective Hamiltonian of the single-band Hubbard model.[3] Zhang and Rice[4] extended this idea to the case of the multiband d-p system. Their scenario to describe the motion of a hole doped into the d-p system is as follows: As was proposed experimentally,[5] the electronic state in the cuprates corresponds to the charge-transfer (CT) type where one hole exists in every $d_{x^2-y^2}$ orbit on Cu ions in the undoped system and additionally doped holes enter into p orbits on O ions. For a state with a doped hole, we first consider combinations of p orbits on four O ions surrounding a central Cu ion. Among these combinations, only the one with the same symmetry as that of $d_{x^2-y^2}$ can hybridize with $d_{x^2-y^2}$. The lowest-energy state is realized if the p hole in the state of this combination and the central d hole have antiparallel spins to enter into a bonding state. A local spin-singlet state thus formed can coherently move through an effective transfer integral t and exchange interaction J. This scenario has been traced and applied to the d-p model by many authors. Some of them supported the validity of the t-J Hamiltonian[6] but the others did not.[7] Aiming to fix the realistic state of the doped hole on the basis of a firm ground, we go back in the present paper to the original d-p model and investigate this system by means of a perturbation theory, in which transfer integrals are expansion parameters.

The first perturbation calculation of the d-p system was done by Zaanen and Oleś.[8] They derived an effective Hamiltonian for the motion of a p hole within the second-order perturbation theory. On the basis of this effective Hamiltonian, they obtained the hole energy band in an assumed linear chain consisting of alternate d and p orbits by making a mean-field approximation for Cu spins. Matsukawa and Fukuyama[9] also made a second-order perturbation calculation to obtain the energy band of the doped hole in the realistic two-dimensional d-p lattice. Although both calculations could demonstrate how the doped hole can move, they are still too crude to clarify the characteristics of the hole motion in the CuO_2 plane. In the present paper, we improve the perturbation theory for the state of the hole doped into the d-p system with an antiferromagnetic spin structure in the following two respects: (i) We calculate the perturbation corrections to the energy of a hole state up to the third order of the transfer integrals between

neighboring d and p, and p and p orbits. The study of the third-order perturbation correction is important for testing the reliability of our low-order perturbation theory of the d-p model.

(ii) Within this accuracy, we take also spin-exchanged states into account, which will be shown to play a vital role in determining low-energy states of the hole.

The present paper is constructed as follows. In the next section, we introduce our d-p model and briefly summarize the properties of the d-p system with a doped hole in the absence of the transfer integral terms. Section III is devoted to get matrix elements between various hole states by use of the perturbation theory. These matrix elements are used in Sec. IV to construct the effective Hamiltonian. Results of numerical calculations are given in Sec. V. In Sec. VI, the present perturbation theory is discussed, being compared with other theories of the hole motion. Finally, conclusions are given in Sec. VII.

II. MODEL HAMILTONIAN AND PRELIMINARIES TO THE PERTURBATION CALCULATIONS

We consider a single CuO_2 plane, in which Cu and O are alternately situated along two, say x and y, directions perpendicular to each other. Until the antiferromagnetic ordering of Cu spins will be taken into consideration in Secs. IV and V, the unit cell is chosen to be the one in a lattice with no specific magnetic ordering, which contains Cu at (0,0), O at ($a/2$, 0), and O at (0, $a/2$), a being the lattice constant. (See Fig. 1.) The electron orbits relevant to our problem are $3d_{x^2-y^2}$ on Cu, $2p_x$ and $2p_y$ on O ions intervening two Cu sites in the x and y directions, respectively. The total Hamiltonian of this d-p system is assumed to be expressed in the hole picture as

$$H = H_0 + H_1 , \tag{1}$$

$$\begin{aligned} H_0 = & \sum_{i,s} \bar{\epsilon}_d b_{is}^{d\dagger} b_{is}^{d} + \sum_{ip} \sum_{s} \bar{\epsilon}_p b_{is}^{p\dagger} b_{is}^{p} \\ & + \tfrac{1}{2} \sum_{i,s} U_d \bar{n}_{is}^{d} \bar{n}_{i,-s}^{d} + \tfrac{1}{2} \sum_{ip} \sum_{s} U_p \bar{n}_{is}^{p} \bar{n}_{i,-s}^{p} \\ & + \sum_{\{id,\, jp\}} \sum_{s,s'} V \bar{n}_{is}^{d} \bar{n}_{js'}^{p} , \end{aligned} \tag{2}$$

$$H_1 = \sum_{\{id,\, jp\}} \sum_{s} (\bar{t}_{ij}^{dp} b_{is}^{d\dagger} b_{js}^{p} + \text{h.c.}) + \sum_{\{ip,\, jp'\}} \sum_{s} \bar{t}_{ij}^{pp'} b_{is}^{p\dagger} b_{js}^{p'} . \tag{3}$$

Here, d and p, $p'=x,y$ are the abbreviations of $d_{x^2-y^2}$, p_x and p_y, respectively, unit cells are numbered by $\mathbf{i} \equiv (i_x, i_y)$, b_{is}^{ν} and $\bar{n}_{is}^{\nu}$ ($\equiv b_{is}^{\nu\dagger} b_{is}^{\nu}$) with $\nu = d$, x and y are, respectively, the annihilation and number operators of a hole with spin s occupying the ν orbit in the ith unit cell, $\bar{\epsilon}_d$ and $\bar{\epsilon}_p$ ($=\bar{\epsilon}_x = \bar{\epsilon}_y$) are the bare energy levels of holes, U_d and U_p ($= U_x = U_y$) are the on-site Coulomb interactions, V is the Coulomb interaction between neighboring d and p holes, $\bar{t}_{ij}^{\nu\nu'}$'s are transfer integrals between the orbits $i\nu$ and $j\nu'$, and finally $\{ \cdots \}$ means pairs of neighboring orbits. When the phases of the orbits are chosen as usually, we have only the two independent transfer integrals $\bar{t}_{ii}^{dx} \equiv -\bar{t}_{dp}$ and $\bar{t}_{ii}^{yx} \equiv \bar{t}_{pp}$, to which other transfer integrals are related as shown in Fig. 1.

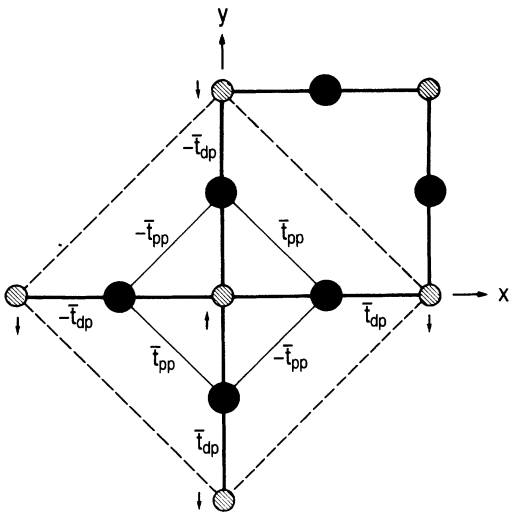

FIG. 1. Unit cells of the CuO_2 plane. The small shaded circles represent Cu atoms with the orbit $d_{x^2-y^2}$. The large black circles represent O atoms with the orbit p_x in the x direction and O atoms with the orbit p_y in the y direction. The bold and thin lines represent the transfer integrals with the magnitudes $|\bar{t}_{dp}|$ and $|\bar{t}_{pp}|$, respectively. The arrows attached to Cu sites represent their spins in the antiferromagnetic (AF) state. The square given by the bold lines is a unit cell assumed in the plane with no specific magnetic structure, while the square given by the thin dashed lines is a unit cell assumed in the plane with the AF state.

Before going into details of the perturbation calculations in the following sections, we here summarize the properties of the d-p system in the absence of both transfer terms. Corresponding to the CT-type state in the cuprates, the ground state is assumed to have one hole per each Cu ion. This ground state is denoted by $|g\rangle$, while other states, which have any charge distributions different from that in $|g\rangle$, are denoted by $|e\rangle$'s. Then, the energies of $|g\rangle$ and $|e\rangle$, E_g^0 and E_e^0, are written as

$$E_g^0 = N\bar{\epsilon}_d , \tag{4}$$

$$\begin{aligned} E_e^0 = E_g^0 + \sum_{i,\nu} & \{\bar{\epsilon}_\nu + \tfrac{1}{2} U_\nu (\langle \bar{n}_i^\nu \rangle_e + \langle \bar{n}_i^\nu \rangle_g - 1)\} \\ & \times \{\langle \bar{n}_i^\nu \rangle_e - \langle \bar{n}_i^\nu \rangle_g\} \\ & + V \sum_{\{id,\, jp\}} \sum \langle \bar{n}_j^p \rangle_e \{\langle \bar{n}_i^d \rangle_e - \langle \bar{n}_i^d \rangle_g\} \\ & + V \sum_{\{id,\, jp\}} \sum \langle \bar{n}_i^d \rangle_g \{\langle \bar{n}_j^p \rangle_e - \langle \bar{n}_j^p \rangle_g\} , \end{aligned} \tag{5}$$

where, $\langle \bar{n}_i^\nu \rangle_{g\ (\text{or}\ e)}$ represents the expected value of $\sum_s \bar{n}_{is}^\nu$ in the state $|g\ (\text{or}\ e)\rangle$, and N is the total number of Cu ions. By use of Eq. (5), the CT energy (i.e., the energy required for transferring a hole in a Cu site into a neighboring O site) is shown to be given by

$$\Delta_0 = -\bar{\epsilon}_d + \bar{\epsilon}_p + V . \tag{6}$$

Since our aim of this paper is to investigate states with

the doped hole, the states $|e\rangle$'s, which will be considered hereafter, are confined to be those with $(N+1)$ holes. By taking into account the experimental results,[5] the lowest-energy states of $|e\rangle$'s thus defined are assumed to have the extra hole on one of the O ions in addition to one hole per each Cu ion. From Eq. (5), we easily find that these $2N$-fold lowest-energy states have the energy

$$E_p^0=E_g^0+\bar{\epsilon}_p+2V \ . \tag{7}$$

The states $|e\rangle$'s are specified by both the charge distribution and the spin configuration. All of those states construct a complete set of orthogonal bases of the system with $(N+1)$ holes. The transfer terms mix $|e\rangle$'s with each other. To calculate the energy changes of low-energy states by the presence of the transfer terms, we further separate $|e\rangle$'s into two groups, i.e., one group, which contains only degenerate states with the lowest energy E_p^0, and the other group, which contains excited states. The states belonging to the former group are denoted by $|\alpha\rangle$'s, while the states belonging to the latter group are denoted by $|\beta\rangle$'s. In the following calculations, we assume that the differences between $E_\alpha^0\ (=E_p^0)$ and E_β^0's are sufficiently larger than the transfer integrals $|\bar{t}_{dp}|$ and $|\bar{t}_{pp}|$, E_β^0 being the energy of an excited state $|\beta\rangle$ in the absence of the transfer terms. Applying the perturbation theory[10] to our system, we express the effective matrix elements in the subspace spanned by the states $|\alpha\rangle$'s as follows:

$$H_{\alpha\alpha'}=\bar{H}_{\alpha\alpha'}+E_p^0\delta_{\alpha\alpha'} \ , \tag{8}$$

$$\bar{H}_{\alpha\alpha'}=(H_1)_{\alpha\alpha'}+\sum_{n=1}^{\infty}\frac{(H_1)_{\alpha\beta_1}(H_1)_{\beta_1\beta_2}\cdots(H_1)_{\beta_n\alpha'}}{[\bar{E}-(\bar{H}_0)_{\beta_1\beta_1}][\bar{E}-(\bar{H}_0)_{\beta_2\beta_2}]\cdots[\bar{E}-(\bar{H}_0)_{\beta_n\beta_n}]} \ , \tag{9}$$

with

$$\bar{E}=E_p-E_p^0 \ , \tag{10}$$

$$(\bar{H}_0)_{\beta_n\beta_n}=(E_{\beta_n}^0-E_g^0)-(E_p^0-E_g^0) \ , \tag{11}$$

where E_p is the total energy of the state with a doped hole in the presence of the transfer terms, and $\delta_{\alpha\alpha'}$ is Kronecker's delta. It is noted here that $\bar{H}_{\alpha\alpha'}$'s given by Eq. (9) are functions of $\bar{E}$, which is one of the eigenvalues of the matrix with the matrix elements $\bar{H}_{\alpha\alpha'}$'s themselves.

III. TRANSFER-INTEGRAL EXPANSION FOR THE MATRIX ELEMENTS

In this section, we derive the expressions of some representative matrix elements $\bar{H}_{\alpha\alpha'}$'s by use of Eq. (9). The derived matrix elements will be used in the next section to build the whole of the matrix, which determines the hole motion. When some of $|\alpha\rangle$'s have the doped hole in the ν ($=x$ or y) orbit on an O ion in the ith unit cell but have different spin configurations, such the states are represented by $|\mathrm{i}\nu\rangle$. Then, the matrix element between $|\mathrm{i}\nu\rangle$ and $|\mathrm{i}'\nu'\rangle$, $\bar{H}_{\mathrm{i}\nu,\mathrm{i}'\nu'}$, thus defined can be expressed in terms of spin operators not only of the doped hole but also of Cu d holes. All perturbation corrections to the matrix elements $\bar{H}_{\mathrm{i}\nu,\mathrm{i}'\nu'}$ are calculated up to the third order of $\bar{t}_{dp}$ and $\bar{t}_{pp}$.

A. The diagonal matrix elements

It is convenient for us to calculate separately the perturbation corrections from different types of ionic clusters (embedded in the lattice) in which all ions necessarily pertain to perturbation processes. In Fig. 2, we show such the clusters, which contribute to $\bar{H}_{\mathrm{ix,ix}}$. In each of the clusters, we look for possible excited states $|\beta\rangle$'s, which are created by transferring holes. For these $|\beta\rangle$'s, we calculate $(\bar{H}_0)_{\beta\beta}$'s by use of Eqs. (11) and (5), and also various matrix elements in Eq. (9), $(\bar{H}_{\alpha\beta})$'s and $(\bar{H}_{\beta\beta'})$'s corresponding to possible transfers of holes.[11] After substituting the obtained quantities into Eq. (9), we arrive at the following expression of $\bar{H}_{\mathrm{ix,ix}}$:

$$\begin{aligned}\bar{H}_{\mathrm{ix,ix}}=&\left\{\left[\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0-U_p+V}+\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}\right][1-2(\mathbf{S}_{\mathrm{i}}+\mathbf{S}_{\{\mathrm{i}+(1,0)\}})\cdot\mathbf{s}]\right\}^{(a)}\\&+(4N-8)\left\{\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0}\right\}^{(b)}+6\left\{\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}\right\}^{(c)}\\&+2\left\{\frac{-2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}[1-2(\mathbf{S}_{\mathrm{i}}+\mathbf{S}_{\{\mathrm{i}+(1,0)\}})\cdot\mathbf{s}]\right\}^{(d)}\\&+(4N-8)\left\{\frac{-2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)^2}\right\}^{(e)}+4\left\{\frac{-2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\right\}^{(f)}\equiv\mathcal{T}_0(\mathbf{S}_{\mathrm{i}},\mathbf{S}_{\{\mathrm{i}+(1,0)\}}) \ .\end{aligned} \tag{12}$$

In this equation, $\mathbf{S}_i$ and $\mathbf{s}$ are, respectively, the spin operator of the Cu d hole in the ith unit cell and that of the itinerant doped hole, whereas the constant terms, which do not contain spin operators, have been defined to give no effect on the spin space. On the right-hand side of Eq. (12), the quantity in $\{\cdots\}^{(b)}$, for example, means the contribution from the cluster (b) in Fig. 2, and its multiplication factor to the bracket is the number of the same type of clusters as that in (b). The clusters (b) and (e) are disconnected to the O ion with the doped hole. This allows the numbers of clusters belonging to (b) and (e) to be $(4N-8)$, which will be derived in Appendix A. A symmetry consideration on the CuO_2 plane proves

$$\overline{H}_{iy,iy}=\mathcal{T}_0(\mathbf{S}_i,\mathbf{S}_{\{i+(0,1)\}}) . \tag{13}$$

B. The matrix elements between the nearest-neighboring x and y orbits

The clusters, which contribute to $\overline{H}_{iy,ix}$, are shown in Fig. 3. We make the perturbation calculations similar to those in Sec. III A for the clusters in Fig. 3 to obtain

$$\begin{aligned}\overline{H}_{iy,ix}=&\{\bar{t}_{pp}\}^{(g)}+\left\{\frac{-\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}(\tfrac{1}{2}-2\mathbf{S}_i\cdot\mathbf{s})+\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}(\tfrac{1}{2}+2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(h)}\\
&+\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}(\tfrac{1}{2}-2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(i)}\\
&+\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)(\bar{E}-\Delta_0-U_p+V)}[1-2(\mathbf{S}_{\{i+(1,0)\}}+\mathbf{S}_{\{i+(0,1)\}})\cdot\mathbf{s}]\right\}^{(j)}+\left\{\frac{-\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}(\tfrac{1}{2}+2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(k)}\\
&+2\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\right\}^{(l)}+\left\{\frac{-\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}(\tfrac{1}{2}+2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(m)}\\
&+3\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)(\bar{E}-\Delta_0)}\right\}^{(n)}+3\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)(\bar{E}-\Delta_0)}\right\}^{(o)}+(4N-12)\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)^2}\right\}^{(p)}\\
&\equiv\mathcal{T}_1(\mathbf{S}_i,\mathbf{S}_{\{i+(1,0)\}},\mathbf{S}_{\{i+(0,1)\}}) ,\end{aligned} \tag{14}$$

where the factor $(4N-12)$ also will be derived in Appendix A.

Making symmetry considerations, we can easily prove the following equations:

$$\overline{H}_{\{i+(0,1)\}x,iy}=-\mathcal{T}_1(\mathbf{S}_{\{i+(0,1)\}},\mathbf{S}_i,\mathbf{S}_{\{i+(1,1)\}}) , \tag{15}$$

$$\overline{H}_{\{i+(1,0)\}y,\{i+(0,1)\}x}=\mathcal{T}_1(\mathbf{S}_{\{i+(1,1)\}},\mathbf{S}_{\{i+(0,1)\}},\mathbf{S}_{\{i+(1,0)\}}) , \tag{16}$$

$$\overline{H}_{ix,\{i+(1,0)\}y}=-\mathcal{T}_1(\mathbf{S}_{\{i+(1,0)\}},\mathbf{S}_{\{i+(1,1)\}},\mathbf{S}_i) . \tag{17}$$

C. The matrix elements between the second-neighboring ν orbits in the ν direction

The clusters that contribute to $\overline{H}_{\{i-(1,0)\}x,ix}$ are shown in Fig. 4. The perturbation calculations for these clusters result in

$$\overline{H}_{\{i-(1,0)\}x,ix}=\left\{\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}(\tfrac{1}{2}+2\mathbf{S}_i\cdot\mathbf{s})+\frac{-\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}(\tfrac{1}{2}-2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(q)}+2\left\{\frac{-2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}(\tfrac{1}{2}+2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(r)}\equiv\mathcal{T}_2(\mathbf{S}_i) . \tag{18}$$

We again make a symmetry consideration to get

$$\overline{H}_{\{i-(0,1)\}y,iy}=\mathcal{T}_2(\mathbf{S}_i) . \tag{19}$$

D. The matrix elements between the second neighboring ν orbits in the $\nu'(\neq\nu)$ direction

The clusters that contribute to $\overline{H}_{\{i+(0,1)\}x,ix}$ are shown in Fig. 5. Making parallel perturbation calculations and symmetry considerations, we get

$$\bar{H}_{\{i+(0,1)\}x,ix}=\left\{\frac{-\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)(\bar{E}-\Delta_0+V)}[2+2(\mathbf{S}_i+\mathbf{S}_{\{i+(1,0)\}}+\mathbf{S}_{\{i+(0,1)\}}+\mathbf{S}_{\{i+(1,1)\}})\cdot\mathbf{s}]\right\}^{(s)}$$
$$\equiv\mathcal{T}_3(\mathbf{S}_i,\mathbf{S}_{\{i+(1,0)\}},\mathbf{S}_{\{i+(0,1)\}},\mathbf{S}_{\{i+(1,1)\}}) , \tag{20}$$
$$\bar{H}_{\{i+(1,0)\}y,iy}=\mathcal{T}_3(\mathbf{S}_i,\mathbf{S}_{\{i+(1,0)\}},\mathbf{S}_{\{i+(0,1)\}},\mathbf{S}_{\{i+(1,1)\}}) . \tag{21}$$

E. The matrix elements between third-neighboring ν orbits

The clusters that contribute to $\bar{H}_{\{i+(-1,1)\}x,ix}$ are shown in Fig. 6. Parallel procedures to those in the above give

$$\bar{H}_{\{i+(-1,1)\}x,ix}=\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)(\bar{E}-\Delta_0)}[1+2(\mathbf{S}_i+\mathbf{S}_{\{i+(0,1)\}})\cdot\mathbf{s}]\right\}^{(t)}\equiv\mathcal{T}_4(\mathbf{S}_i,\mathbf{S}_{\{i+(0,1)\}}) , \tag{22}$$
$$\bar{H}_{\{i+(0,1)\}x,\{i-(1,0)\}x}=\mathcal{T}_4(\mathbf{S}_i,\mathbf{S}_{\{i+(0,1)\}}) , \tag{23}$$
$$\bar{H}_{\{i-(1,1)\}x,ix}=\bar{H}_{\{i-(0,1)\}x,\{i-(1,0)\}x}=\mathcal{T}_4(\mathbf{S}_i,\mathbf{S}_{\{i-(0,1)\}}) , \tag{24}$$
$$\bar{H}_{\{i-(1,1)\}y,iy}=\bar{H}_{\{i-(1,0)\}y,\{i-(0,1)\}y}=\mathcal{T}_4(\mathbf{S}_i,\mathbf{S}_{\{i-(1,0)\}}) , \tag{25}$$
$$\bar{H}_{\{i+(1,-1)\}y,iy}=\bar{H}_{\{i+(1,0)\}y,\{i-(0,1)\}y}=\mathcal{T}_4(\mathbf{S}_i,\mathbf{S}_{\{i+(1,0)\}}) . \tag{26}$$

F. The matrix elements between the fourth-neighboring ν orbits

The only cluster which contributes to $\bar{H}_{\{i-(1,0)\}y,ix}$ is shown in Fig. 7. For this cluster, we get

$$\bar{H}_{\{i-(1,0)\}y,ix}=\left\{\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)(\bar{E}-\Delta_0+V)}(\tfrac{1}{2}+2\mathbf{S}_i\cdot\mathbf{s})\right\}^{(u)}\equiv\mathcal{T}_5(\mathbf{S}_i) , \tag{27}$$

$$\begin{aligned}\bar{H}_{\{i+(1,-1)\}y,\{i-(1,0)\}x}&=-\bar{H}_{\{i-(1,1)\}y,ix}\\&=-\bar{H}_{\{i+(1,0)\}y,\{i-(1,0)\}x}=\bar{H}_{\{i-(0,1)\}x,iy}\\&=\bar{H}_{\{i+(-1,1)\}x,\{i-(0,1)\}y}=-\bar{H}_{\{i-(1,1)\}x,iy}\\&=-\bar{H}_{\{i+(0,1)\}x,\{i-(0,1)\}y}=\mathcal{T}_5(\mathbf{S}_i) .\end{aligned} \tag{28}$$

The matrix elements given by Eqs. (12) and (14) contain terms proportional to N. As will be proved in Appendix B, those terms should give the perturbation correction to the unperturbed energy E_g^0 of the undoped d-p system, $(E_g-E_g^0)$, E_g being the total energy of the undoped system in the presence of the transfer terms.[11] In the following calculations, therefore, we drop out all terms proportional to N from the expressions of the matrix elements by replacing E_p^0 in Eqs. (8), (10), and (11) by $E_p^0+(E_g-E_g^0)$. Then, E_p is given by

$$E_p=(E_g+\bar{\epsilon}_p+2V)+\bar{E} , \tag{29}$$

where $\bar{E}$ is an eigenvalue of the new matrix independent of N.

IV. HOLE MOTION IN THE ANTIFERROMAGNETIC STATE

Spins of neighboring Cu d holes interact with each other through the superexchange interaction J, which is of the fourth order of the transfer integrals.[4,8,9,11] The interaction J orders Cu spins antiferromagnetically in the undoped and doped systems. We are, therefore, interested in the motion of the hole doped into a p orbit in the antiferromagnetic (AF) background of Cu d spins. The unit cell of the AF state is chosen to be the one which is shown also in Fig. 1. This new lattice is separated into sublattices specified by spins ↑ and ↓. In the ↑ sublattice, cells are numbered by $\mathbf{i}=(i_x,i_y)$ with $i_x+i_y=2l$, l being any integers, and all d holes are assumed to have ↑ spins, while in the ↓ sublattice, cells are numbered by $\mathbf{i}=(i_x,i_y)$ with $i_x+i_y=2l+1$, and all Cu d holes are assumed to have ↓ spins. Without loss of generality, we assume that a hole with ↓ spin is doped into the AF d-p system. (Notice that the doped-hole states with ↑ spin and with ↓ spin are energetically degenerate in the AF background.) Then, the doped hole on one of O ions can transfer to neighboring Cu d orbits in the ↑ sublattice. Therefore, it is convenient for us to choose unit cells so that the ith unit cell in the ↑ sublattice contains the orbits $\mathbf{i}d$, $\mathbf{i}x$, $\mathbf{i}y$, $\{\mathbf{i}-(1,0)\}x(\equiv\mathbf{i}\bar{x})$ and $\{\mathbf{i}-(0,1)\}y(\equiv\mathbf{i}\bar{y})$, and the ith unit cell in the ↓ sublattice contains only the $\mathbf{i}d$ orbit.

As has been studied in the preceding section, the doped hole can itinerate in the crystal not only through the direct transfer term $\bar{t}_{pp}$ but also through the indirect transfer terms given by the perturbation corrections.

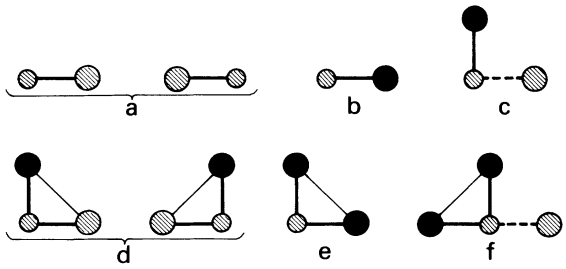

FIG. 2. Types of clusters that contribute to $\overline{H}_{ix,ix}$. The small shaded circles represent Cu sites with $d_{x^2-y^2}$ occupied by a hole, while the large black circles represent O sites with p_x and p_y occupied by no hole. The large shaded circles represent the O site with the ix orbit occupied by the doped hole. The bold and thin lines represent the transfer integrals, which are all used in the perturbation processes. The bold dotted lines represent the Coulomb interactions V, which affect the perturbation corrections. It is noted that the clusters (b) and (e) are disconnected to the O site with the doped hole.

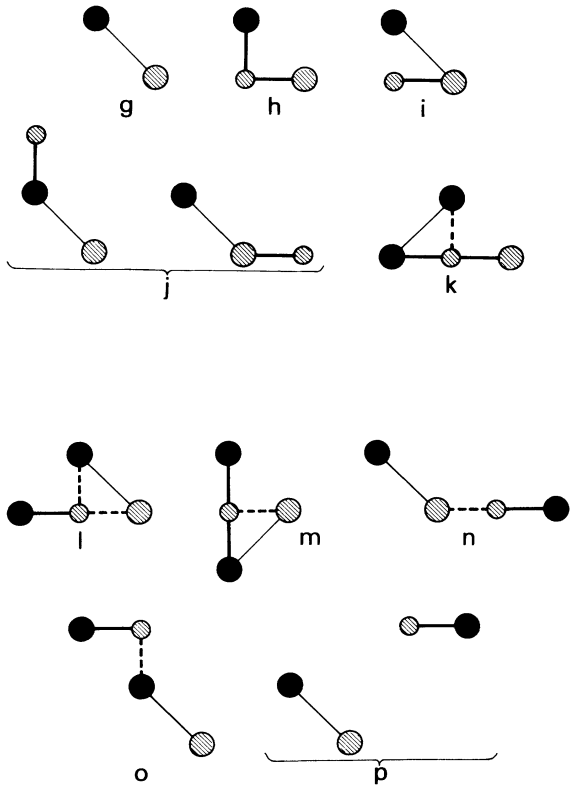

FIG. 3. Types of clusters that contribute to $\overline{H}_{iy,ix}$. The large shaded circles are O sites with the ix orbit occupied by the doped hole. Their nearest neighboring, large black circles [the upper one in the case of (m)] are O sites with the iy orbit to which the doped hole transfers. Note that the cluster (p) consists of two subclusters, which are disconnected from each other. For other symbols, see Fig. 2.

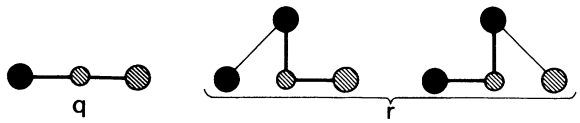

FIG. 4. Types of clusters that contribute to $\overline{H}_{\{i-(1,0)\}x,ix}$. The large shaded circles are O sites with the ix orbit occupied by the doped hole. Their second neighboring, large black circles are O sites with the $\{i-(1,0)\}x$ orbit to which the doped hole transfers. For other symbols, see Fig. 2.

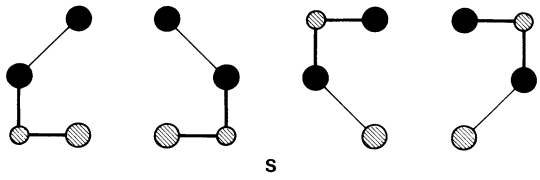

FIG. 5. Type of clusters that contribute to $\overline{H}_{\{i+(0,1)\}x,ix}$. The large shaded circles are O sites with the ix orbit occupied by the doped hole. Their second neighboring, large black circles are O sites with the $\{i+(0,1)\}x$ orbit to which the doped hole transfers. For other symbols, see Fig. 2.

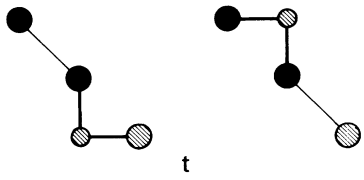

FIG. 6. Type of clusters that contribute to $\overline{H}_{\{i+(-1,1)\}x,ix}$. The large shaded circles are O sites with the ix orbit occupied by the doped hole. Their second neighboring, large black circles are O sites with the $\{i+(-1,1)\}x$ orbit to which the doped hole transfers. For other symbols, see Fig. 2.

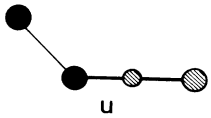

FIG. 7. Type of clusters that contribute to $\overline{H}_{\{i-(1,0)\}y,ix}$. The large shaded circle is the O site with the ix orbit. Its second-neighboring, large black circle is the O site with a $\{i-(1,0)\}y$ orbit to which the doped hole transfers. For other symbols, see Fig. 2.

This itineracy is done with and without fluctuating spins of d and p holes. This means that all of the states with various p orbits occupied by the doped hole and various spin configurations produced by the hole itineracy can be included by the group $|\alpha\rangle$'s, which has been defined in Sec. II.

In order to find $|\alpha\rangle$'s relevant to our interest, we first consider the case where the doped hole can itinerate only in a unit cell, say the ith unit cell, of the $\uparrow$ sublattice. Within the third-order perturbation approximation, the hole itineracy in this case produces the following twelve states:

$$
\begin{aligned}
&|\mathbf{i}x1\rangle \equiv |\mathbf{i}d\uparrow, \mathbf{i}x\downarrow, \{\mathbf{i}+(1,0)\}d\downarrow\rangle \ , \\
&|\mathbf{i}y1\rangle \equiv |\mathbf{i}d\uparrow, \mathbf{i}y\downarrow, \{\mathbf{i}+(0,1)\}d\downarrow\rangle \ , \\
&|\mathbf{i}\bar{x}1\rangle \equiv |\mathbf{i}d\uparrow, \{\mathbf{i}-(1,0)\}x\downarrow, \{\mathbf{i}-(1,0)\}d\downarrow\rangle \ , \\
&|\mathbf{i}\bar{y}1\rangle \equiv |\mathbf{i}d\uparrow, \{\mathbf{i}-(0,1)\}y\downarrow, \{\mathbf{i}-(0,1)\}d\downarrow\rangle \ , \\
&|\mathbf{i}x2\rangle \equiv |\mathbf{i}d\downarrow, \mathbf{i}x\uparrow, \{\mathbf{i}+(1,0)\}d\downarrow\rangle \ , \\
&|\mathbf{i}y2\rangle \equiv |\mathbf{i}d\downarrow, \mathbf{i}y\uparrow, \{\mathbf{i}+(0,1)\}d\downarrow\rangle \ , \\
&|\mathbf{i}\bar{x}2\rangle \equiv |\mathbf{i}d\downarrow, \{\mathbf{i}-(1,0)\}x\uparrow, \{\mathbf{i}-(1,0)\}d\downarrow\rangle \ , \\
&|\mathbf{i}\bar{y}2\rangle \equiv |\mathbf{i}d\downarrow, \{\mathbf{i}-(0,1)\}y\uparrow, \{\mathbf{i}-(0,1)\}d\downarrow\rangle \ , \\
&|\mathbf{i}x3\rangle \equiv |\mathbf{i}d\downarrow, \mathbf{i}x\downarrow, \{\mathbf{i}+(1,0)\}d\uparrow\rangle \ , \\
&|\mathbf{i}y3\rangle \equiv |\mathbf{i}d\downarrow, \mathbf{i}y\downarrow, \{\mathbf{i}+(0,1)\}d\uparrow\rangle \ , \\
&|\mathbf{i}\bar{x}3\rangle \equiv |\mathbf{i}d\downarrow, \{\mathbf{i}-(1,0)\}x\downarrow, \{\mathbf{i}-(1,0)\}d\uparrow\rangle \ , \\
&|\mathbf{i}\bar{y}3\rangle \equiv |\mathbf{i}d\downarrow, \{\mathbf{i}-(0,1)\}y\downarrow, \{\mathbf{i}-(0,1)\}d\uparrow\rangle \ .
\end{aligned}
\tag{30}
$$

In the above definitions, $|\mathbf{i}\nu\mu\rangle$ represents the state, which has the μth spin configuration and the doped hole in the ν orbit around the ith unit cell belonging to the $\uparrow$ sublattice. $|\mathbf{i}\nu s, \mathbf{i}'\nu' s', \mathbf{i}''\nu'' s''\rangle$, on the other hand, represents the state in which the orbits $\mathbf{i}\nu$, $\mathbf{i}'\nu'$, and $\mathbf{i}''\nu''$ have holes with spins s, s', and s'', respectively, and all other d holes have the same spin directions as those in the AF state. In the states $|\mathbf{i}\nu 1\rangle$'s, any d-hole spin is not exchanged by any other spins, while in the states $|\mathbf{i}\nu 2\rangle$'s and $|\mathbf{i}\nu 3\rangle$'s, some of d-hole spins are exchanged by other d-hole spins or the doped-hole spin. In this paper, the former states are called spin-unexchanged states and the latter states are called spin-exchanged states.

We second consider the case where the doped hole in the ith unit cell is released to transfer into p orbits in neighboring unit cells. Since local states around the doped hole have their own spin configurations, some of the hole transfers leave spin configurations distort from that of the AF state. Successive operations of such the transfers result in many different states in which d-spin directions are different from those in the AF state even in regions far from the doped hole. The resultant states can gain the transfer energies to attain their low energies but cannot become coherent states of the hole motion spread over the crystal. Contrary to these hole transfers, other hole transfers conserve or repair spin configurations around the ith unit cell to be that in the AF state. In other words, the doped hole itinerates in the crystal by accompanying spin configurations distorted only in a definite region around the mobile hole. Such hole transfers result in coherent states of the hole motion. It is noted here that these coherent states are not entirely free from the incoherent states discussed above. This is because they still mix with each other by repairing wrong directions of d spins via spin-exchange and higher-order perturbation processes. In this paper, we focus our attention on the coherent states by neglecting effects of the incoherent states. Then, a hole transfer between p orbits can be regarded as a transfer from one state $|\mathbf{i}\nu\mu\rangle$ into another state $|\mathbf{i}'\nu'\mu'\rangle$ in our approximation. The above considerations prove that the group of $|\alpha\rangle$'s consists of the states $|\mathbf{i}\nu\mu\rangle$'s with any $\mathbf{i}$, ν, and μ whose total number is $12(N/2)$.

Our effective Hamiltonian in the subspace spanned by $|\mathbf{i}\nu\mu\rangle$'s can be expressed as

$$
\begin{aligned}
\bar{H} &= \sum_{\mathbf{i}\mathbf{i}'} \sum_{\nu\nu'} \sum_{\mu\mu'} \bar{H}_{\mathbf{i}\nu\mu,\mathbf{i}'\nu'\mu'} B^{\dagger}_{\mathbf{i}\nu\mu} B_{\mathbf{i}'\nu'\mu'} \\
&= \sum_{\mathbf{k}} \sum_{\nu\nu'} \sum_{\mu\mu'} \bar{H}_{\nu\mu,\nu'\mu'}(\mathbf{k}) B^{\dagger}_{\nu\mu}(\mathbf{k}) B_{\nu'\mu'}(\mathbf{k}) \ .
\end{aligned}
\tag{31}
$$

Here, $B_{\mathbf{i}\nu\mu}$ is the annihilation operator of the state $|\mathbf{i}\nu\mu\rangle$ and $\bar{H}_{\mathbf{i}\nu\mu,\mathbf{i}'\nu'\mu'}$ is the matrix element between $|\mathbf{i}\nu\mu\rangle$ and $|\mathbf{i}'\nu'\mu'\rangle$. Their Fourier components have been defined by

$$
B_{\nu\mu}(\mathbf{k}) = \sqrt{2/N} \sum_{\mathbf{i}} B_{\mathbf{i}\nu\mu} e^{-i\mathbf{k}\cdot\mathbf{R}_{\mathbf{i}}} \ , \tag{32}
$$

$$
\bar{H}_{\nu\mu,\nu'\mu'}(\mathbf{k}) = \sum_{\mathbf{i}} \bar{H}_{\mathbf{i}\nu\mu,\mathbf{i}'\nu'\mu'} e^{-i\mathbf{k}\cdot(\mathbf{R}_{\mathbf{i}}-\mathbf{R}_{\mathbf{i}'})} \ , \tag{33}
$$

where $\mathbf{R}_{\mathbf{i}}$ is the position vector of the ith unit cell belonging to the $\uparrow$ sublattice and a wave vector $\mathbf{k}$ is in the first Brillouin zone of the AF state shown in Fig. 8. As the result, an eigenvalue $\bar{E}$ of the matrix $\bar{\mathbf{H}}(\mathbf{k})$ $(\equiv\{\bar{H}_{\nu\mu,\nu'\mu'}(\mathbf{k})\})$ gives the energy of a coherent state of the hole motion, while a linear combination of $B_{\nu\mu}(\mathbf{k})$'s corresponding to the eigenvalue gives the annihilation operator of the coherent state.

For our arguments, it is convenient to decompose the matrix $\bar{\mathbf{H}}(\mathbf{k})$ into the submatrices $\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})$'s as follows:

$$
\bar{\mathbf{H}}(\mathbf{k}) \equiv \{\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})\} \quad (\mu,\mu' = 1,\ 2,\ \text{and}\ 3) \ , \tag{34}
$$

$$
\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k}) \equiv \{\bar{H}_{\nu\mu,\nu'\mu'}(\mathbf{k})\} \quad (\nu,\nu' = x,\ y,\ \bar{x},\ \text{and}\ \bar{y}) \ . \tag{35}
$$

$\bar{\mathbf{H}}_{11}(\mathbf{k})$ has the matrix elements between only the states with the ground configuration of Cu d spins and, therefore, the eigenvalues of $\bar{\mathbf{H}}_{11}(\mathbf{k})$ give the energies of the hole motion accompanying no spin fluctuation. On the other hand, the eigenvalues of $\bar{\mathbf{H}}_{22}(\mathbf{k})$ and $\bar{\mathbf{H}}_{33}(\mathbf{k})$ give the energies of the localized states, which cannot itinerate in the AF background without the aid of spin fluctuations. (See Appendix C.) The nonvanishing matrices' $\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})$'s with μ or $\mu'=1$ mix those itinerant and localized states so that even the states with the spin configurations $\mu=2$ and 3 can have dispersions.

To derive $\bar{\mathbf{H}}(\mathbf{k})$ or $\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})$'s, we first calculate by use of Eqs. (12)–(28) the matrix elements of the spin Hamiltonians $\bar{H}_{\mathbf{i}\nu,\mathbf{i}'\nu'}$'s between the spin states $\mu=1$, 2, and 3 to obtain $\bar{H}_{\mathbf{i}\nu\mu,\mathbf{i}'\nu'\mu'}$'s, and second substitute $\bar{H}_{\mathbf{i}\nu\mu,\mathbf{i}'\nu'\mu'}$ into Eq. (33) to arrive at $\bar{H}_{\nu\mu,\nu'\mu'}(\mathbf{k})$'s. The obtained results are summarized in Appendix C. The final procedure we

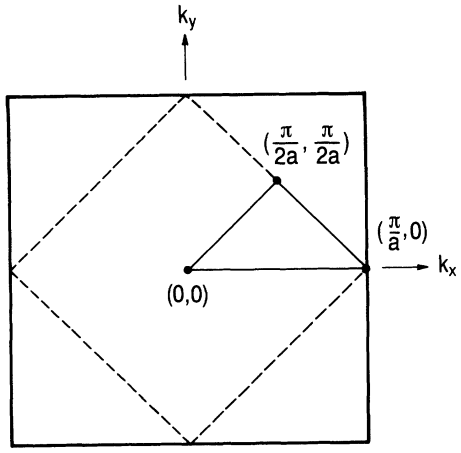

FIG. 8. First Brillouin zones of the CuO_2 plane. The zone in the CuO_2 plane with no spin structure is given by the bold lines, while the zone in the CuO_2 plane with the AF state is given by the dashed lines. The calculations of the hole bands were done along the thin lines.

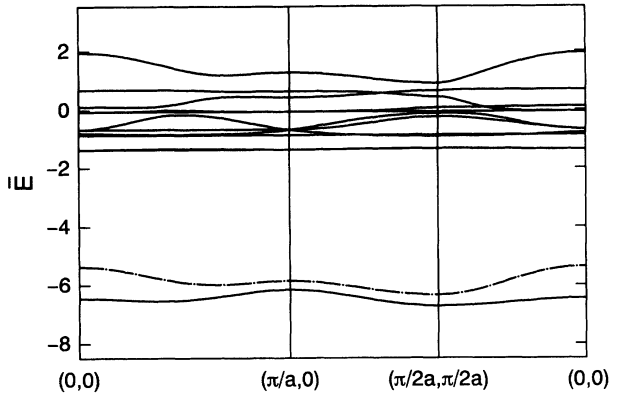

FIG. 9. Energy bands of the hole motion. The solid lines are the energy bands, which were calculated by taking account of the perturbation corrections up to the second order of the transfer integrals $\bar{t}_{dp}$ and $\bar{t}_{pp}$. The dotted chain line is the lowest band, which was calculated by taking account of the perturbation corrections up to the third order of $\bar{t}$'s. The parameter values used are given in (36). Energies are in units of eV.

must do is to look for the eigenvalues $\bar{E}$'s of $\bar{\mathbf{H}}(\mathbf{k})$. When we get $\bar{E}$'s within the accuracy up to the second order of $\bar{t}$'s, we can neglect all $\bar{E}$'s in the expressions of matrix elements. This is because $\bar{E}$ should begin with the first order of $\bar{t}_{pp}$ if $\bar{E}$ can be expanded in powers of $\bar{t}$'s. When, on the other hand, we improve the accuracy up to the third order of $\bar{t}$'s, we get $\bar{E}$ in the following way. We neglect $\bar{E}$'s in all third-order terms, but we expand $\bar{E}$'s in the denominators of all second-order terms in powers of $\bar{E}$'s to retain the terms up to the first order of $\bar{E}$. $\bar{E}$'s in the resultant expressions of the effective matrix elements are replaced by the expected value of the Hamiltonian for $\bar{t}_{pp}\neq 0$ but $\bar{t}_{dp}=0$, which is taken in the eigenstate with the eigenvalue $\bar{E}$. We can perform these procedures by using iteration method.

V. RESULTS OF NUMERICAL CALCULATIONS

Some authors[12] estimated theoretically the values of the parameters in Eqs. (2) and (3). Among them, Hybertsen, Schlüter, and Christensen[12] obtained for La_2CuO_4, a prototype of the cuprate oxides, the following energy values in units of eV:

$$\bar{\epsilon}_p-\bar{\epsilon}_d=3.6,\quad \bar{t}_{dp}=1.3,\quad \bar{t}_{pp}=0.65\ ,$$
$$U_d=10.6,\quad U_p=4.0,\quad \text{and}\quad V=1.2\ . \tag{36}$$

(Hereafter, the same units are used for all energy values.) These values give further Δ_0 defined by Eq. (6) and the exchange constant J[4,8,9,11] as

$$\Delta_0=4.8\quad \text{and}\quad J=0.07\ . \tag{37}$$

Our numerical calculations of the doped-hole states were done around these parameter values.

First, we show in Fig. 9 the energy dispersions of the doped hole, which were calculated with the accuracies up to the second and third orders of t's. Observing the band structure which was calculated in the absence of the third-order perturbation correction, we can find the following properties: The band structure consists of a group of 11 upper bands and the lowest single band, which is split off far away from the upper bands. Most of their band widths, including the lowest-band one, are less than 1. The lowest-band width is reduced considerably compared with that expected by a tight-binding model, which neglects the spin-exchanged states. (See also Fig. 11.) However, our band width is still much larger than J given in Eq. (37), which has been already found to give the order of the band width in the t-J model.[13,14] The lowest band exhibits a local top at $\mathbf{k}=(\pi/a,0)$ but the bottom at $(\pi/2a,\pi/2a)$. This result means, in accordance with the result obtained by other methods,[14,15] that extra holes in the d-p system enter into band states around $(\pi/2a,\pi/2a)$ in the lowest band so long as the concentration of doped holes is small. All the above qualitative properties of the lowest band are unchanged by the third-order perturbation correction. However, this correction shifts upward energies of the lowest-band states by about 1 at most for the parameter values given by Eq. (36).

To see how the lowest band depends on $\bar{t}_{dp}$ and $\bar{t}_{pp}$, we show in Fig. 10 the dispersions of the lowest band for some choices of their values. This figure teaches us the following: When $\bar{t}_{dp}$ is increased under a constant $\bar{t}_{pp}$, the lowest band is rapidly pushed downward to be split off from upper bands. The $\bar{t}_{pp}$ term lifts the degeneracies of the lowest-band states on the wave-vector line from $(\pi/a,0)$ to $(\pi/2a,\pi/2a)$ and is responsible for appearance of the band bottom at $(\pi/2a,\pi/2a)$. When $\bar{t}_{pp}$ is decreased to become negative, the band bottom moves to $(\pi/a,0)$. Here, we are aware that $|\bar{E}|$'s of the lowest-band states calculated for the parameter values given by Eq. (36) become larger than Δ_0. Nevertheless, we expect that the present perturbation calculation can give reliable band states enough to clarify the properties of the doped-hole state. We will discuss again in the next sec-

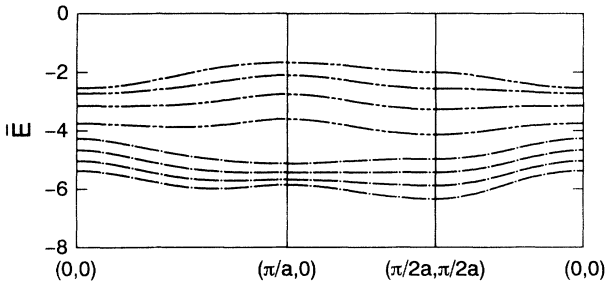

FIG. 10. Transfer-integral dependence of the lowest band of the hole motion. All lines were calculated by taking account of the perturbation corrections up to the third order of $\bar{t}$'s. The dotted chain lines were obtained for $\bar{t}_{dp}=1.3$; among these lines, the lines from the lowest to the highest correspond to $\bar{t}_{pp}/\bar{t}_{dp}=0.5$, 0.25, 0.0, and -0.25, respectively. The doubly dotted chain lines were obtained for $\bar{t}_{pp}=0.65$; among these lines, the lines from the lowest to the highest correspond to $\bar{t}_{dp}/\bar{t}_{pp}=1.5$, 1.25, 1.0, and 0.75, respectively. Energies are in units of eV.

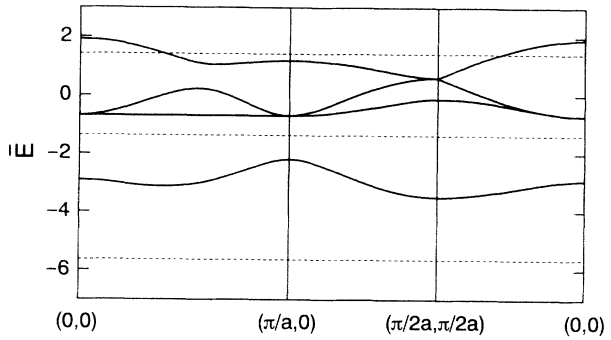

FIG. 11. Energy bands of the hole motion in the two assumed cases under no third-order perturbation correction. The solid lines are the energy bands calculated in the absence of the spin-exchanged states. The dotted lines show the energy levels of the hole states, which were calculated by allowing the spin-exchanged states but neglecting all off-diagonal matrix elements in $\bar{H}_{11}(\mathbf{k})$. The lowest, middle, and top dotted lines correspond, respectively, to the lowest level of all energy levels, the bottom and top levels of the group of the upper levels. The parameter values used are the same as those in Fig. 9. Energies are in units of eV.

tion the applicability of the perturbation theory to the d-p model with such the values of $\bar{t}$'s.

The origins of the above-mentioned characteristics of the lowest band can be revealed by going into detail of wave functions of the band states. In Table I, we give the weights of the states $|\nu\mu;\mathbf{k}\rangle$'s, $|a(\nu\mu;\mathbf{k})|^2$'s in some lowest-band states. It can be found in this Table that $|\nu 1;\mathbf{k}\rangle$'s and $|\nu 2;\mathbf{k}\rangle$'s have comparable weights, but the weights of $|\nu 3;\mathbf{k}\rangle$'s are much smaller than those of $|\nu\mu;\mathbf{k}\rangle$'s with $\mu=1$ and 2, irrespective to $\mathbf{k}$. The lowest-band states, therefore, contain spin-singlet states localized around Cu sites in the ↑ sublattice in their large parts. This spin-singlet nature of a doped-hole state has been already proposed by Zhan and Rice.[4] In order to see the important role of the spin-exchanged states $|\nu 2;\mathbf{k}\rangle$'s in the formation of the lowest-band states, we show in Fig. 11 the band structure, which was calculated by neglecting all spin-exchanged states $|\nu 2;\mathbf{k}\rangle$'s and $|\nu 3;\mathbf{k}\rangle$'s. It is remarked that the lowest band in this figure is very different from that in Fig. 9. Figure 11 gives also the energy levels of the hole states, which were calculated by taking account of the spin fluctuations but by forcing all off-diagonal matrix elements of $\bar{H}_{11}(\mathbf{k})$ to be zero. All hole states in this assumed case do not exhibit any dispersion in the absence of the third-order perturbation correction. This is because the states $|i\nu\mu\rangle$'s with $\mu=2$ and 3 can itinerate only by repairing the fluctuating d-spin directions in those states but such the itineracy can become possible only in the third-order perturbation processes in the present theory. Nevertheless, energies of the lowest-band states $\bar{E}$ are still fairly close to energies of the lowest-band states in Fig. 9. This proves that the formation of a spin-singlet state, rather than the motion itself of the spin-singlet state, dominates the energy lowering of the lowest band. The small weights of $|\nu 3;\mathbf{k}\rangle$'s in the lowest-band states imply that effects of the formation of a spin-singlet state is well localized around the Cu site neighboring the O site with the doped hole in the ↑ sublattice.

TABLE I. Weights of the states $|\nu\mu;\mathbf{k}\rangle$'s in some lowest-band states. The obtained $|a(\nu\mu;\mathbf{k})|^2$'s do not depend on ν. The parameter values used are the same as those in Fig. 9.

$\mathbf{k}$	$\lvert a(\nu 1;\mathbf{k})\rvert^2$	$\lvert a(\nu 2;\mathbf{k})\rvert^2$	$\lvert a(\nu 3;\mathbf{k})\rvert^2$
(0,0)	0.095	0.153	0.002
$(\pi/a,0)$	0.091	0.156	0.003
$(\pi/2a,\pi/2a)$	0.126	0.122	0.002

We are especially interested in cases where some of the parameters have extreme values so as to reduce the present model to other simplified model. In the first case, $\bar{t}_{pp}$ is assumed to be zero but other parameters remain to have the same values as those in Eqs. (36) and (37). Then, all matrix elements in $\bar{\mathbf{H}}(\mathbf{k})$ contain only the second-order terms of $\bar{t}_{dp}$. [See Eqs. (C1)–(C13).] We show in Fig. 12 the band structure for $\bar{t}_{pp}=0$. A small width of the lowest band and also a large energy separation between the lowest and upper bands are reproduced also in this case. The weights $|a(\nu\mu;\mathbf{k})|^2$'s of the lowest-band state at $(\pi/2a,\pi/2a)$, which is given in Table II, show the spin-singlet nature of the lowest band even for $\bar{t}_{pp}=0$. These results and comparisons between Figs. 9, 10, and 12 clarify that the $\bar{t}_{dp}$ term is responsible for the appearance of the spin-singlet nature but the $\bar{t}_{pp}$ term also contributes to the energy lowering of the lowest band. In the second case we are interested in, both U_p and V are assumed to be zero under the same values of other parameters including Δ_0 as those given by Eqs. (36) and (37). Then, various energy levels of the unperturbed excited states become one of Δ_0 and $U_d-\Delta_0$, but the perturbation processes are not affected by this assumption. Figure 13 shows the band structure of this case. The gross feature of this band structure is found to be unchanged in comparison with that in Fig. 9. The spin-singlet nature of its lowest band is also conserved, as seen in Table II. These results prove that a simplified d-p model without U_p and V terms in Eq. (2) approximates well to the d-p

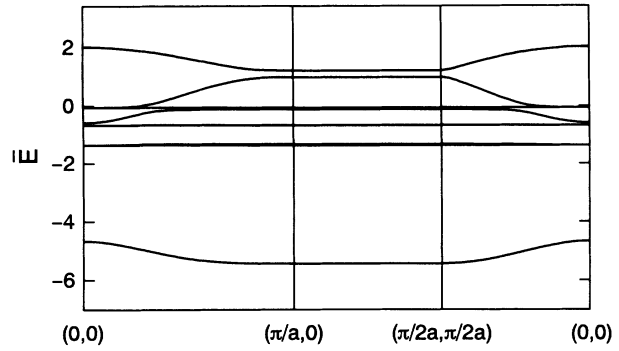

FIG. 12. Energy bands of the hole motion for $\bar{t}_{pp}=0$. The parameter values used are the same as those in Fig. 9 except for the value of $\bar{t}_{pp}$. It is noted that the lowest band is flat on the wave-vector line from $(\pi/a,0)$ to $(\pi/2a,\pi/2a)$. Energies are in units of eV.

model with the full terms if Δ_0 is rechosen suitably. In the final case, we assume $U_d\to\infty$ under the fixed value 4.8 of Δ_0. As shown in Fig. 14, the lowest band in this case is still split off but its energies increased drastically compared with that for $U_d=10.5$. This large energy increase can be understood as follows: For a definite U_d, $|\nu\mu;\mathbf{k}\rangle$'s with $\mu=1$ and 2 mix with each other also through perturbation processes via excited states with a d orbit doubly occupied by holes. Since there are many such processes, they contribute to the large energy decreases of the spin-singlet states in spite of a small value of $\bar{t}_{dp}^2/U_d$ itself. The infinite U_d makes those mixing processes impossible. From Table II, we see that the lowest band in this case has still the spin-singlet nature. This is because $|\nu 1;\mathbf{k}\rangle$ and $|\nu' 2;\mathbf{k}\rangle$ with $\nu\neq\nu'$ can still mix with each other through the $\bar{t}_{dp}$ term without the aid of any doubly occupied d orbit. In order to prove that the $\bar{t}_{pp}$ term is also important as well as the $\bar{t}_{dp}$ term in this case, we show in Fig. 15 the band structure for $U_d\to\infty$ and $\bar{t}_{pp}=0$ under $\Delta_0=4.8$. Comparing Figs. 9, 14, and 15, we know that a d-p model with $U_d\to\infty$ can not become a good approximation to the d-p model with realistic parameter values.

Finally in this section, we mention about the origin of the small band width of the lowest band. As has been already discussed on Fig. 11, the dispersion of the lowest band arises mainly from the off-diagonal matrix elements between $|\nu 1;\mathbf{k}\rangle$'s. On the other hand, the weights of $|\nu 1;\mathbf{k}\rangle$'s in the lowest-band states are very small, because any lowest-band state consists of many localized states $|i\nu 1\rangle$'s and $|i\nu 2\rangle$'s with comparable weights. These two properties of the lowest-band states result in such the small band width.

TABLE II. Weights of the state $|\nu\mu;\mathbf{k}\rangle$ in the lowest-band state with $\mathbf{k}=(\pi/2a,\pi/2a)$ in some assumed cases. The obtained $|a(\nu\mu;\mathbf{k})|^2$'s do not depend on ν. For the parameter values used, see Figs. 12–14.

Case	$\lvert a(\nu 1;\mathbf{k})\rvert^2$	$\lvert a(\nu 2;\mathbf{k})\rvert^2$	$\lvert a(\nu 3;\mathbf{k})\rvert^2$
$\bar{t}_{pp}=0$	0.120	0.128	0.002
$U_p=V=0$	0.115	0.132	0.003
$U_d\to\infty$	0.136	0.113	0.001

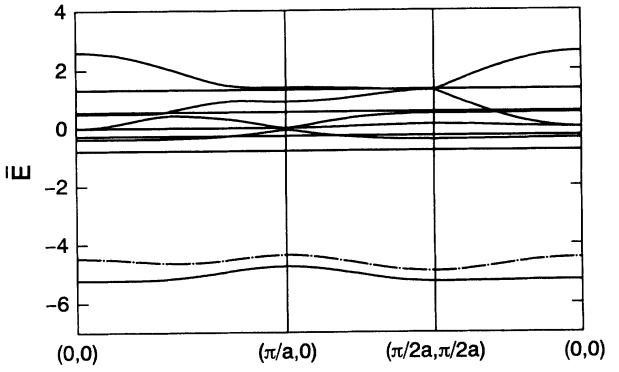

FIG. 13. Energy bands of the hole motion for $U_p=V=0$. This figure was obtained for the same values of the parameters other than U_p and V and of Δ_0 as those given in (36) and (37). Energies are in units of eV.

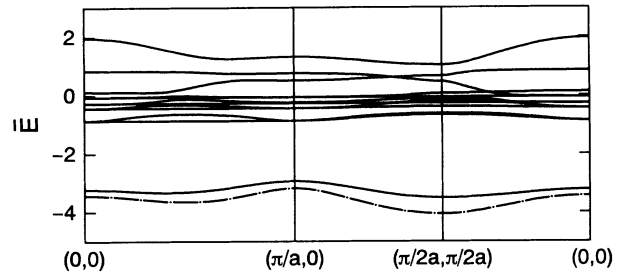

FIG. 14. Energy bands of the hole motion for $U_d\to\infty$. The solid lines are the energy bands, which were calculated by taking account of the perturbation corrections up to the second order of $\bar{t}_{dp}$ and $\bar{t}_{pp}$. The dotted chain line is the lowest band, which was calculated in the presence of the third-order perturbation correction. The used values of the parameters other than U_d and of Δ_0 are given in (36) and (37). Energies are in units of eV.

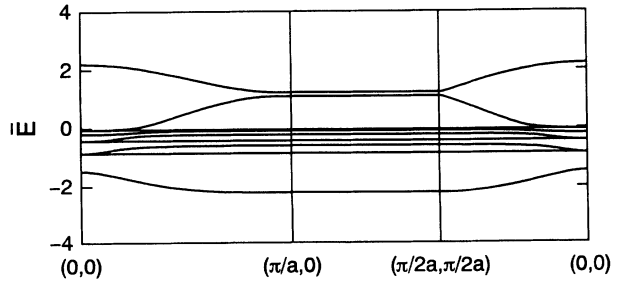

FIG. 15. Energy bands of the hole motion for $U_d\to\infty$ and $\bar{t}_{pp}=0$. The used values of the parameters other than U_d and $\bar{t}_{pp}$ and of Δ_0 are given in (36) and (37). Energies are in units of eV.

VI. DISCUSSION

In the beginning of this section, we discuss the applicability of the present perturbation theory to the d-p model of the CuO_2 plane. It is of no doubt that this theory should give good calculated results so long as the transfer integrals $|\bar{t}_{dp}|$ and $|\bar{t}_{pp}|$ are sufficiently smaller than the energy separations between the degenerate ground states and other excited states, $(E_e^0-E_g^0)$, which is typically the charge-transfer gap Δ_0. In the present system, however, there are many ground states $|\alpha\rangle$'s, which can mix with each other not only through the direct-transfer terms proportional to $|\bar{t}_{pp}|$ but also through indirect-transfer terms resulting from perturbation corrections. The mixings between these many states give rise to considerable changes of both eigenenergies and eigenfunctions. This makes the applicability of the perturbation theory to be more stringent. In fact, as was already seen in the preceding section, the energy gain by forming the lowest-band states of a doped hole exceeded some of the $(E_e^0-E_g^0)$'s for the values of $\bar{t}_{dp}$ and $\bar{t}_{pp}$ given in Eq. (36). Since, however, we were interested in the perturbation corrections up to the third-order $\bar{t}$'s, $\bar{E}$'s in denominators in the expressions of the perturbation corrections were replaced by expected values of the $\bar{t}_{pp}$ term in resulting eigenstates, whose magnitudes are still sufficiently smaller than $(E_e^0-E_g^0)$'s. Furthermore, it was found that the third-order perturbation correction is small enough for both qualitative and quantitative natures of the lowest-band states to be unchanged. These will allow us to believe that the obtained characteristics of the motion of a doped hole in the AF background are conserved even if the accuracy of the perturbation calculation is improved.[16]

We here compared the present theory with the perturbation theories of the d-p model, which have been reported until now. Zaanen and Oleś,[8] and Matsukawa and Fukuyama[9] did not consider spin-exchanged states $|i\nu\mu\rangle$'s with $\mu=2,3$ for degenerate ground states in calculating the band states of a doped hole. Nevertheless, we have seen in the preceding section that the spin-exchanged states play a vital role in determining the lowest-band states of the doped hole. They did not also take into account the third-order perturbation corrections of $\bar{t}$'s. Our theory, however, proved that the third-order perturbation correction cannot change essential features of the lowest-band states.

We are especially interested in a comparison between calculated results on the bases of the d-p and t-J models. Comparing our lowest band of the hole motion with that given by the t-J model,[14] we found that both the lowest bands have some common features such as their spin-singlet nature and the appearance of the band bottom at $\mathbf{k}=(\pi/2a,\pi/2a)$, but they are very different from each other in their band widths. In the t-J model, a local spin-singlet state formed around a Cu site transfers into one of its neighboring Cu sites by accompanying an inversion of a d-spin direction in the AF background. For the spin-singlet state to move coherently, the inverted spin direction should be repaired mainly by the exchange interaction J. This situation suppresses the band width to be of the order of J in the t-J model.[13,14] Zhan and Rice[4] supposed that J can be the superexchange interaction constant. The band width in the t-J model thus estimated is much smaller than the lowest-band width in our theory. Notice that our theory of the hole motion completely neglected the exchange interaction J. From the above arguments, we know that the t-J and d-p models give quite different mechanisms of the transfer of a local spin-singlet state.

The d-p model is sometimes reduced to be a more simplified model by assuming $U_d\rightarrow\infty$. This infinite-U_d d-p model is usually investigated theoretically by use of the slave-boson technique, which forbids d orbits to be doubly occupied by holes.[17] As was already shown in Sec. V, the simplification of the model by assuming $U_d\rightarrow\infty$ causes a large quantitative change in the band structure. This shows that the slave-boson technique is applied to a d-p model with realistic parameter values at the cost of accuracies.

VII. CONCLUSION

We presented a perturbation theory for the motion of a hole doped into the d-p system of the antiferromagnetic CuO_2 plane. The present theory assumes the expansion parameters to be the transfer integrals, and calculates the perturbation corrections up to their third-order terms. It was found that the third-order perturbation correction cannot change the qualitative nature of the band structure. Some spin-exchanged states among the degenerate ground states were confirmed to play a vital role in determining the lowest band of the hole motion.

The band structure obtained here consists of the lowest single band and a group of all other upper bands, which are well separated from the lowest band. The large energy lowering of the lowest band originates mainly from the formation of local spin-singlet states by use of d and p holes with antiparallel spins. On the other hand, the small band width compared with the energy lowering is due to the fact that the spin-singlet states contain only small weights of the spin-unexchanged states, which can propagate without distorting directions of d spins in the AF state. The energy terms of hole transfers between neighboring d and p orbits are responsible for the formation of the spin-singlet states, but the terms of hole transfers between neighboring p orbits are also important for quantitative properties of the hole states. Especially, the latter terms lift the degeneracies of the lowest-band states on the wave-vector line from $(\pi/a,0)$ to $(\pi/2a,\pi/2a)$ to give rise to the band bottom at $(\pi/2a,\pi/2a)$.

The simplification of the d-p model by assuming $U_d\rightarrow\infty$ was found to cause a large quantitative change of the band structure. However, the assumption $U_p=V=0$ was confirmed numerically to cause no serious modifications of the band structure under a suitable value of the charge-transfer gap Δ_0. The large difference between the band widths calculated on the bases of the d-p and t-J models reveals that the transfer mechanisms of the doped hole in the two models are very different from each other.

APPENDIX A: NUMBERS OF CLUSTERS (OR CLUSTERS INCLUDING SUBCLUSTERS) DISCONNECTED TO THE O SITE WITH A HOLE

Here, we count the numbers of the same types of cluster as the clusters (b) and (e) in Fig. 2 and (p) in Fig. 3. In the crystal with no doped hole, there are $4N$ clusters belonging to (b). When an extra hole is doped, two and six clusters among those $4N$ clusters change to be the clusters (a) and (c), respectively. As the result, the number of the clusters (b) in the doped crystal becomes $(4N-8)$. A parallel argument can be applied to the case of the cluster (e). We have $4N$ clusters belonging to (e) in the undoped crystal, among which four clusters each change to be clusters (d) and (f) in the doped crystal. This results again in $(4N-8)$ clusters belonging to (e) in the doped crystal. In clusters belonging to (p), on the other hand, the pair of O ions with the ix and iy orbits is fixed so that there are $4N$ clusters if any interference between O-O and Cu-O subclusters were neglected. Among those $4N$ clusters, 12 clusters have Cu sites nearest neighboring one of O ions in the fixed O-O pair. Since these 12 clusters belong to other clusters in Figs. 2 and 3, we get $(4N-12)$ clusters allowed for the type of the cluster (p).

APPENDIX B: TREATMENT OF THE TERMS PROPORTIONAL TO N IN THE MATRIX ELEMENTS

We show that the terms proportional to N in the matrix elements give the perturbation correction to the energy of the undoped system. For simplicity, we consider only the two states $|\mathrm{ix}1\rangle$ and $|\mathrm{iy}1\rangle$, so that the doped hole can move only in a pair of nearest-neighboring p orbits without accompanying spin fluctuations. By use of Eqs. (12) and (14), the diagonal and off-diagonal matrix elements between the two states are shown to have the following forms within the accuracy up to the third order of t's:

$$\bar{H}_{\mathrm{ix}1,\mathrm{ix}1}=\bar{H}_{\mathrm{iy}1,\mathrm{iy}1}=\eta(\bar{E})\bar{t}_{dp}^2+\xi\,\bar{t}_{dp}^2\bar{t}_{pp}+\frac{4N\,\bar{t}_{dp}^2}{\bar{E}-\Delta_0}-\frac{8N\,\bar{t}_{dp}^2\bar{t}_{pp}}{\Delta_0^2}\ , \tag{B1}$$

$$\bar{H}_{\mathrm{iy}1,\mathrm{ix}1}=\bar{t}_{pp}+\eta'(\bar{E})\bar{t}_{dp}^2+\xi'\bar{t}_{dp}^2\bar{t}_{pp}+\frac{4N\,\bar{t}_{dp}^2\bar{t}_{pp}}{\Delta_0^2}\ , \tag{B2}$$

where, $\eta(\bar{E})$, $\eta'(\bar{E})$, ξ, and ξ' are constants independent of N and are known by use of Eqs. (12) and (14). One of the eigenvalues of the 2×2 matrix with these elements is expressed by

$$\bar{E}=-\bar{t}_{pp}+\{\eta(\bar{E})-\eta'(\bar{E})\}\bar{t}_{dp}^2+(\xi-\xi')\bar{t}_{dp}^2\bar{t}_{pp}+\frac{4N\,\bar{t}_{dp}^2}{\bar{E}-\Delta_0}-\frac{12N\,\bar{t}_{dp}^2\bar{t}_{pp}}{\Delta_0^2}\ . \tag{B3}$$

Solving this equation for $\bar{E}$ by an iteration, we arrive at

$$\bar{E}=-\bar{t}_{pp}+\{\eta(-\bar{t}_{pp})-\eta'(-\bar{t}_{pp})\}\bar{t}_{dp}^2+(\xi-\xi')\bar{t}_{dp}^2\bar{t}_{pp}+(E_g-E_g^0)\ , \tag{B4}$$

with

$$(E_g-E_g^0)=N\left\{-\frac{4\bar{t}_{dp}^2}{\Delta_0}-\frac{8\bar{t}_{dp}^2\bar{t}_{pp}}{\Delta_0^2}\right\}\ . \tag{B5}$$

It is noted that the terms of N in Eqs. (B1) and (B2) created $(E_g-E_g^0)$ in Eq. (B4), which becomes just the perturbation correction to the total energy of the undoped system as was already proved in Ref. 11. The same arguments can be done also for the other eigenvalue. The above consideration is to be extended to the general case where the doped hole itinerates on all p orbits by accompanying spin fluctuations.

APPENDIX C: CONSTRUCTION OF THE SUBMATRICES $\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})$'s

We summarize here the obtained expressions of $\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})$'s. To simplify their expressions, we define the following quantities:

$$\Sigma_1=\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0-U_p+V}+\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}+\frac{6\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}-\frac{8\bar{t}_{dp}^2}{\bar{E}-\Delta_0}-\frac{4\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}+\frac{16\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)^2}-\frac{8\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\ , \tag{C1}$$

$$\Sigma_2=\frac{2\bar{t}_{dp}^2}{\bar{E}-\Delta_0-U_p+V}+\frac{2\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}+\frac{6\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}-\frac{8\bar{t}_{dp}^2}{\bar{E}-\Delta_0}-\frac{8\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}+\frac{16\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)^2}-\frac{8\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\ , \tag{C2}$$

$$K_1=-\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0-U_p+V}-\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}+\frac{4\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}\ , \tag{C3}$$

$$K_2=\bar{t}_{pp}-\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}+\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}+\frac{2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}+\frac{6\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)(\bar{E}-\Delta_0)}-\frac{12\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)^2}\ , \tag{C4}$$

$$K_3=\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}+\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}-\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0-U_p+V)(\bar{E}-\Delta_0+V)}-\frac{2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\ , \tag{C5}$$

$$K_4=-\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}\ , \tag{C6}$$

$$K_5=\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}+\frac{\bar{t}_{dp}^2}{\bar{E}+\Delta_0-U_d+V}-\frac{4\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\ , \tag{C7}$$

$$K_6=K_2+\frac{2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)(\bar{E}-\Delta_0-U_p+V)}\ , \tag{C8}$$

$$K_7=-\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)(\bar{E}-\Delta_0-U_p+V)}\ , \tag{C9}$$

$$T_1=\frac{\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)(\bar{E}-\Delta_0)}\ , \tag{C10}$$

$$T_2=\bar{t}_{pp}+\frac{\bar{t}_{dp}^2}{(\bar{E}-\Delta_0+V)}+\frac{2\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)(\bar{E}-\Delta_0-U_p+V)}+\frac{6\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)(\bar{E}-\Delta_0)}-\frac{12\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0)^2}\ , \tag{C11}$$

$$T_3=\frac{\bar{t}_{dp}^2}{\bar{E}-\Delta_0+V}-\frac{4\bar{t}_{dp}^2\bar{t}_{pp}}{(\bar{E}-\Delta_0+V)^2}\ , \tag{C12}$$

$$T_4=K_7\ . \tag{C13}$$

Among these quantities, Σ's are self-energies, which contribute to the diagonal elements, K's are transfer energies between different orbits in same unit cells, and T's are transfer energies between two orbits in different unit cells. Then, $\bar{\mathbf{H}}_{\mu\mu'}(\mathbf{k})$'s are expressed as follows:

$$\bar{\mathbf{H}}_{11}(\mathbf{k})=\begin{pmatrix}
\Sigma_1+4T_1c_xc_y & K_2+T_2e_{\bar{}}^{*} & K_4+T_3e_{2x} & -K_2-T_2e_X \\
 & -T_1(e_{2x}+e_{2y}^{*}) & -2T_1(e_X+e_Y^{*}) & +T_1(e_{2x}+e_{2y}) \\
K_2+T_2e_Y & \Sigma_1+4T_1c_xc_y & -K_2-T_2e_X & K_4+T_3e_{2y} \\
-T_1\{e_{2x}^{*}+e_{2y}\} & & +T_1(e_{2x}+e_{2y}) & -2T_1(e_X+e_Y) \\
K_4+T_3e_{2x}^{*} & -K_2-T_2e_X^{*} & \Sigma_1+4T_1c_xc_y & K_2+T_2e_Y \\
-2T_1(e_X^{*}+e_Y) & +T_1(e_{2x}^{*}+e_{2y}^{*}) & & -T_1(e_{2x}^{*}+e_{2y}) \\
-K_2-T_2e_X^{*} & K_4+T_3e_{2y}^{*} & K_2+T_2e_Y^{*} & \Sigma_1+4T_1c_xc_y \\
+T_1(e_{2x}^{*}+e_{2y}^{*}) & -2T_1(e_X^{*}+e_Y^{*}) & -T_1(e_{2x}+e_{2y}^{*}) &
\end{pmatrix}\ , \tag{C14}$$

$$\bar{\mathbf{H}}_{12}(\mathbf{k})=\begin{bmatrix} K_1 & K_3 & K_5 & -K_3 \\ +T_1(e_X+e_Y^*) & -T_1e_X+T_4e_Y^* & -T_1(e_X+e_Y^*) & -T_4e_X+T_1e_Y^* \\ K_3 & K_1 & -K_3 & K_5 \\ +T_4e_Y-T_1e_X & +T_1(e_X+e_Y) & -T_4e_X+T_1e_Y & -T_1(e_X+e_Y) \\ K_5 & -K_3 & K_1 & K_3 \\ -T_1(e_X^*+e_Y) & -T_4e_X^*+T_1e_Y & +T_1(e_X^*+e_Y) & +T_4e_Y-T_1e_X^* \\ -K_3 & K_5 & K_3 & K_1 \\ +T_4e_X^*+T_1e_Y^* & -T_1(e_X^*+e_Y^*) & +T_4e_Y^*-T_1e_X^* & +T_1(e_X^*+e_Y^*) \end{bmatrix}, \tag{C15}$$

$$\bar{\mathbf{H}}_{13}(\mathbf{k})=0\mathbf{1}\ , \tag{C16}$$

$$\bar{\mathbf{H}}_{22}(\mathbf{k})=\begin{bmatrix} \Sigma_2 & K_6 & K_4 & -K_6 \\ K_6 & \Sigma_2 & -K_6 & K_4 \\ K_4 & -K_6 & \Sigma_2 & K_6 \\ -K_6 & K_4 & K_6 & \Sigma_2 \end{bmatrix}, \tag{C17}$$

$$\bar{\mathbf{H}}_{23}(\mathbf{k})=\begin{bmatrix} K_1 & K_7 & 0 & -K_7 \\ K_7 & K_1 & -K_7 & 0 \\ 0 & -K_7 & K_1 & K_7 \\ -K_7 & 0 & K_7 & K_1 \end{bmatrix}, \tag{C18}$$

$$\bar{\mathbf{H}}_{33}(\mathbf{k})=\Sigma_1\mathbf{1}\ . \tag{C19}$$

Here, we have used the 4×4 matrix $\mathbf{1}$ and the following abbreviations:

$$\begin{aligned} &c_x\equiv\cos(ak_x),\quad c_y\equiv\cos(ak_y)\ , \\ &e_{2x}\equiv\exp(2iak_x),\quad e_{2y}\equiv\exp(2iak_y)\ , \\ &e_X\equiv\exp[ia(k_x+k_y)],\quad e_Y\equiv\exp[ia(-k_x+k_y)]\ . \end{aligned} \tag{C20}$$

[1]Physica C **185-189**, 1417 (1991).

[2]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[3]L. N. Bulaevskii, É. L. Nagaev, and D. I. Khomskii, Zh. Eksp. Teor. Fiz. **54**, 1562 (1968) [Sov. Phys. JETP **27**, 836 (1968)]; J. E. Hirsch, Phys. Rev. Lett. **54**, 1317 (1985); C. Gros, R. Joynt, and T. M. Rice, Phys. Rev. B **36**, 381 (1987); S. A. Trugman, *ibid.* **37**, 1597 (1988).

[4]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[5]N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegenheimer, and Z. X. Zhao, *ibid.* **39**, 6619 (1989); J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and Youwen Xu, *ibid.* **42**, 6299 (1990).

[6]A. Ramšak and P. Prelovšek, Phys. Rev. B **40**, 2239 (1989); F. C. Zhang, *ibid.* **39**, 7375 (1989); V. I. Belinicher and A. L. Chernyshev, *ibid.* **47**, 390 (1993).

[7]V. J. Emery and G. Reiter, Phys. Rev. B **38**, 11 938 (1988); V. Cataudella and M. Nylén, Phys. Scr. **40**, 122 (1989); J. L. Shen and C. S. Ting, Phys. Rev. B **41**, 1969 (1990); R. J. Gooding and V. Elser, *ibid.* **41**, 2557 (1990); A. V. Sherman, *ibid.* **46**, 6400 (1992).

[8]J. Zaanen and A. M. Oleś, Phys. Rev. B **37**, 9423 (1988).

[9]H. Matsukawa and H. Fukuyama, J. Phys. Soc. Jpn. **58**, 3687 (1989).

[10]P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[11]M. Kataoka, J. Phys. Soc. Jpn. **62**, 215 (1993).

[12]Zhi-xun Shen *et al.*, Phys. Rev. B **36**, 8414 (1987); A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *ibid.* **35**, 8814 (1987); A. K. McMahan, R. M. Martin, and S. Satpathy, *ibid.* **38**, 6650 (1988); E. B. Stechel and D. R. Jennison, *ibid.* **38**, 8873 (1988); H. Chen and J. Callaway, **40**, 8800 (1989); M. S. Hybertsen, M. Schlüter, and N. E. Christensen, *ibid.* **39**, 9028 (1989).

[13]C. L. Kane, P. A. Lee, and N. Read, Phys. Rev. B **39**, 6880 (1989).

[14]J. Inoue and M. Maekawa, J. Phys. Soc. Jpn. **59**, 2110 (1990); R. Eder, K. W. Becker, and W. H. Stephan, Z. Phys. B **81**, 33 (1990).

[15]S. A. Trugman, Phys. Rev. Lett. **65**, 500 (1990); I. R. Pimentel and R. Orbach, Phys. Rev. B **46**, 2920 (1992); J. Igarashi and P. Fulde, *ibid.* **48**, 998 (1993).

[16]When we try to improve the present perturbation theory by calculating also the fourth- and higher-order perturbation corrections, the initially chosen space spanned by $|i\nu\mu\rangle$'s is insufficient to the subspace spanned by $|\alpha\rangle$'s in Eq. (9). Then, this space must be expanded so as to include not only the degenerate ground states but also a sufficient number of low-lying excited states.

[17]P. Coleman, Phys. Rev. B **35**, 5072 (1987).