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# Parameters of a Hubbard Hamiltonian to describe superconducting Cu oxides

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The parameters of a Hubbard Hamiltonian to describe superconducting Cu oxides are derived on the basis of (i) band-structure calculations for the hopping integrals through a tight-binding fit; (ii) photoemission and optical absorption for on-site energies and Coulomb repulsion within a cluster analysis of the experimental data. The undoped material described by this Hamiltonian is a Mott insulator; its antiferromagnetism can be accounted for by superexchange theory. An extra hole localized around a Cu atom is shown to form a singlet with the hole already present in the undoped material. It is argued that this local singlet is a good starting point to describe the holes created in the Cu oxide layers upon doping.

## I. INTRODUCTION

To determine the mechanism of superconductivity in Cu-oxide compounds,[1,2] a major step (probably the crucial one) will be to understand the electronic properties of these materials. When the underlying approximations turn out to be justified, the *ab initio* band-structure calculations give a very accurate description of both the ground state and the excited states of the system, as well as a very useful description in terms of a one-body Hamiltonian. But in the case of the superconducting Cu oxides, it is now generally admitted that this description is not satisfactory. For such highly correlated materials, the excitations of the system are totally beyond the scope of band-structure approximations, and one is faced with a double problem. Which effective Hamiltonian should one take? How should one solve it? In this paper, we propose a full answer to the first question, and some preliminary remarks concerning the second one.

The relevant physics of such compounds is believed to be contained in a simple model Hamiltonian, the so-called Hubbard Hamiltonian. The kinetic energy of the electrons is included in a tight-binding description. To study the low-energy properties, we need only a few orbitals per atom. In fact, the various *ab inito* band-structure calculations relative to $La_2CuO_4$ (Refs. 3 and 4) show clearly that the electronic properties near the Fermi level are strongly dominated by the O $2p$ and Cu $3d$ orbitals of the Cu oxide layers that can be found in all the materials. Moreover, the coupling between a layer and the rest of the crystal is small,[3] and it is a good approximation to consider that the layers are independent objects. As we shall deal with nearly filled Cu $3d$ and O $2p$ shells, it is convenient to use hole notation. We take the vacuum to be the state with 10 electrons in the Cu $3d$ shells and 6 electrons in the O $2p$ shells. We denote by $p^\dagger$ and $d^\dagger$ (respectively $p$ and $d$) the operators that create (respectively destroy) a hole in the various O $2p$ and Cu $3d$ orbitals of the layers. The Hubbard Hamiltonian can be written

$$H_{\text{hole}} = H^{\text{at}}_{\text{hole}} + H^{\text{hyb}}_{\text{hole}} + H^{\text{corr}}_{\text{hole}} . \tag{1}$$

$H^{\text{at}}_{\text{hole}}$ includes the hole on-site energies and we write it

$$H^{\text{at}}_{\text{hole}} = \sum_l \left[ \sum_{p,\sigma} \varepsilon_p p^\dagger_\sigma(l) p_\sigma(l) + \sum_{d,\sigma} \varepsilon_d d^\dagger_\sigma(l) d_\sigma(l) \right] , \tag{2}$$

where $l$ is the unit-cell index.

$H^{\text{hyb}}_{\text{hole}}$ describes the hybridization between the various orbitals

$$H^{\text{hyb}}_{\text{hole}} = \sum_{p,p',\sigma} (t_{pp'} p^\dagger_\sigma p'_\sigma + \text{H.c.}) + \sum_{d,d',\sigma} (t_{dd'} d^\dagger_\sigma d'_\sigma + \text{H.c.}) + \sum_{p,d,\sigma} (t_{pd} d^\dagger_\sigma p_\sigma + \text{H.c.}) . \tag{3}$$

$H^{\text{corr}}_{\text{hole}}$ describes the Coulomb repulsion between orbitals. Including only the *a priori* biggest terms, we write it

$$H^{\text{corr}}_{\text{hole}} = \sum_{(d,d')} U_d d^\dagger_\uparrow d_\uparrow d'^\dagger_\downarrow d'_\downarrow + \sum_{(p,p')} U_p p^\dagger_\uparrow p_\uparrow p'^\dagger_\downarrow p'_\downarrow + \sum_{\langle p,d \rangle,\sigma,\sigma'} U_{pd} d^\dagger_\sigma d_\sigma p^\dagger_{\sigma'} p_{\sigma'} , \tag{4}$$

where $(d,d')$ [respectively $(p,p')$] means that the orbitals are on the same atom, while $\langle p,d \rangle$ means that the orbitals refer to nearest neighbors.

To get the effective Hamiltonian that describes the system, we need the values of the various parameters. This is certainly a very important question, as the numerous theories proposed up to now are only valid in a (usually rather) limited range of parameters. Let us summarize the main current points of view.

Some people have considered that band-structure calculations provide a good starting point. The correlation parameters $U$ are then treated as a perturbation. This weak-coupling approach[5] is of course valid only for small $U$'s.

If, on the contrary, $U_d$ is very large, the situation depends critically on $\varepsilon_p - \varepsilon_d$. If $\varepsilon_p - \varepsilon_d$ is large enough as compared to the $t$'s, the undoped system has essentially one hole/Cu atom. It is a Mott insulator, and is antiferromagnetic due to superexchange between the localized holes. What happens then upon doping? If $\varepsilon_p - \varepsilon_d > U_d$, then an extra hole will tend to go on a Cu site, and will interact through Hund's rule coupling with the hole already there to form a local triplet.[6] But if $\varepsilon_p - \varepsilon_d < U_d$, an extra hole will go into the O band. If the direct hopping between O atoms can be neglected, the extra hole will form a local singlet through the hybridization with the wave function of a localized hole of the undoped system.[7] It is then possible to get rid of the O orbitals, thus obtaining an effective *one*-band Hubbard Hamiltonian, i.e., the starting point of resonating-valence-bond (RVB) theories.[8] This becomes questionable if one assumes big values for the O-O hopping integrals. The description of an extra hole in such a case remains very controversial.

On the other hand, if $\varepsilon_p - \varepsilon_d$ is small, the system is a semiconductor. There is in fact no localization effect, and the antiferromagnetism is bandlike. Only preliminary results have been obtained along these lines.[9] If $U_{pd}$ is also a substantial parameter, other pairing mechanisms have been proposed.[10-12]

The previous mechanisms suppose that the holes created upon doping go into orbitals that hybridize with those occupied by the holes already present in the undoped materials. Actually, most models include only one orbital/O atom. But this is no longer satisfactory if the on-site energies $\varepsilon_p$ of the various O $2p$ orbitals are very different. It has been argued that this can happen due to important ionic corrections, and the consequences of such a hypothesis have been analyzed.[13]

The first goal of this paper is to propose values for the parameters of $H_{\text{hole}}$. This has been done as follows. The hopping integrals have been obtained from the *ab initio* band-structure calculations by performing a tight-binding fit. The other parameters have then been determined on the basis of valence-band photoemission and optical-absorption data that we have interpreted within a cluster approximation. Let us briefly justify the choices we have made. In principle, the most direct source of information concerning the electronic properties close to the Fermi level is the valence-band photoemission spectroscopy, and a number of groups have already used these data to propose parameters.[14,15] While the values reported for $U_d$ are always large, there is no agreement on $\varepsilon_p - \varepsilon_d$ and on the hopping integrals. This difficulty is a serious one, as the different sets of parameters put the system in different regimes of the Hubbard Hamiltonian. So, we clearly need something else to get some confidence in the parameters we propose.

For the hopping integrals, the band-structure calculations appear to be the most reliable source. The local-density approximation is believed to describe correctly the charge distribution in the ground state. The hopping integrals, that are matrix elements of the Coulomb potential, should then also be satisfactorily described. Let us note that a number of *ab initio* determinations of the other parameters of the Hubbard Hamiltonian have been proposed.[16-18] There is a general agreement on a large value for $U_d$, but no agreement at all for $U_{pd}$, $U_p$, and $\varepsilon_p - \varepsilon_d$. At the present time, it seems difficult to choose between the different methods, and we decided to take the alternative way, that is to rely on experimental data. What we urgently need is in fact an independent source of information on $\varepsilon_p - \varepsilon_d$. This is provided by the optical-absorption measurements, as we shall argue below.

As we are interested in the Cu-oxide layers, we have tried to use only experimental data relative to $La_{2-x}Sr_xCuO_4$. This is no problem for photoemission. For optical data, the position of the absorption edge has been reported for $La_{2-x}Sr_xCuO_4$,[19] but absolute measurements of intensity have been reported (to our knowledge) only for $YBa_2Cu_3O_{7-x}$,[20] and we shall have to rely on these data. Let us remark that doping has very little influence on the data we have used. In valence-band photoemission, the spectra relative to $La_2CuO_4$ and $La_{2-x}Sr_xCuO_4$ exhibit no relevant difference up to $x = 0.2$.[15] In optical absorption, the position of the main absorption edge is independent of $x$ in the range $0 \leq x \leq 0.3$ where data have been reported.[19] As a consequence, the parameters of our effective Hamiltonian are independent of doping within the error bars of our analysis, and the different materials can be described by merely changing the number of electrons.

Having a Hamiltonian at hand, we then want to analyze the physical properties of the system that it describes. To do this, we distinguish between undoped and doped materials.

For the undoped materials, the filling corresponds to one hole/Cu atom. The main issue is the following: Do we have a magnetic insulator with holes localized on Cu due to a Mott phenomenon? We shall argue that, for our parameters, the answer is yes. In particular, there is no essential difficulty to explain antiferromagnetism with superexchange, a point questioned in previous reports on the problem.[15]

For the doped material, the first step is to determine what is the nature of the system with *one* extra hole. The analysis we propose is based on a cluster $CuO_6$. We shall see that the *magnetic* energy to be gained by forming a local singlet is bigger than the *kinetic* energy to be gained by delocalizing the hole in the O band. So, our conclusion is that we are in a regime where the formation of a local singlet is the main effect and is a good starting point for a better description of one extra hole. Further investigation will be devoted to the motion of this local singlet in a layer described by the Hamiltonian we have found.

The paper is organized as follows. In Sec. II, we present the tight-binding fit of the band-structure calculation. In Sec. III, we analyze photoemission and optical data to obtain the on-site energies and Coulomb integrals of our effective Hamiltonian. Finally, we draw a number of conclusions concerning the properties of both undoped and doped materials in Sec. IV.

## II. ANALYSIS OF BAND-STRUCTURE CALCULATIONS

The first band-structure calculations of $La_2CuO_4$ were done by Mattheiss[3] and by Yu and co-workers,[4] with very similar results. For our purpose, Mattheiss's results are more convenient because he quotes the dispersion curves along two directions parallel to the Cu-oxide planes, and we shall use his results. In the band picture, the Fermi level crosses a set of 17 dispersion curves that have the following characteristics: (i) they come from the Cu $3d$ and

O 2*p* orbitals; (ii) they are relatively well separated from the other bands; (iii) they show little dispersion in the direction perpendicular to the Cu-oxide layers. Points (i) and (ii) insure that a good description should be obtained by a tight-binding Hamiltonian with only Cu 3*d* and O 2*p* orbitals. Point (iii) shows that the interaction between Cu oxide layers is small and can be neglected. Hence, the 17 dispersion curves should be correctly reproduced by a tight-binding description of the Cu-oxide layer depicted on Fig. 1. Note that the stoichiometry of this layer is $CuO_4$ due to the O atoms above and below each Cu, hence the 17 bands (5 for each Cu, 3 for each O). In such a model, the high-symmetry directions $\Delta$ and $U$ of the body-centered tetragonal Brillouin zone reduce to the $\Gamma X$ direction of our square lattice, while the directions $\Gamma X$ and $ZX$ in the body-centered-tetragonal (bct) Brillouin zone are both equivalent to $\Gamma M$ in our model. In Mattheiss's calculation, the dispersion along $\Delta$ and $U$ (respectively $\Gamma X$ and $ZX$) are actually very similar, which is an extra reason to believe the model is relevant.

It is more usual to fit the band structure with a tight-binding Hamiltonian written in electron notation, a convention we follow in this section. To clearly distinguish it from the Hubbard Hamiltonian introduced in the previous section, we use capital letters for the parameters: $E$ for the on-site energies, $T$ for the hopping integrals. In this section, $p^\dagger$ and $d^\dagger$ (respectively $p$ and $d$) create (respectively destroy) an *electron* in the corresponding orbital.

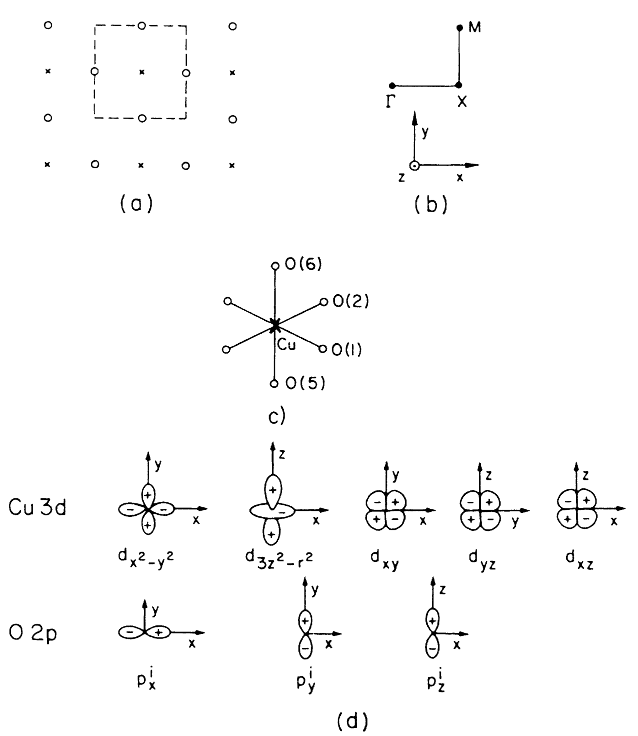

FIG. 1. Cu-oxide layer used for the fit of the band-structure calculation. (a) Top view. The dashed line is the unit cell. (b) High symmetry points of the Brillouin zone. (c) Atoms of the unit cell. (d) Phase convention for the 3*d* and 2*p* orbitals.

The tight-binding Hamiltonian can be written

$$H_{\mathrm{el}} = H_{\mathrm{el}}^{\mathrm{at}} + H_{\mathrm{el}}^{\mathrm{hyb}} . \tag{5}$$

The atomic part includes the on-site energies of the various orbitals and reads

$$H_{\mathrm{el}}^{\mathrm{at}} = \sum_l \left[ \sum_{p,\sigma} E_p p_\sigma^\dagger(l) p_\sigma(l) + \sum_{d,\sigma} E_d d_\sigma^\dagger(l) d_\sigma(l) \right] , \tag{6}$$

where $l$ is the unit-cell index. Using the Slater-Koster basis,[21] we denote the Cu orbitals by $d_{x^2-y^2}$, $d_{3z^2-r^2}$, $d_{xy}$, $d_{xz}$, $d_{yz}$ and the 2*p* orbitals of atom O($i$) by $p_x^i$, $p_y^i$, and $p_z^i$. The phase conventions are given in Fig. 1(d). Due to the symmetry of the layer, the atoms O(1) and O(2) [respectively O(5) and O(6)] of the unit cell [see Fig. 1(c)] are equivalent, and we need only to define the on-site energies of, e.g., the O(1), O(5), and Cu orbitals, that is, 11 parameters. To avoid working with too many parameters, we have given the same energy to some orbitals: $E_d^1$ to $d_{x^2-y^2}$, $d_{xy}$ (in-plane Cu orbitals), $E_d^2$ to $d_{3z^2-r^2}$, $d_{xz}$, $d_{yz}$ (out-of-plane Cu orbitals), $E_p^1$, $E_p^2$, and $E_p^3$ to $p_x^1$, $p_y^1$, $p_z^1$, respectively. The orbitals of O(5) have been given a single energy, and it appeared that it was a good approximation to take it equal to $E_p^1$. So we have five independent parameters describing the on-site energies: $E_d^1$, $E_d^2$, $E_p^1$, $E_p^2$, $E_p^3$.

The general form of the Hamiltonian that describes the hybridization between orbitals is

$$H_{\mathrm{el}}^{\mathrm{hyb}} = \sum_{p,p',\sigma} (T_{pp'} p_\sigma^\dagger p'_\sigma + \mathrm{H.c.}) + \sum_{d,d',\sigma} (T_{dd'} d_\sigma^\dagger d'_\sigma + \mathrm{H.c.}) + \sum_{p,d,\sigma} (T_{pd} d_\sigma^\dagger p_\sigma + \mathrm{H.c.}) , \tag{7}$$

where $p,p'$ (respectively $d,d'$) are orbitals of *different* O atoms (respectively Cu atoms). To reduce the number of independent parameters, we include only the *a priori* most important integrals, that is, those between O(1)-O(2), Cu-O(1), Cu-O(5), and equivalent pairs. According to the Slater-Koster tables,[21] each pair is described by two parameters: $(V_{pp\sigma}, V_{pp\pi})$, $(V_{pd\sigma}, V_{pd\pi})$, $(V'_{pd\sigma}, V'_{pd\pi})$ for O(1)-O(2), Cu-O(1), Cu-O(5), respectively. Moreover, to simplify matters, we have only included the hopping integrals of the pairs $p_x^1 - p_y^2$ and $p_y^1 - p_y^2$ for the atoms O(1) and O(2), which is certainly safe as the other ones are very small if they do not vanish for symmetry reasons.

To determine the parameters, we have used only the results between $\Gamma$ and $M$, so that the dispersion curves between $\Gamma$ and $X$ provide a test of the validity of the fit. To go from Mattheiss's results to our 11 parameters, we have worked in two steps. First, we have determined at $\Gamma$ and $M$ the symmetry of the most dispersive branches by comparing the relative dispersions of the various symmetries. The representations of the 14 wave functions that we have identified are indicated in Fig. 2. (The orbitals that enter the various representations at $\Gamma$ and $M$ are listed in Table I.) Then, we have used the equations within the different representations at $\Gamma$ and $M$ to determine the 11 parameters from the 14 constraints given by the energies of the identified wave functions. In spite of the overdetermination that we have imposed, a good fit was possible. The values of the parameters are listed in Table II. With these

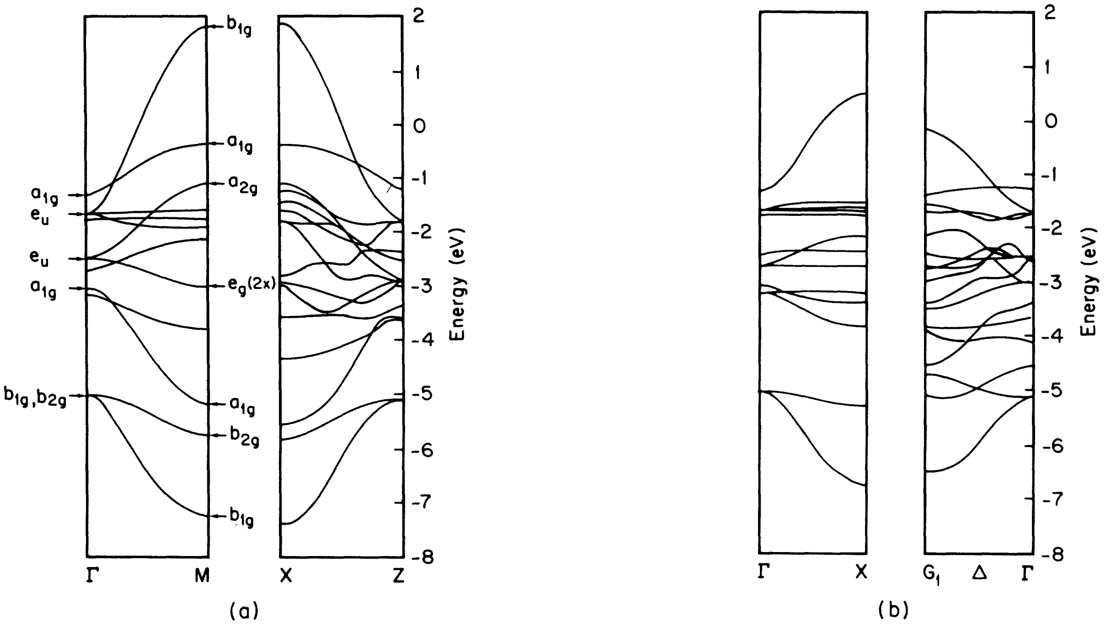

FIG. 2. Dispersion curves along two high symmetry directions. The left part of each panel is our fit; the right part is Mattheiss's results. (a) Between Γ and $M$. The representations at Γ and $M$ of the points used for the fit are indicated. (b) Between Γ and $X$.

parameters, we have calculated the 17 dispersion curves between Γ and $M$ and between Γ and $X$ (Fig. 2). The good qualitative agreement between our results and Mattheiss's calculation between Γ and $X$ [Fig. 2(b)] shows that our parametrization of the band structure is basically correct.

The important information contained in this section is the following. First, we have obtained the values of the hopping integrals that should describe the Cu-oxide layers. The hope is that these values depend mainly on the local charge density, which is believed to be well described in a band-structure approach even for highly correlated materials, so that we can use them for a description of the system in terms of a Hubbard Hamiltonian although they were derived for a tight-binding one. To discuss the physical content of these results, it is convenient to go from the Slater-Koster coefficients to the hopping integrals between Cu and O orbitals. Their values are listed in Table III. The biggest hopping integral is between $d_{x^2-y^2}$ and $p_x^1$, a result already recognized by Mattheiss[3] who proposed a fit of the upper and lower branches neglecting all other parameters. But the dispersion of these branches is also partly due to $T_1$, the main hopping term between O orbitals. Nevertheless, we shall see in Sec. IV that our value is small enough to favor *a priori* the approaches where this parameter is considered to be negligible.

Second, it has been argued by Aharony and coworkers[13] that an extra hole would be created in the nonbonding orbital $p_y^1$ rather than in the antibonding mixture of $p_x^1$ and $d_{x^2-y^2}$, because the on-site energy of $p_y^1$ is considerably increased as compared to $p_x^1$ due to ionic corrections. While this point of view agrees with Guo *et al.* *ab initio* calculations,[18] it contradicts our results, as we actually find $E_p^2$ slightly lower than $E_p^1$. This strongly questions their hypothesis, as the band-structure calculations are believed to reproduce satisfactorily the charge density

TABLE I. Orbitals entering the various representations at Γ and $M$. At both points, the group of the **q** vector is $G(\mathbf{q})=D_{4h}$. The representations $a_{1u}$, $b_{1u}$, and $b_{2u}$ are not mentioned as they are empty in both cases.

| | Γ | $M$ |
|---|---|---|
| $a_{1g}$ | $d_{3z^2-r^2}$, $p_z^5-p_z^6$ | $d_{3z^2-r^2}$, $p_x^1+p_y^2$, $p_z^5-p_z^6$ |
| $a_{2g}$ | Empty | $p_y^1-p_x^2$ |
| $b_{1g}$ | $d_{x^2-y^2}$ | $d_{x^2-y^2}$, $p_x^1-p_y^2$ |
| $b_{2g}$ | $d_{xy}$ | $d_{xy}$, $p_y^1+p_x^2$ |
| $e_g$ | $d_{xz}$, $d_{yz}$, $p_x^5-p_x^6$, $p_y^5-p_y^6$, $p_z^1$, $p_z^2$ | $d_{xz}$, $d_{yz}$, $p_x^5-p_x^6$, $p_y^5-p_y^6$, $p_z^1$, $p_z^2$ |
| $a_{2u}$ | $p_z^5+p_z^6$ | $p_z^5+p_z^6$ |
| $e_u$ | $p_x^1$, $p_y^2$, $p_y^1$, $p_x^2$, $p_x^5+p_x^6$, $p_y^5+p_y^6$ | $p_x^5+p_x^6$, $p_y^5+p_y^6$ |

TABLE II. Values in eV of the parameters derived from the fit of the band structure. The origin of the energies is the same as in Mattheiss's calculation, which gives $\varepsilon_d^1 = -5$ eV.

| | |
|---|---|
| $E_d^1$ | −5 |
| $E_d^2$ | −2.59 |
| $E_p^1$ | −1.73 |
| $E_p^2$ | −2.39 |
| $E_p^3$ | −3.16 |
| $V_{pp\sigma}$ | 0.395 |
| $V_{pp\pi}$ | −0.265 |
| $V_{pd\sigma}$ | −1.59 |
| $V_{pd\pi}$ | 0.43 |
| $V'_{pd\sigma}$ | −0.54 |
| $V'_{pd\pi}$ | 0.21 |

and include the Hartree energy, which is the relevant quantity for ionic corrections.

## III. PHOTOEMISSION AND OPTICAL EXPERIMENTS

### A. The model Hamiltonian

The model Hamiltonian proposed in Sec. I [Eqs. (1)-(4)] has a lot of independent parameters, in fact much more than we can expect to derive from the interpretation of photoemission and optical data. In this subsection we make a number of assumptions that will lead to a reasonable number of adjustable parameters.

Let us start with $H_{\text{hole}}^{\text{at}}$ [Eq. (2)]. While in the previous section the introduction of five parameters was necessary to find accurate values for the hopping integrals, such a hypothesis would be meaningless here given the relatively raw information contained in experimental data. We thus include only two parameters: $\varepsilon_p$ and $\varepsilon_d$ for a hole on any O or Cu orbital, respectively.

For $H_{\text{hole}}^{\text{hyb}}$ [Eq. (3)], we note that written in electron notation this Hamiltonian would have the form $H_{\text{el}}^{\text{hyb}}$ of Eq. (7) with $T_{\alpha\beta} = -t_{\alpha\beta}$ $(\alpha,\beta = p,d)$. As we mentioned before, the most reliable source of information for this Hamiltonian seems to be the band-structure calculations, and we use the results of Sec. II for $H_{\text{el}}^{\text{hyb}}$. $H_{\text{hole}}^{\text{hyb}}$ thus involves seven different hopping integrals given by

$$t_i = -T_i, \quad i = 1, \ldots, 7, \tag{8}$$

the values of $T_i$ being listed in Table III.

TABLE III. Values in eV of the hopping integrals in electron notations. The bond described by each integral is also indicated.

| | | |
|---|---|---|
| $p_x^1 - p_y^2$ | $T_1$ | −0.33 |
| $p_y^1 - p_y^2$ | $T_2$ | .065 |
| $d_{x^2-y^2} - p_x^1$ | $T_3$ | −1.38 |
| $d_{3z^2-r^2} - p_x^1$ | $T_4$ | −0.80 |
| $d_{3z^2-r^2} - p_z^5$ | $T_5$ | −0.54 |
| $d_{xy} - p_y^1$ | $T_6$ | 0.43 |
| $d_{xz} - p_x^6$ | $T_7$ | 0.21 |

For $H_{\text{hole}}^{\text{corr}}$ [Eq. (4)], we make the assumption that $U_d$, $U_p$, and $U_{pd}$ do not depend on which particular $3d$ or $2p$ orbital is concerned. Now, when interpreting photoemission and optical data in transition-metal compounds, one usually drops $U_p$ and $U_{pd}$ to keep only the parameter describing the repulsion on the transition-metal ion. But in the case of superconducting Cu oxides, $U_p$ and $U_{pd}$ have been invoked to explain superconductivity, and it is important to keep them to show what we can learn on these parameters from experimental data.

### B. The data

The photoemission data we used[15] have been obtained on $La_2CuO_4$ compounds. The contributions that have been attributed to Cu and O consist of three peaks: a main peak at 4 eV of the Fermi level and two satellites of this main peak, a small one at 5 eV and a big one at 8 eV (see Fig. 5). The most probable interpretation is the following. In the undoped materials, with a filling of one hole/Cu atom, the holes are known to sit mainly on Cu. With the notations of the cluster approximation,[22] this corresponds to the configuration $d^9$. The main contribution to the photoemission spectrum should then come from the creation of an extra hole on an O atom ($d^9\underline{L}$ configuration, where $\underline{L}$ stands for a hole in the ligand orbitals) or the creation of a second hole on a Cu atom ($d^8$). But it is known from resonant photoemission[15] that the main satellite at 8 eV corresponds to the $d^8$ configuration. So, the main peak is $d^9\underline{L}$. The only possibility for the small satellite is then to be $d^{10}\underline{LL}'$, i.e., two holes on O atoms. Actually, there are two possibilities, as the two holes can be on the same atom or on different ones. For the relevant cluster in the case of $La_2CuO_4$, i.e., $CuO_6$, the configurations in which the two holes are on different O atoms are much more numerous than the configurations where there are on the same atom, and the spectral weight of the last case should be negligible. This point has two consequences. First, if the two holes are on different O atoms, we expect no resonance when varying the incident photon energy. Experimentally, this is still controversial.[23,24] Second, the energy of the configuration with two holes on different O atoms does not include $U_p$. We shall come back later to this point when interpreting the data in terms of the model Hamiltonian introduced before.

The interpretation of optical data is much less straightforward for two reasons. First, a number of features of the absorption spectrum are not yet reproducible. Second, the spectrum has several differences with that of NiO,[25,26] which is to date the best understood transition-metal oxide. Nevertheless, we believe that this spectrum gives strong evidence in favor of a large value of the charge-transfer energy ($\varepsilon_p - \varepsilon_d$), a very controversial point at present, and which deserves special attention. The two reliable features of the optical-absorption spectrum of $La_{2-x}Sr_xCuO_4$ (Ref. 19) at the present time are (i) a strong edge starting at approximately 5-6 eV; (ii) a relatively large intensity below this edge with a broad and flat maximum between 2 and 3 eV. This last point is at variance with NiO, for which the intensity decreases by two orders of magnitude below the edge. As a consequence, the interpretation of the main absorption edge as the first dipole allowed transition in a cluster approximation has been questioned.[9] But we believe it remains the most probable interpretation for two reasons. First, if the charge-transfer excitations $p \rightarrow d$ were to correspond to the 2 eV peak, it is very difficult to understand why it is so narrow. Given the width ($\sim$4 eV) of the O $2p$ band, one expects an increase in intensity over a wide range of energy, which is effectively present after the main absorption edge at 5–6 eV. Second, the intensity of the main absorption edge is $5\times10^5$ cm$^{-1}$ for NiO, a value not reached before 6 eV for $\mathrm{YBa_2Cu_3O_{7-x}}$.[20] (Unfortunately, no such data have been reported for $\mathrm{La_{2-x}Sr_xCuO_4}$ to our knowledge.) The sizable absorption below the main edge is probably due to the dispersion effects that are neglected in the cluster approximation. Moreover, the 2–3 eV peak could be due to an excitonic effect. Another possibility is proposed in Sec. IV.

The other piece of information that one would hope to get from optical data is the position of the dipole-forbidden $d$-$d$ transitions. These transitions have been unambiguously identified in NiO,[25] with an absorption coefficient of approximately $10^3$ cm$^{-1}$. As the features observed in $\mathrm{YBa_2Cu_3O_{7-x}}$ (Ref. 20) have an absorption coefficient two orders of magnitude bigger, their interpretation in terms of $d$-$d$ transitions is not conclusive, and we shall not attempt to fit these data.

### C. Preliminary analysis

The Hamiltonian can be solved exactly in the limit where all the hopping integrals are set to 0. Let us estimate the other parameters in this limit. In the undoped material (i.e., a filling of one hole/Cu atom), the holes are known to sit mainly on Cu,[27] which implies $\varepsilon_d < \varepsilon_p$. So, the ground state of our simplified Hamiltonian consists of one hole on each Cu atom and no hole on O atoms. Its energy is $N\varepsilon_d$ ($N$ is the number of Cu atoms). In this picture, the first dipole-allowed transition corresponds to the hopping of a hole from a Cu atom to a neighboring O atom. The energy of this state is $(N-1)\varepsilon_d+\varepsilon_p+U_{pd}$. Note that the hole that sits on the O atom feels the repulsion of only *one* Cu site, the Cu atom on which it was in the ground state being now empty. So, the energy of the transition is $\varepsilon_p+U_{pd}-\varepsilon_d$. After the discussion of the previous paragraph, we know the experimental value for this transition is $\sim$5–6 eV. Hence, the optical data yield the relation $\varepsilon_p+U_{pd}-\varepsilon_d \simeq 5$–$6$ eV.

In a photoemission experiment, one creates an extra hole in the layer. The energies of the various configurations can be easily deduced with our simplified Hamiltonian. If one starts with one hole on each Cu atom and creates a hole on an O atom, one reaches a configuration equivalent to $d^9\underline{L}$ in the cluster approximation. Its energy is $N\varepsilon_d+\varepsilon_p+2U_{pd}$, as the extra hole feels the repulsion of both the neighboring Cu atoms. Now, if the extra hole is created on a Cu atom, it is in a $d^8$ configuration, and the energy is $N\varepsilon_d+\varepsilon_d+U_d$. Finally, one gets the configuration $d^{10}\underline{LL}'$ by putting two holes around an empty Cu atom. If the holes are on the same O atom, the energy is $(N-1)\varepsilon_d+2\varepsilon_p+2U_{pd}+U_p$, while if they are on different O atoms, it is $(N-1)\varepsilon_d+2\varepsilon_p+2U_{pd}$. As we saw before, only this latter case should be detected with a sizable cross section, and we neglect the former one. The positions of the two satellites with respect to the main peak are now easily written as a function of the parameters of the model Hamiltonian:

$$E(d^8)-E(d^9\underline{L})=\varepsilon_p-\varepsilon_d+U_d-2U_{pd}\,, \tag{9a}$$

$$E(d^{10}\underline{LL}')-E(d^9\underline{L})=\varepsilon_p-\varepsilon_d\,. \tag{9b}$$

The experimental value of the position of the small satellite is $\sim$5 eV. Comparing this with $\varepsilon_p+U_{pd}-\varepsilon_d \simeq 5$–$6$ eV obtained from the position of the main absorption edge, we get $U_{pd}\simeq 0$–$1$ eV. So, according to our interpretation of the experimental data, $U_{pd}$ is a very small quantity. This is in agreement with the theoretical analysis by Schluter, Hybertsen, and Christensen[16] who reported a value $U_{pd}\simeq 2$ eV and question several mechanisms proposed to explain superconductivity.[10,11]

The value of $U_d$ is now obtained from Eq. (9a) and from the experimental value of the position of the main satellite relative to the main peak (8 eV): $U_d \simeq 13$ eV. This number is a little larger than the usual values in transition-metal oxides. We shall see in the next section that a more careful analysis yields a slightly smaller value.

Finally, let us comment on the only parameter we have not determined, $U_p$. Although big theoretical values have been reported [$U_p\sim$4–5 eV (Ref. 16)], this parameter should not be important for the explanation of superconductivity. To see this, let us treat the O degrees of freedom in mean-field theory. Then, the on-site energy is renormalized by a term $U_p(\delta n_p)$ at most, where $\delta n_p$ is the occupation of the $2p$ orbitals of the O atom under concern. But superconductivity has been reported for small doping, which corresponds to values of $\delta n_p \lesssim 0.1$. So, the renormalization effects are expected to be very small for the materials that we intend to describe.

The previous analysis has been made assuming vanishing hopping integrals. As the parameters that determine the position of the satellites, $U_d$ and $\varepsilon_p-\varepsilon_d$, are bigger than these hopping integrals, the results of this preliminary analysis should be qualitatively correct.

### D. Cluster analysis

To go beyond this simplified version is not a straightforward task, as the Hamiltonian we get after we include the hopping integrals, sometimes called the *lattice* Anderson Hamiltonian, is an unsolved problem. The simplest approximation, known as the cluster approximation, consists in replacing the system by a cluster that includes only one transition-metal atom and the ligand atoms around it. In the present case, the cluster to be considered is made of a Cu atom and its six O neighbors (Fig. 3). Taking into account the different bond length for the in-plane and out-of-plane Cu-O pairs, the symmetry of this cluster is $D_{4h}$, and the wave functions will be classified according to the 10 irreducible representations of this group.

After the analysis of the previous section, we expect the

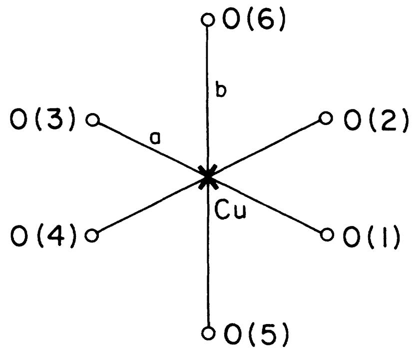

FIG. 3. Cluster $CuO_6$ used in Secs. III and IV. $a = 1.89$ Å and $b = 2.43$ Å being different, the point group is $D_{4h}$.

parameters not to be too far from $U_{pd} = 0-1$ eV, $\varepsilon_p - \varepsilon_d = 5$ eV, $U_d = 13$ eV. Actually, given the experimental uncertainty and the approximate nature of our approach, it is hopeless to derive a meaningful value for a parameter as small as $U_{pd}$, and we take $U_{pd} = 0$. Finally, the parameter $U_p$, that has been shown to be irrelevant for the dopings we are interested in, has little effect on the following analysis, as it merely shifts a few contributions to the photoemission spectrum that are expected to have very small cross sections, and we have also set $U_p = 0$.

Within the cluster approximation, the undoped system corresponds to one hole on the cluster. The optical absorption is then described by the transitions from the one-hole ground state to the one-hole excited states of the cluster. For the hopping integrals we have included, the one-hole problem can be solved explicitly. The results are listed in Table IV. A numerical application with $\varepsilon_p - \varepsilon_d = 4$ eV is given in Fig. 4. The ground state $\phi_g$ has been found to belong to $b_{1g}$, that is to be a mixing of $d_{x^2-y^2}$ and $P^{(S)} = (p_x^1 - p_y^2 - p_x^3 + p_y^4)/2$. There are two reasons for that. First, the hopping term $t_1$ between the O orbitals entering $P^{(S)}$ is *positive*. Hence, the self-energy of $P^{(S)}$ is $\varepsilon_p - 2t_1$, i.e. it is lowered with respect to the atomic value $\varepsilon_p$. Second, the hopping term $t_3$ between $d_{x^2-y^2}$ and $P^{(S)}$ is the biggest one, so the kinetic energy to be gained is also the biggest. The ground state $\phi_g$ being $b_{1g}$, the dipole allowed transitions correspond to final states of symmetry $b_{2u}$ and $e_u$, the lowest in energy being at $\varepsilon_p - 2t_2$. As $t_2$ is very small, $\varepsilon_p - \varepsilon_d = 4$ eV is enough to explain the position of the main absorption edge (see Fig. 4). So, if we compare this analysis with the preliminary one of the previous paragraph, we see that the main effect of hybridization is to increase the optical gap for a given value of $\varepsilon_p - \varepsilon_d$. Another interesting effect is the crystal-field splitting between the various $3d$ orbitals due to their mixing with O $2p$ orbitals. With respect to the ground state ($d_{x^2-y^2}$), the other $d$ levels are at 0.95 eV ($d_{3z^2-r^2}$), 1.41 eV ($d_{xy}$), and 1.45 eV ($d_{xz}, d_{yz}$) (see Fig. 4). Although these values are in qualitative agreement with the two lowest values reported by Geserich *et al.*,[20] we will not go further in this direction for reasons given in Sec. III B.

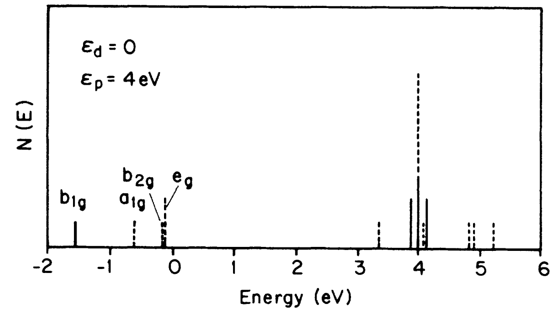

FIG. 4. One-hole energy states of a cluster $CuO_6$. The hopping integrals are taken from Table III. The thick solid line at $-1.56$ eV is the ground state. The solid (dashed) lines are the states accessible from the ground state by a dipole-allowed (-forbidden) transition. The height of a line gives the number of states having the corresponding energy. The symmetry of the five lowest lying states that correspond to crystal-field splitting of Cu $3d$ orbitals is also indicated.

To compute the photoemission spectrum, we take advantage of the fact that at the incident energies used in the experiments we shall interpret[15] the emission from a Cu $3d$ state has a much bigger cross section than the emission from an O $2p$ state, so that we can neglect the latter. Hence, the accessible states are two-hole states that result from creating a hole in a $3d$ orbital in a system that already has a hole in its ground state $\phi_g$. But such states are not eigenstates of the Hamiltonian. So the procedure to calculate the photoemission spectrum consists in determining the eigenstates of the two-hole problem, and then in calculating their cross section by projecting them on the accessible two-hole states. The first step is straightforward but cumbersome, as the dimension of the two-hole space is 1035. Thanks to the possibility of including only $d$ emission, an important number of these states are known *a priori* to have a vanishing cross section. Nevertheless, the details are too long to be reported here, and we quote only the results. Assuming the value $\varepsilon_p - \varepsilon_d = 4$ eV which gives the correct result for optical measurements, it was possible to reproduce the position of the various peaks by taking $U_d = 10$ eV, a value slightly smaller than that given by the preliminary analysis. In Fig. 5, the results are compared with the experimental data of Shen *et al.*[15] The length of the vertical lines gives the relative cross sections of the states that contribute to the signal. So the rel-

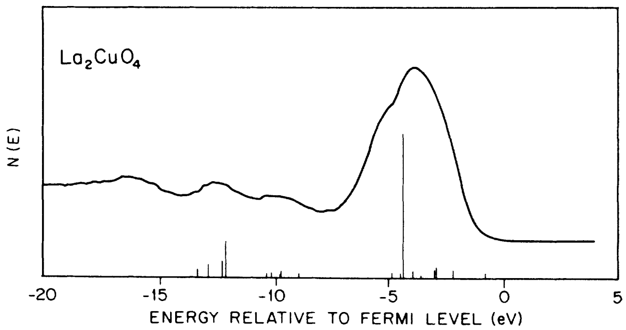

FIG. 5. Photoemission spectrum of $La_2CuO_4$. The solid curve is the experimental result of Shen *et al.* The vertical lines are the results of our cluster calculation.

TABLE IV. Solution of the one-hole problem for the cluster CuO$_6$ with $D_{4h}$ symmetry. For each representation, the orbitals and the eigenenergies are listed. For $a_{1g}$, we quote the secular equation, as it is of degree 3. $a_{1u}$ and $b_{1u}$ are missing because they are empty.

| | Orbitals | Eigenenergies |
|---|---|---|
| $a_{1g}$ | $\frac{1}{2}(p_x^1+p_y^2-p_x^3-p_y^4)$<br>$d_{3z^2-r^2}$, $\frac{1}{\sqrt{2}}(p_z^5-p_z^6)$ | $(\varepsilon_p+2t_1-E)[(\varepsilon_d-E)(\varepsilon_p-E)-2t_5^2]-4t_4^2(\varepsilon_p-E)=0$ |
| $a_{2g}$ | $\frac{1}{2}(p_y^1-p_x^2-p_y^3+p_x^4)$ | $\varepsilon_p-2t_1$ |
| $b_{1g}$ | $d_{x^2-y^2}$<br>$\frac{1}{2}(p_x^1-p_y^2-p_x^3+p_y^4)$ | $\frac{1}{2}(\varepsilon_d+\varepsilon_p-2t_1\pm\{(\varepsilon_d-\varepsilon_p+2t_1)^2+16t_3^2\}^{1/2})$ |
| $b_{2g}$ | $d_{xy}$<br>$\frac{1}{2}(p_y^1+p_x^2-p_y^3-p_x^4)$ | $\frac{1}{2}(\varepsilon_d+\varepsilon_p+2t_1\pm\{(\varepsilon_d-\varepsilon_p-2t_1)^2+16t_6^2\}^{1/2})$ |
| $e_g$ | $d_{xz}$, $d_{yz}$<br>$\frac{1}{\sqrt{2}}(p_z^1-p_z^3)$, $\frac{1}{\sqrt{2}}(p_z^2-p_z^4)$<br>$\frac{1}{\sqrt{2}}(p_x^6-p_x^5)$, $\frac{1}{\sqrt{2}}(p_y^6-p_y^5)$ | $\varepsilon_p$<br>$\frac{1}{2}(\varepsilon_p+\varepsilon_d\pm\{(\varepsilon_p-\varepsilon_d)^2+8(t_6^2+t_7^2)\}^{1/2})$ |
| $a_{2u}$ | $\frac{1}{2}(p_z^1+p_z^2+p_z^3+p_z^4)$<br>$\frac{1}{\sqrt{2}}(p_z^5+p_z^6)$ | $\varepsilon_p$ |
| $b_{2u}$ | $\frac{1}{2}(p_z^1-p_z^2+p_z^3-p_z^4)$ | $\varepsilon_p$ |
| $e_u$ | $\frac{1}{\sqrt{2}}(p_x^1+p_x^3)$, $\frac{1}{\sqrt{2}}(p_y^2+p_y^4)$<br>$\frac{1}{\sqrt{2}}(p_y^1+p_y^3)$, $\frac{1}{\sqrt{2}}(p_x^2+p_x^4)$<br>$\frac{1}{\sqrt{2}}(p_x^6+p_x^5)$, $\frac{1}{\sqrt{2}}(p_y^6+p_y^5)$ | $\varepsilon_p$<br>$\varepsilon_p+2t_2$<br>$\varepsilon_p-2t_2$ |

ative intensities of the three peaks are very well reproduced by our model, which gives extra confidence in the parameters derived through this fit.

In conclusion, by adjusting the value of only two parameters ($\varepsilon_p-\varepsilon_d=4$ eV and $U_d=10$ eV), it is possible, within a cluster analysis, to reproduce the position of the main absorption edge in an optical experiment and the position and intensity of the three peaks that have been attributed to the Cu-oxide layers in the photoemission spectrum.

## IV. DISCUSSION AND CONCLUSION

Let us summarize the results of Secs. II and III in terms of the model Hamiltonian of Eqs. (1)-(4). In Eq. (2), it is a good approximation to give all the O 2$p$ orbitals (respectively Cu 3$d$ orbitals) the same on-site energy. Measuring the energies with respect to the Cu 3$d$ on-site energy $\varepsilon_d$, the relevant parameter is the relative position of the O 2$p$ levels $\varepsilon_p-\varepsilon_d$. Both photoemission and optical measurements give $\varepsilon_p-\varepsilon_d=4$ eV. For the hybridization, the inclusion of the seven hopping integrals of Table III is enough. The parameters of Eq. (3) are given by $t_i=-T_i$, $i=1,\dots,7$. Finally, in Eq. (4), it should be a good approximation to neglect $U_{pd}$ because it is small and $U_p$ because it has very little effect in the concentration range under study. The correlation effects are then described by a single parameter $U_d=10$ eV. Our parameters, as well as these of other groups whose work has been mentioned in the text, are summarized in Table V.[28]

Now, we want to analyze the properties of the system described by this Hamiltonian in both the cases of undoped and doped materials. The first thing to do is to see where we are in the map outlined in the Introduction. With our parameters, three possibilities are *a priori* ir-

TABLE V. Comparison of the parameters obtained by several groups: (a) Ref. 14; (b) Ref. 15; (c) Ref. 16; (d) Ref. 17; (e) our results.

| | (a) | (b) | (c) | (d) | (e) |
|---|---|---|---|---|---|
| $t_3$ | 1.9 | 2.3 | ? | 1.55 | 1.38 |
| $t_1$ | ? | ? | ? | 0.65 | 0.33 |
| $\varepsilon_p-\varepsilon_d$ | 0 | 0.3 | 2 | 1.2 | 4 |
| $U_d$ | 5.5 | 6.5 | 10-12 | 8.5 | 10 |
| $U_p$ | ? | ? | 6-8 | 4.1-7.3 | ? |
| $U_{pd}$ | ? | ? | $<4$ | $>0.6$ | 0-1 |

relevant: (i) the weak-coupling limit,[5] because $U_d=10$ eV; (ii) the theories based on a large $U_{pd}$,[10,11] because we showed this parameter is small; (iii) the theories that put the extra hole in a nonbonding orbital,[13] as evidence has not been found for the ionic corrections that would justify this hypothesis. Clearly, we are in the case of a large $U_d$. But $\varepsilon_p-\varepsilon_d=4$ eV is *not* very large compared to the biggest hopping integrals, and the main issue is the following: Is $\varepsilon_p-\varepsilon_d$ large enough to localize the holes in the undoped materials? If it is the case, we do not expect the formation of a triplet[6] due to Hund's rule coupling between two holes on Cu upon doping because $\varepsilon_p-\varepsilon_d=4$ eV $\ll U_d=10$ eV. But the O-O hopping integral $t_1=0.33$ eV is *not* negligible. Does the formation of a singlet still provide the biggest energy to be gained by an extra hole? Let us answer these questions.

### A. Undoped materials

As mentioned before, the undoped materials correspond to a filling of one hole/Cu atom. Given the large value of the Hubbard parameter for Cu 3*d* orbitals ($U_d=10$ eV), the Mott localization is likely to be effective if, in the ground state, the holes tend to sit mainly on Cu. This depends on the hybridization with the O 2*p* orbitals and can be analyzed within a cluster approximation. The calculations have in fact already been performed in Sec. III D when studying the optical spectrum. The ground state was found to be a mixing of $d_{x^2-y^2}$ and $P^{(S)}$. What is now of interest is the weight of the wave function on the different orbitals. With our parameters, the probability of finding the hole on Cu is 0.75. In electron notation, this means that the ground-state configuration is $d^{9.25}$. So, the hybridization is relatively small, and the ground state is likely to be the *magnetic state*[29] that constitutes the basis of the theory of magnetic insulators.

To test this hypothesis, let us first see whether the magnetic properties of the undoped materials can be accounted for in this context. $La_2CuO_4$ has been reported to be antiferromagnetic with a coupling constant $J\simeq0.1$ eV within the Cu-oxide layers. For magnetic insulators, the antiferromagnetism is explained by superexchange theory that predicts

$$J=4\frac{t_3^4}{(\varepsilon_p-\varepsilon_d)^2}\left[\frac{1}{U_d}+\frac{1}{\varepsilon_p-\varepsilon_d}\right]. \tag{10}$$

While the previous authors who tried to use this formula for $La_2CuO_4$ found 1.5 eV,[15] our parameters yield $J=0.32$ eV. The difference originates from the fact that the value we report for $\varepsilon_p-\varepsilon_d$ (4 eV) is bigger than the values reported before. Our result for $J$ has the correct order of magnitude, although it is a little too big. This could be due to the neglect of $U_p$. The formula giving $J$ when $U_p$ is not vanishing is

$$J=4\frac{t_3^4}{(\varepsilon_p-\varepsilon_d)^2}\left[\frac{1}{U_d}+\frac{1}{(\varepsilon_p-\varepsilon_d)+U_p/2}\right] \tag{11}$$

and yields a smaller value of the coupling constant. So, this is no essential problem in explaining the antiferromagnetism of $La_2CuO_4$ with superexchange theory.

The other point to check is that, although $\varepsilon_p-\varepsilon_d$ is not so large, we have an insulator. So, we need an estimation of the conductivity gap. Let us note that this gap is *not* given by the first dipole-allowed transition in a cluster approximation. In fact, the process to be considered for conductivity is the following: (i) remove a hole from its localized orbital; (ii) put it far away, i.e., in a region where all the Cu sites are already occupied; (iii) let it delocalize. But steps (ii) and (iii) are equivalent to adding a hole to the undoped material, that is to doping. So, let us see what we can say about doped materials.

### B. Doped materials

The first step is to understand the nature of the system with one extra hole. In fact, we shall not attempt to go to finite doping here. Starting from the magnetic ground state of the undoped material in which all the Cu sites are nearly filled with one hole, an extra hole will prefer to go in an O orbital of energy $\varepsilon_p$ due to the large $U_d$. Now, it can gain energy due to two hopping processes: (i) O-O hopping, by which it will tend to delocalize; (ii) O-Cu hopping, which corresponds to an interaction with the localized spins. Let us estimate the energy to be gained by each process separately.

By delocalizing in the O band, the hole can gain half the bandwidth, i.e., $4t_1=1.32$ eV. If we assume that $\varepsilon_d=0$, then $\varepsilon_p=4$ eV and the energy of the extra hole is 2.68 eV.

If, on the contrary, we want to stress the interaction with the localized spins, then the relevant problem is that of two holes on a cluster $CuO_6$. This problem has already been solved in Sec. III when fitting the photoemission spectrum. Let us describe in more detail the results we obtained. The ground state is a singlet. The orbital part of its wave function involves the configurations $d^2_{x^2-y^2}$, $d_{x^2-y^2}P^{(S)}$, and $(P^{(S)})^2$. It is constructed out of the one-hole wave functions that enter the one-hole ground state, which is not surprising given the important crystal-field splitting that separates the one-hole ground state from the first one-hole excited state. Still assuming $\varepsilon_d=0$, the energy of this singlet is $-0.32$ eV (see Table VI), while the energy of *one* hole is $-1.56$ eV (see Fig. 4). So, if such a singlet is formed, the energy of $N+1$ holes on a cluster with $N$ Cu atoms is $(N-1)(-1.56)+(-0.32)$, whereas the energy of $N$ holes is $N(-1.56)$. The difference gives the effective energy required to introduce an extra hole

TABLE VI. Symmetry, total spin, and energy of the lowest-lying two-hole states of $CuO_6$ with $\varepsilon_d=0$, $\varepsilon_p=4$ eV, and $U_d=10$ eV, the hopping integrals being taken from Table III.

| Representation | Energy | Total spin |
|---|---|---|
| $a_{1g}$ | −0.32 | $S=0$ |
| $b_{1g}$ | 1.13 | $S=0$ or 1 |
| $b_{2g}$ | 1.78 | $S=0$ or 1 |
| $e_g$ | 1.86 | $S=0$ or 1 |
| $a_{2g}$ | 1.93 | $S=0$ or 1 |
| $e_u$ | 2.31 | $S=0$ or 1 |

and create such a singlet $\varepsilon_{\rm eff}=-0.32+1.56=1.24$ eV.

This effective energy $\varepsilon_{\rm eff}$ is 1.44 eV less than the energy of an extra hole in the O band. So, the magnetic energy to be gained by forming a local singlet is the biggest. As a consequence, a good description of the ground state should be obtained by taking this local singlet as a starting point and by allowing it to delocalize by switching on the hopping integrals that are set to 0 in the cluster approximation. This procedure is valid only if the effective hopping integrals of this singlet are small compared to the energy that separates it from the first excited state. The 6 lowest two-hole energy states are listed in Table VI; the first excited state is 1.45 eV above the ground state. The calculation of the hopping integrals of this singlet is in progress.

Finally, let us go back to the problem of the conductivity gap. The energy to remove a hole is 1.56 eV, while the energy required to create it in a region with already one hole/Cu atom is $\varepsilon_{\rm eff}=1.24$ eV (if we neglect the delocalization energy of this singlet). So, we get a conductivity gap of $1.56+1.24=2.8$ eV, and the undoped material is a good insulator. Moreover, this gap provides a possible explanation of the feature observed in optical absorption between 2 and 3 eV.[19,30]

*Note added in proof.* The tight-binding fit in Sec. II is not unique. In particular, M. Schluter (private communication) has informed me that a fit with values of $\varepsilon_p-\varepsilon_d\approx 0$ agrees better with the character of the wave functions in the Mattheiss band-structure calculation. However, since in Sec. III this parameter is adjusted empirically to fit the optical properties and since the overlap matrix elements which determine the bandwidth are not sensitive to details of the tight-binding fit, the conclusions of the paper are not altered.

## ACKNOWLEDGMENTS

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