Electronic structure of La_2CuO_4 and $YBa_2Cu_3O_6$: A local-spin-density approximation with on-site Coulomb-U correlation calculations

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The electron-electron correlation has been considered by using the local-spin-density approximation (LSDA) with on-site Coulomb interaction in the first-principles discrete variational cluster method. Based on the correction to LSDA, we have carried out self-consistent electronic-structure calculations for the strongly correlated electronic systems of La_2CuO_4 and $YBa_2Cu_3O_6$. In contrast to LSDA, the LSDA+U calculations reveal the experimentally observed antiferromagnetic and insulating ground state. The energy gap for these compounds is of a charge-transfer character, and the values of the energy gap and Cu magnetic moment are in good agreement with experiments. The orbital character of the states near the Fermi level in La_2CuO_4 and $YBa_2Cu_3O_6$ is discussed and a comparison with experiments is made.

I. INTRODUCTION

Since the discovery of the high-T_c superconductivity in the copper oxide systems, large efforts have been made to the superconducting mechanism and the electronic properties of these materials. Among these efforts, the electronic-structure calculations based on the local-density approximation (LDA) or the local-spin-density approximation (LSDA) have been shown to give a good description for the optical phonon frequencies and Fermi surface,[1-4] but they fail in predicting the deeper levels of these materials and the antiferromagnetic and insulating ground state[5] for the parent compounds of high-T_c superconductors La_2CuO_4 and $YBa_2Cu_3O_6$. The situation resembles that of the Mott insulating $3d$ monoxides MnO, FeO, CoO, and NiO, which are indicated by many experiments to be wide-gap insulators but LSDA theory predict as a metal (FeO and CoO) or a small-gap semiconductor (MnO and NiO).[6] It is obvious that a correct electronic structure can provide a basis for understanding the superconductivity in these copper oxides. The physical origin of the failure of LSDA theory can be traced back to the mean-field character of the Kohn-Sham equations,[7,8] by which the electron-electron correlation potential is underestimated for the compounds with strong electron-electron correlation. Several attempts to improve the LSDA have been made, such as the self-interaction correction (SIC),[9] the generalized gradient approximation (GGA),[10] quasiparticle,[11] etc., but the formalism of those corrections is complicated. It should be pointed out that the electronic correlation effect is partially considered in LDA (or LSDA), therefore, repeat calculation of electron-electron correlation must be avoided when deal with this problem. It is generally accepted that strongly correlated system can be quite well described by the Hubbard model or Anderson-lattice model.[12] The essential point of these models is that the on-site Coulomb interaction as a strong correlation of d or f electrons is included in the model Hamiltonian. The parameter of this interaction U is defined as

$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n), \tag{1}$$

i.e., the Coulomb energy cost to place two electrons at the same site. Recently, Anisimov, Zaanen, and Anderson[8] proposed a modified LDA method (LDA + U) in their linear-muffin-tin-orbital (LMTO) band calculations. This method emphasized that the localization was controlled by the on-site Coulomb interaction U rather than the Stoner exchange interaction I. They added a spin- and orbital-dependent one-electron potential to the LDA theory. Their calculated results for $3d$-transition-metal oxide[8] and $La_{2-x}Sr_xCuO_4$ (Ref. 13) showed that this method was successful in description of the electronic structure of a variety of $3d$ insulators, yielding order-of-magnitude improvements on conventional LDA results. Another advantage of this method is that it is easy to introduce the correlation correction in the conventional LDA theory. The electronic structure of La_2CuO_4 material considering the correction of electron-electron correlation has been calculated by several authors, Svane[9] in their LSD+SIC calculations obtained magnetic moment of Cu $0.47\mu_B$, energy gap 1.4 eV; Anisimov *et al.*[13] using LDA+U method obtained magnetic moment of Cu $0.74\mu_B$, energy gap 2.3 eV. All of these calculated results are in agreement with the experimental results of about $0.4\mu_B$ (Ref. 14) and 2.0 eV (Ref. 15), and show good improvement on LDA (LSDA) calculations. But for $YBa_2Cu_3O_6$ compound, according to our knowledge, there is no similar electronic structure calculations published. In this paper, we apply our first-principals discrete variational (DV) cluster method, with a similar manner to take into account of the on-site Coulomb interaction U correlation in the local-spin-density-approximation (LSDA+U), to study the electronic structure of La_2CuO_4 and $YBa_2Cu_3O_6$ compounds. The magnetic moment, energy gap, orbital character of states near Fermi energy and the possible

excitations from occupied energy levels to unoccupied energy levels are analyzed and compared with experiments. The results show that this method can give a correct description of the antiferromagnetic and insulating ground state of these materials.

II. METHOD OF CALCULATION

It is well known that compounds of La_2CuO_4 and $YBa_2Cu_3O_6$ are both strongly correlated antiferromagnetic insulators. To this kind of system, the LSDA is not enough to consider the correlation interaction. However, the correlation effect is very important for the above system to understand its ground state. One of the convenient and useful method considering this effect is including on-site Coulomb interaction in LSDA.[8] In this approach, one must subtract the exchange-correlation part, which has been underestimated considered in LSDA. The simple approximate method to take into account of this problem is replacing the $n_{m\sigma}$ with spin σ and orbital m Hubbard-like U term by its fluctuation from the average number n^o, i.e., $n_{m\sigma} - n^o$. In our calculations, n^o is taken as the occupancy number obtained by LSDA calculation in a self-consistent manner, which may be a little bit different from the average occupancy of one d orbital ($n^o = n_d/10$) as proposed by Ref. 8. In this way, we write the total-energy functional as

$$E = E^{\mathrm{LSD}} + \frac{1}{2}\sum_{m,m',\sigma} U(n_{m\sigma} - n^o)(n_{m'\sigma-} - n^o) + \frac{1}{2}\sum_{m,m'(m\neq m'),\sigma} U(n_{m\sigma} - n^o)(n_{m'\sigma} - n^o)$$
$$-\frac{1}{2}\sum_{m,m'(m\neq m'),\sigma} J(n_{m\sigma} - n^o_\sigma)(n_{m'\sigma} - n^o_\sigma), \tag{2}$$

where E^{LSD} is the usual LSDA total energy, U and J are on-site Coulomb energy and exchange energy, respectively. For simplification, we approximate U and J as independent to orbital parameter m. ${n_\sigma}^o$ is the average spin occupancy due to the band splitting for different spin. In this approximation, the zero fluctuation is corresponding to the usual LSDA. In analogy with the formulation of usual LSDA, the single-particle potential can be derived from the total energy Eq. (2) in the following form:

$$V_{m\sigma} = V^{\mathrm{LSD}} + U\sum_{m'}(n_{m'\sigma-} - n^o) + U\sum_{m'\neq m}(n_{m'\sigma} - n^o) - J\sum_{m'\neq m}(n_{m'\sigma} - n^o_\sigma), \tag{3}$$

where V^{LSD} is the usual LSDA potential, corresponding to the charge density and spin density with the number of d electrons given by $n_d = \Sigma_{m,\sigma} n_{im\sigma}$. We use this kind of potential (LSDA+U) in our DV-SCF cluster calculations. For $3d$ electrons of Cu in La_2CuO_4 and $YBa_2Cu_3O_6$ compounds, the parameter U_d and J are chosen to be 6.5 eV and 0.98 eV, respectively. These data are obtained from U_{eff} and J of Anisimov *et al.*, which may be reasonable as pointed out by Ref. 8. In our calculations, an embedded cluster model[16] is used to simulate the La_2CuO_4 and $YBa_2Cu_3O_6$ crystals. In this model, a CuO_6 cluster is considered for La_2CuO_4. This CuO_6 cluster is constructed with one Cu ion at center and four strongly bonded planar O(1) neighbors at a distance of 1.89 Å and two more weakly bonded apical O(2) neighbors at a distance of 2.41 Å.[17] For $YBa_2Cu_3O_6$ crystal, we choose a Cu_4O_{10} cluster, which composed of two layers of Cu(2)-$O(2)_2$ plane, two apical O(4) and two Cu(1) ions. The lattice parameters for this crystal are obtained from experimental values.[18] These clusters CuO_6 and Cu_4O_{10} are embedded in an antiferromagnetic La_2CuO_4 or $YBa_2Cu_3O_6$ crystallite, respectively. The Coulomb potential and exchange-correlation potential raised from the ions in the crystallite (with 1892 and 1598 ions, respectively) surrounding the clusters are considered in the one-electron Hamiltonian. The long-distance Coulomb potentials generated by the ions outside the crystallite to infinity are also involved using the Ewald method.[19] The $3d$, $4s$ electrons of Cu ions and the $2s$, $2p$ electrons of O ions are adopted as valence electrons, which should respond to the variation in the self-consistent processes, and the more tightly bound core electrons, remain in their atomic state in a frozen-core approximation. To get the electronic densities of states (DOS) from the discrete energy level ϵ_i, the Lorentz expansion scheme is used, the total DOS is defined as

$$D(E) = \sum_{n,l,\sigma} D^\sigma_{nl}(E) \tag{4}$$

with the partial densities of states (PDOS) for atomic orbital labeled by n, l quantum number, and spin σ:

$$D^\sigma_{nl}(E) = \sum_i A^\sigma_{nl,i}\frac{\delta/\pi}{(E-\epsilon_i)^2 + \delta^2}, \tag{5}$$

where i labels the eigenlevel and a broadening factor δ=0.12 eV is used. $A^\sigma_{nl,i}$ is the Mulliken population number for corresponding atomic orbital.

III. RESULTS AND DISCUSSION

The electronic structure of La_2CuO_4 and $YBa_2Cu_3O_6$ are calculated self-consistently by DV cluster method in above LSDA+U formalism. For comparison, the LSDA calculations for the same clusters are also carried out. Figures 1–4 show the calculated total density of states (TDOS) and the partial density of states (PDOS) of Cu

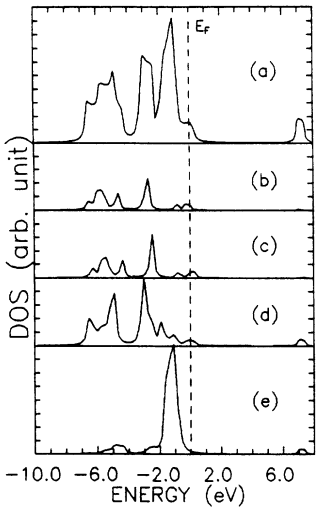

FIG. 1. The densities of states (DOS) for La_2CuO_4 in LSDA calculations. (a) The total DOS; (b) the partial DOS of the spin-up Cu $3d$ orbitals; (c) the spin-down Cu $3d$ orbitals; (d) the planar O(1) $2p$ orbitals; (e) the apical O(2) $2p$ orbitals.

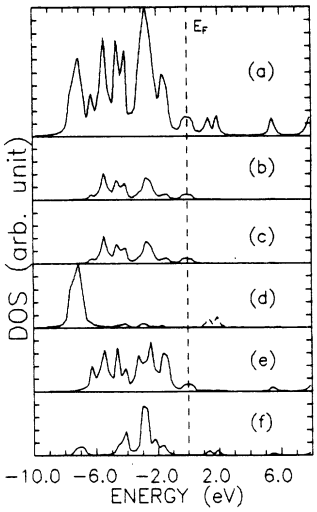

FIG. 3. The densities of states (DOS) for $YBa_2Cu_3O_6$ in LSDA calculations. (a) The total DOS; (b) the partial DOS of the spin-up Cu(2) $3d$ orbitals; (c) the spin-down Cu(2) $3d$ orbitals; (d) the Cu(1) $3d$ orbitals and $4s$ orbital (dashed line); (e) the planar O(2) $2p$ orbitals; (f) the apical O(1) $2p$ orbitals.

$3d$, $4s$, and O $2p$ orbitals in both LSDA and LSDA+U cases. The calculated values of the energy gaps, the magnetic moments of Cu, and the corresponding experimental values are given in Table I. It can be seen from Table I that there are energy gaps of about 0.3 eV (which are obtained from the energy difference between the highest occupied and the lowest unoccupied energy level) for La_2CuO_4 and $YBa_2Cu_3O_6$ in our LSDA cluster calculations, but in the TDOS shown in Figs. 1 and 3, the small energy gaps are smeared out by the broadening factor in Eq. (5). Compared to the experimental observed wide gaps (about 2.0 eV), our LSDA cluster calculated gaps are too small and fail to show the insulating character of these materials. In this respect, the results of our LSDA cluster calculations are similar to those of conventional LSDA band theory. It is noted that our calculated gaps and magnetic moments are somewhat larger than the ones of corresponding band calculations (by which they are nonmagnetic and metallic). The main reason for this is that the translational symmetry is ignored in the real-space cluster approach, which can be considered as a weighted sum of contributions over the part of k points

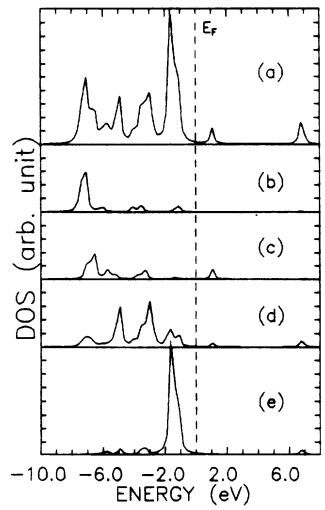

FIG. 2. The densities of states (DOS) for La_2CuO_4 in LSDA+U calculations. (a) The total DOS; (b) the partial DOS of the spin-up Cu $3d$ orbitals; (c) the spin-down Cu $3d$ orbitals; (d) the planar O(1) $2p$ orbitals; (e) the apical O(2) $2p$ orbitals.

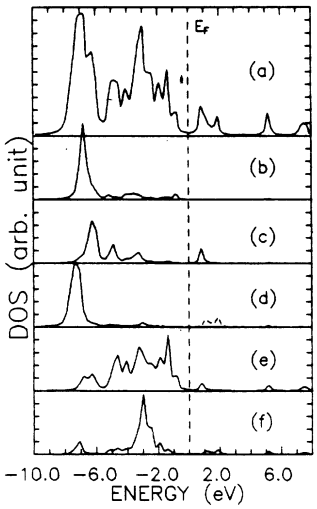

FIG. 4. The densities of states (DOS) for $YBa_2Cu_3O_6$ in LSDA+U calculations. (a) The total DOS; (b) the partial DOS of the spin-up Cu(2) $3d$ orbitals; (c) the spin-down Cu(2) $3d$ orbitals; (d) the Cu(1) $3d$ orbitals and $4s$ orbital (dashed line); (e) the planar O(2) $2p$ orbitals; (f) the apical O(1) $2p$ orbitals.

TABLE I. The comparison of the magnetic moments (m, in μ_B) and energy gaps (E in eV) of the La_2CuO_4 and $YBa_2Cu_3O_6$ compounds between the experimental (expt) results and the cluster model with LSDA and LSDA+U calculations.

	$E_{\rm LSD}$	$E_{\rm LSD+U}$	$E_{\rm expt}$	$m_{\rm LSD}$	$m_{\rm LSD+U}$	$m_{\rm expt}$
La_2CuO_4	0.30	2.17	2.0	0.47	0.59	0.40
$YBa_2Cu_3O_6$	0.33	1.69	1.7	0.02	0.52	0.48

around the Γ point of the reciprocal space. Therefore, in the cluster method, the role of Γ point may be emphasized as compared with usual band theory calculations. Chen and Callaway,[20] in their study for La_2CuO_4 by using CuO_6 cluster, obtained the same order-of-magnitude gap (0.44 eV) and moment ($0.64\mu_B$) as ours. If more atoms are include in the cluster, such as the larger cluster Cu_3O_{16}, which is also considered in the calculations of Chen and Callaway,[20] the reduction of magnetic moment of Cu is presented and may yield a negligible moment in the limit of a larger system for LSDA calculations. This situation is also shown in our LSDA calculation for $YBa_2Cu_3O_6$, in this case the relative larger cluster Cu_4O_{10} is used, and a very small moment of about 0.02 μ_B (see Table I) is obtained, which is in good agreement with the nonmagnetic result of conventional LSDA band theory. However, on the other hand, the object of this paper is to study the effect of the local on-site Coulomb interaction on the LSDA calculations, the adopted cluster model may be more reasonable to study the localized character in detail. In the use of the LSDA+U correction, the results show an essential reconstruction of the PDOS for Cu 3d orbitals. The d band of Cu has been split into a occupied lower Hubbard band (LHB) and an unoccupied upper Hubbard band (UHB). The LHB lies about 6.5 eV ($\sim U_d$) below the Fermi energy E_F, and the UHB, which is mainly contributed by spin-down empty Cu 3d orbitals, lies just above E_F. It is indicated that the on-site Coulomb interaction respond to the much larger d-band splitting comparing with LSDA calculations, and leads to the increasement of the Cu magnetic moment due to the potential difference between levels for different spin for the partial polarized case. The occupied O 2p band (see Figs. 2 and 4) lies between LHB and UHB, and a gap obviously arise from O 2p to UHB. Therefore, due to the possible transition of O 2p to Cu 3d, the compounds La_2CuO_4 and $YBa_2Cu_3O_6$ are all charge-transfer insulators as shown by experiments. On the whole, it can be seen from Table I that our LSDA+U calculated energy gaps and magnetic moments of Cu ions show order-of-magnitude improvements on the results of LSDA calculations, and are in good agreement with experimental values.[14,15,21,22]

As shown in Fig. 2 for the LSDA+U calculated DOS for La_2CuO_4, the total O 2p band width is about 6.4 eV, which is in accord with Svane[9] (SIC-LSD) calculated value of about 6.2 eV. The O 2p band are contributed by a major bell-shaped structure in the region of 0–4.2 eV below the E_F and a tail towards larger binding energies. The O 2p PDOS has a maximum at about −1.65 eV with another peak at about −3.4 eV. In photoemission experiment,[23] the O 2p derived structure has a similar form with a width of 4.5 eV and the peak maximum located at −2.8 eV below the E_F. The shoulder observed in the experiment at 1.7 eV below the primary peak may match the theoretical structure at −3.4 eV, which is derived from in-plane O(1) and Cu. These two O 2p peaks were also confirmed by the calculations of Svane[9] at −1.5 eV and −2.7 eV. Since the on-site Coulomb interaction pulls the major occupied Cu 3d states to higher binding energies, only little admixture of it is found in the O 2p band, and the hybridization of Cu 3d orbitals is more at peak −3.4 eV than the one at peak −1.65 eV. This is also in agreement with the experimental observation that the primary O 2p peak has more pure O 2p character than the shoulder.[23] Our calculations indicate that the peak at −1.65 eV is composed of two overlapping levels actually. One of the levels is attributed to the hybridization between 65% in-plane O(1) $2p_{x,y}$ and 27% Cu $3d_{x^2-y^2}$ orbitals. Another one is the apical hybridization state between Cu $3d_{3z^2-r^2}$ (11%) and O(2) $2p_z$ (74%), which is only 0.17 eV below the former. Therefore, we can predicate rationally that the motion of the two apical O(2) along the Cu-O(2) bond axis ["anti-Jahn-Teller (JT) polaron"] may lead some additional holes of the doped La_2CuO_4 localize in the $(3z^2 - r^2)$-like orbital. Anisimov *et al.*[13] also suggested that the anti-JT polaron lies very close to the ground state. The coexistence of these small polarons with more bandlike carriers has been used account for the anomalous normal-state properties.[24] For unoccupied states, the analyses of the polarization-dependent x-ray-absorption spectroscopy[25] indicated that UHB are predominantly composed of in-plane orbitals in the CuO_2 plane with Cu $3d_{x^2-y^2}$ and O $2p_{x,y}$ symmetry, and other orbitals, such as O $2p_z$ or Cu $3d_{3z^2-r^2}$ is about one order of magnitude lower. The three-band model cluster calculations[26,27] also confirmed that La_2CuO_4 is a charge transfer insulator with an upper Hubbard band composed of about 80% Cu $3d_{x^2-y^2}$ and 20% O(1) $2p_{x,y}$ states. In our calculations, the UHB consist of about 53% Cu $3d_{x^2-y^2}$, 37% O(1) $2p_{x,y}$ and 10% O(1)2s. The main reason for more contributions from oxygen orbitals in our calculations as compared with band calculation may be due to the cluster CuO_6 we chose, where the proportion of in-plane oxygen and copper in this cluster is 4:1, which is two times of the proportion (2:1) in the unit cell of La_2CuO_4. After a rough estimate, taking the proportion 2:1 into account, the composition become to about 70% Cu $3d_{x^2-y^2}$, 24% O(1) $2p_{x,y}$, and 6% O(1)2s, which is in agreement with experiment.[25]

$YBa_2Cu_3O_6$ are generally more complicated than that

for La_2CuO_4 because of the more complex unite cell,[18] where there are two kinds of Cu ions [Cu(1) and planar Cu(2)]. The LSDA+U calculations for the magnetic moments of Cu(2) and Cu(1) show that the magnetic moments of the two Cu(2) ions in adjacent CuO_2 planes are equal in magnitude and opposite in sign, and the magnetic moment of Cu(1) is nearly zero. This result correctly display the antiferromagnetic structure (AFM) of the compound. The calculated DOS for $YBa_2Cu_3O_6$ is shown in Fig. 4, the occupied states are mainly the hybridization band of Cu $3d$ and O $2p$ orbitals in the region of -1--7 eV. Similar to the case of La_2CuO_4, the low binding energy part of the DOS is dominated by O $2p$ orbitals, while Cu $3d$ orbitals, due to the on-site Coulomb U_d interaction, are mainly distributed in the high binding energy part of DOS. The planar O(2) $2p$ derived band with hybridization of Cu(2) $3d$ covers entire range of valence band. Otherwise, the apical O(4) $2p$ orbitals with small admixture of Cu(1) $3d$ form a narrow, localized hybridization band (the "dumbbell band"). For the unoccupied states just above E_F, our calculated DOS suggest that it consist of two parts. One is the in-plane hybridization state between Cu(2) $3d_{x^2-y^2}$ (64%) and O(2) $2p_{x,y}$(27%) orbitals, as well as small admixture of O(2) $2p_z$ (4%) and O(2) $2s$ (5%) orbitals. Another is due to the out-of-plane Cu(1) $4s$ and O(4) $2p_z$ orbitals. On the whole, this distribution of states near Fermi energy E_F is in accord with experiments. Particularly, when additional holes are induced by increasing the oxygen content, the Fermi energy E_F will shift to lower energy. Thus most of the holes will distribute on the in-plane O(2) $2p_{x,y}$ orbitals, which is in agreement with experiment[28] indicating that the hole has oxygen character for this kind of superconductors.

It has been observed from experiments of the resonant Raman scattering[22] and the visible-near-uv optical spectra[29] that there are four electronic transitions in the low-energy range for insulator $YBa_2Cu_3O_6$. The energy of the four transitions are 1.7 eV, 2.1 eV, 2.5 eV, and 4.1 eV, respectively. According to the analyses of experiments,[22,29] the resonances near 1.7 eV and 2.5 eV can be attributed to "charge-transfer transitions" from the plane O p_x or p_y bands to the upper Hubbard band having mainly planar Cu $3d$ character. The initial state for the transition 4.1 eV is the apical O(4) x-polarized p orbital,[22] and Cu(1) $4s$ orbital may play the final state in this transition.[29] The experimental results[22] about the transition of 2.1 eV are quite confused. For xx polarization, the resonance near 2.1 eV seems similar transition as 1.7 and 2.5 eV peaks. However, the zz weak resonance at 2.1 eV is likely due to transition from the occupied Cu(1) dumbbell orbital to the upper Hubbard band too. Therefore, this transition should be further identified by experiments. In our LSDA+U calculations (see DOS in Fig. 4), we find four peaks at -0.8, -1.3, -1.8, and -2.9 eV just below E_F. The peaks of -0.8 and -1.8 eV are predominantly derived from in-plane O(2) $2p_{x,y}$ orbitals, while the peak of -1.3 eV also comes from in-plane O(2) but with $2p_z$ orbital symmetry. The fourth peak of -2.9 eV is contributed by the apical O(4) $2p_{x,y}$ orbitals from dumbbell band. One of the empty states having mainly Cu $3d_{x^2-y^2}$ character reside at about 0.89 eV above the E_F, the Cu(1) $4s$ empty orbitals have the energies of 1.1 eV and 1.9 eV above the E_F. The transition of electron from above occupied states to empty states will lead the peaks observed by experiments. Since our calculations show that the "dumbbell" band is narrow and does not seem to be hybridized significantly with the other bands. Electronically, the two subsystems, CuO_2 plane and dumbbell, are almost isolated from each other. This point of view was also suggested by experiment[22] due to the dipole matrix elements between them are small. Therefore, the transitions between the states within the two CuO_2 plane is possible, and the transitions from dumbbell band to the UHB may be very weak. In this way, our calculations predict that there are mainly four possible transitions of 1.69, 2.19, 2.69, and 4.0 eV in low-energy range. The peaks of 1.69 and 2.69 eV are attributed to the transitions from the charge-transfer band (CTB) of in-plane O(2) $2p_{x,y}$ states to the UHB of Cu $3d_{x^2-y^2}$–O(2) $2p_{x,y}$ orbitals. The transition of 4.0 eV are from the O(4) $2p_{x,y}$ state in the dumbbell band to the empty state of Cu(1) $4s$. It is obvious that our calculated transition energies and the polarization character of states are in good agreement with the experiments.[22,29] For the controversial transition of 2.19 eV, our results suggest that the initial state of this transition is the in-plane O(2) $2p_z$ orbitals derived from the CTB, and the final state is the UHB the same as other two in-plane transitions.

IV. CONCLUSION

We have considered the electron-electron correlations by using LSDA+U formalism in the DV cluster method. The first-principal self-consistent electronic-structure calculations confirm that La_2CuO_4 and $YBa_2Cu_3O_6$ are all charge-transfer insulators. The calculated energy gap and magnetic moment of Cu ions is in good agreement with experimental results, and show order-of-magnitude improvements on conventional LSDA calculations. For the analyses of the orbital character of states near the Fermi level, our results indicate that the Cu $3d$ orbitals have been splitting into the LHB and the UHB (having mainly spin-down Cu $3d_{x^2-y^2}$ characters). The in-plane O $2p_{x,y}$ symmetry derived from the CTB just below the E_F is in accord with the hole states of O $2p_{x,y}$ character for this kind of copper oxide superconductors suggested by experiments.[28] The prediction of the four low-energy transitions for $YBa_2Cu_3O_6$ insulator is also in good agreement with experiments.[22,29] It is conclusive that our DV cluster calculations in the LSDA+U formalism give a correct description for the antiferromagnetic and insulating ground state of the strong correlated La_2CuO_4 and $YBa_2Cu_3O_6$ systems.

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