

## Correlation-corrected energy bands of $\text{YBa}_2\text{Cu}_3\text{O}_7$ : A mutually consistent treatment

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The band structures and density of states (DOS) of important subunits (Cu-O planes and chains, both including apical oxygens) in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  were computed. As a first step we employed an *ab initio* Hartree-Fock (HF) crystal-orbital method to both subunits in a mutually consistent way embedding them also in a partially self-consistent Madelung potential of the 3D crystal. Afterwards the bands were corrected for correlation by a Green's-function method in second order of the Møller-Plesset many-body perturbation theory. The main purpose of these rather large-scale calculations was to obtain reliable unfilled energy bands to be used in subsequent exciton bands calculations. This will make it possible to look more thoroughly at the proposed excitonic (polarization) mechanism of high- $T_c$  superconductivity. A comparison with calculations based on a local-density-functional (LDF) approximation showed good agreement to our approach in the valence-band energy region above  $-8$  eV while the LDF results agree well with experimental photoelectron spectra. In contrast to the LDF methods, we detected between  $-8$  and  $-12$  eV flat Cu $3d$  energy bands, which correspond to satellite structures observed by experiment. [S0163-1829(97)01613-5]

### I. INTRODUCTION

In 1986 Bednorz and Müller<sup>1</sup> discovered superconductivity in the ceramic material  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  above 30 K. This initiated numerous experimental and theoretical investigations on various cuprates to explain the existence of Cooper pairs in these materials. The ordinary BCS approach<sup>2</sup> based on phonon-electron coupling seems not to be exclusively valid in regions of higher temperature. Many different models have been proposed [e.g., based on narrow filled band(s) polarization (excitonic) (Refs. 3–5) or spin-dependent<sup>6–8</sup> mechanisms], but up to now no theoretical description of the complex situation could rule out the others.

Many similarities between the different cuprates have been detected, e.g., the common feature of containing  $\text{CuO}_2$  layers, which play an important role in high- $T_c$  superconductivity. Among the different high- $T_c$  cuprates we want to concentrate on the electronic structure of the superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ,<sup>9</sup> with a critical temperature of  $T_c=92$  K for  $x=0$ .

The orthorhombic unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is shown in Fig. 1. According to Siegrist *et al.*<sup>10</sup> the lattice vectors of the  $x$ - $y$  plane ( $a=3.856$  Å,  $b=3.870$  Å) are nearly equal in contrary to the one in the  $z$  direction ( $c=11.666$  Å). The rare-earth element Y lies between two  $\text{CuO}_2$  layers. An apical oxygen atom O(4) connects each plane with a Cu-O chain [Cu(1), O(1)]. We have focused our approach on these regions.

Many theoretical calculations using the local-density-functional approximation were performed on this material.<sup>11–16</sup> In this way resulting filled bands (close to the Fermi level), DOS and Fermi surfaces are in quite good agreement with the experimental observations.<sup>17–19</sup> It seems that this approach is applicable to ceramic materials for reproducing important features of the complicated electronic structures.

On the other hand, these methods use approximations [e.g., LAPW, (linear augmented plane wave); LMTO (linearized muffin-tin-orbitals)] to save computer time. Therefore

they were criticized with respect to their applicability to ceramic materials.<sup>20</sup> This was one reason to try the hard way of the band-structure calculation,<sup>21</sup> namely the *ab initio* Hartree-Fock (HF) method. The resulting bands were corrected afterwards for correlation. Because of the large computational time and storage place we had to choose rather small subunits to be able to perform these calculations for the energy bands, Fermi surface, and density of states (DOS). Further we wanted to answer the question of whether our two-dimensional (2D) treatment leads to similar characteristics, as the full three-dimensional (3D) band structures (calculated by LDF methods).

This means that we want to show the possibility to obtain significant information about the electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  using suitable subunits of the total system. We take two units into account; each containing one copper and three oxygen atoms: Cu(2), O(2), O(3), O(4) (plane cell) and

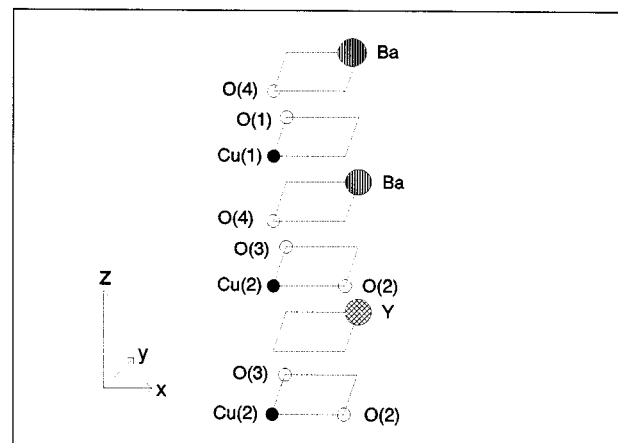


FIG. 1. The elementary cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  including two  $\text{CuO}_2$  planes and one  $\text{Cu-O}$  chain, connected by the apical oxygen atom O(4).

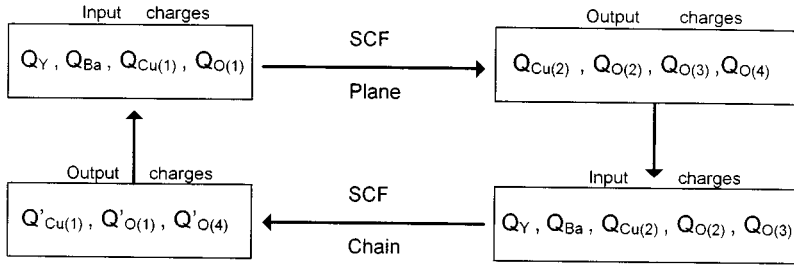


FIG. 2. One cycle of the mutually consistent treatment containing one chain and one plane SCF calculation.

Cu(1), O(1),  $2 \times O(4)$  (chain cell). In each substructure we had to include the apical oxygen O(4) to obtain reasonable results. The reason for this is that interatomic distances [Cu(2)-O(2): 1.946 Å, Cu(2)-O(4): 2.382 Å; Cu(1)-O(1): 1.928 Å, Cu(1)-O(4): 1.785 Å] are comparable.

In the next section we shall introduce the method of mutually consistent treatment, which ‘reconnects’ the cells under consideration. Afterwards the HF results are corrected for correlation by a Green’s-function method using the Møller-Plesset many-body perturbation theory (MBPT) for the self-energy. Finally we discuss our results in comparison to the LDF approaches.

The main purpose of our calculation was, however, to also obtain the unfilled bands (and the unfilled parts of the valence band) in a reasonable approximation (the LDF method is known to be unreliable in these regions). Namely, if one uses the filled narrow band(s) polarization model of high- $T_c$  superconductivity of Ginzburg<sup>3</sup> in first order (the first-order term in the polarization propagator), one obtains the excitonic superconductor model.<sup>3–5</sup> To be able to calculate the excitonic bands and from them the effective interaction potential of this model one, of course, also needs unfilled energy bands in an acceptable (correlation corrected) approximation.

## II. MUTUALLY CONSISTENT SCF CALCULATIONS

Our approach can be viewed as the further developed method of Saalfrank and Ladik,<sup>22</sup> where no mutual relations between the plane and chain cell were taken into account. In our model both subunits have to be understood as an elementary cell spanned by the lattice vectors  $\mathbf{a}$  and  $\mathbf{b}$ . This results in 2D band structures of  $C_{2v}$  symmetry. Naturally we must consider in both cases all atoms lying outside the regions (for their charges certain reasonable values were taken) of the explicit HF calculation. This means we have to embed the subunits in a 3D surrounding modeled by a Madelung potential. Therefore the HF LCAO crystal orbital (CO) method<sup>21</sup> had to be modified appropriately. The usual Fock matrix  $\mathbf{F}^0$ , which describes the region of full calculation without external charges, was corrected by a Madelung matrix  $\mathbf{V}^M$ . This leads to the following reformulation of the generalized eigenvalue problem:

$$\mathbf{F}(\mathbf{k})\mathbf{C}_n(\mathbf{k}) = \epsilon_n(\mathbf{k})\mathbf{S}(\mathbf{k})\mathbf{C}_n(\mathbf{k}), \quad (1)$$

with

$$\mathbf{F} = \mathbf{F}^0 + \mathbf{V}^M. \quad (2)$$

This equation has to be solved for different  $\mathbf{k}$  (quasimomentum) values to obtain the energy eigenvalues  $\epsilon_n(\mathbf{k})$  and eigenvectors  $\mathbf{C}_n(\mathbf{k})$  for each band  $n$ .

The Madelung matrix itself consists of two parts: The first one,  $\mathbf{V}^{M,\text{fix}}$ , depends on fixed charges, which stem from those atoms, which are not contained in the subunit under consideration. The second term  $\mathbf{V}^{M,\text{SCF}}$  depends on the HF calculation of the corresponding plane or chain layer. It contains the four atomic charges computed in every SCF cycle with the aid of Mulliken’s population analysis<sup>23</sup> to get the same values for the copper and oxygen atoms inside and outside the explicitly calculated zone. The actual form of  $\mathbf{V}^M$  can be taken from Ref. 24. Its evaluation is based on lattice summations using Ewald’s method.<sup>25</sup>

To make this description more concrete the Madelung matrices for the plane calculation ( $\mathbf{V}_{\text{Pl}}^M$ ) and for the chain ( $\mathbf{V}_{\text{Ch}}^M$ ) are written as functions of the corresponding charges:

$$\mathbf{V}_{\text{Pl}}^M = \mathbf{V}_{\text{Pl}}^{M,\text{fix}}(Q_Y, Q_{\text{Ba}}, Q_{\text{Cu}(1)}, Q_{\text{O}(1)}) + \mathbf{V}_{\text{Pl}}^{M,\text{SCF}}(Q_{\text{Cu}(2)}, Q_{\text{O}(2)}, Q_{\text{O}(3)}, Q_{\text{O}(4)}), \quad (3)$$

$$\mathbf{V}_{\text{Ch}}^M = \mathbf{V}_{\text{Ch}}^{M,\text{fix}}(Q_Y, Q_{\text{Ba}}, Q_{\text{Cu}(2)}, Q_{\text{O}(2)}, Q_{\text{O}(3)}) + \mathbf{V}_{\text{Ch}}^{M,\text{SCF}}(Q_{\text{Cu}(1)}, Q_{\text{O}(1)}, Q_{\text{O}(4)}). \quad (4)$$

After determining the fixed charges, one can establish a mutually consistent HF treatment of the plane and the chain. The only really fixed charges are  $Q_{\text{Ba}}$  and  $Q_Y$ . We have taken for the Ba atoms always a positive charge of 2.00. This choice is based on cluster calculations.<sup>26–28</sup> The decision for identifying  $Q_Y$  with 2.80 was not so easy. Cluster calculation results vary from 2.63 to 2.83.<sup>29</sup> These values indicate that the formal charge of 3.00 is too large for Y. Test calculations with our method showed that charges on Y from 2.60 to 2.75 led to unreasonable band structures. Using charges between 2.76 and 2.85 the results became realistic, stable, and nearly independent on the charge of Y within this interval. One should point out that this choice of the Y charge was not guided by LDA band structures of the ‘‘123’’ system, but only on the basis of the criterion to obtain reasonable band structures *per se*.

The other atoms outside the explicitly calculated region were treated in a consistent way (illustrated in Fig. 2): Starting with the SCF calculation of the plane layer, an initial guess for  $Q_{\text{Cu}(1)}$  and  $Q_{\text{O}(1)}$  had to be made, e.g., +1.00 and –2.00, respectively. The converged result leads to charges for  $Q_{\text{Cu}(2)}$ ,  $Q_{\text{O}(2)}$ ,  $Q_{\text{O}(3)}$  (and  $Q_{\text{O}(4)}$ ). Now they can be used as fixed charges for the computation of the chainlike substructure, which then produces new guesses  $Q'_{\text{Cu}(1)}$  and  $Q'_{\text{O}(1)}$  to be used for a further plane calculation, etc.

This mutually consistent treatment stops if the charges of cycle  $n$  agree with the input values of cycle  $(n-1)$ . Because of charge neutrality of the total system this criterion forces

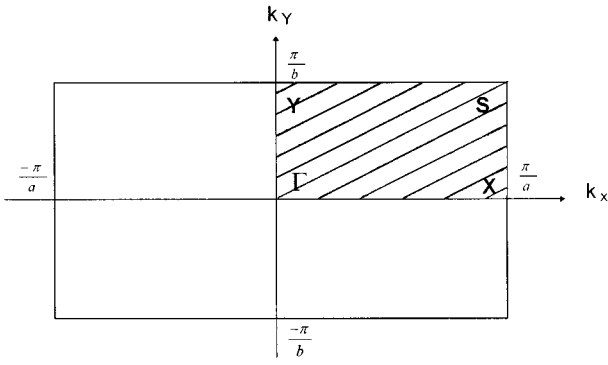


FIG. 3. First Brillouin zone of the 2D substructures. The irreducible part is surrounded by  $\Gamma$ -X-S-Y- $\Gamma$ .

both HF computations in the last cycle to produce the needed identity between  $Q_{O(4)}$  and  $Q'_{O(4)}$  (no more change in the charge of  $Q_{O(4)}$ ).

To program this method we modified the HF LCAO CO code CRYSTAL 88 (Ref. 30) to deal with charged unit cells and Madelung corrections. For oxygen<sup>31</sup> and copper<sup>32</sup> basis sets of double- $\zeta$  quality were taken into account. Furthermore, the copper basis was improved with a set of 4p polarization functions. In the HF calculation we have used a cut off radius 11.6 Å for the integrals (this was provided by the CRYSTAL 88 program with an integral threshold  $10^{-7}$  a.u.). This radius corresponds in the plane to fourth-neighbor interactions. We have noticed, however, that the third- and fourth-neighbor contributions were very small, their neglect did not change the band structure at all. Therefore in the subsequent correlation calculation we had used only a second-neighbor interaction approximation. We solved the eigenvalue equation (1) for 25 vectors  $\mathbf{k}$  in the irreducible part of the Brillouin zone (see Fig. 3). As a convergency criterion for one SCF calculation, an energy difference of  $10^{-6}$  a.u. was used.

The mutually consistent treatment converges within a few cycles (each cycle containing two complete HF calculations). As expected the converged charges are independent of the initial guess for  $Q_{Cu(1)}$  and  $Q_{O(1)}$  (naturally very wrong initial values prevent the first SCF computation from converging at all).

The corresponding band structures are given in Figs. 4 (plane case) and 5 (chain case). Both plots show four important characteristics: The two lowest unoccupied bands dominated by Cu3s, Cu3d, O2s, and O2p atomic orbitals, a partially occupied band mainly consisting of Cu3d, Cu4p, and O2p contributions, an intermediate valence energy region (nine O2p-like bands, weakly hybridized with Cu3d orbitals) and four flat bands with predominantly Cu3d character. The last ones may play an important role in an excitonic mechanism of superconductivity.<sup>33</sup>

A more detailed analysis of the band structure and comparisons to other approaches is carried out after we have corrected our results for correlation (see below). Although the curvature of our bands at the HF level is similar to the LDF results, the obtained energy range is still too broad.

### III. CORRELATION CORRECTED BAND STRUCTURES

Going beyond the HF level we wrote a program for correlation corrections for 2D systems of  $C_{2v}$  symmetry. The

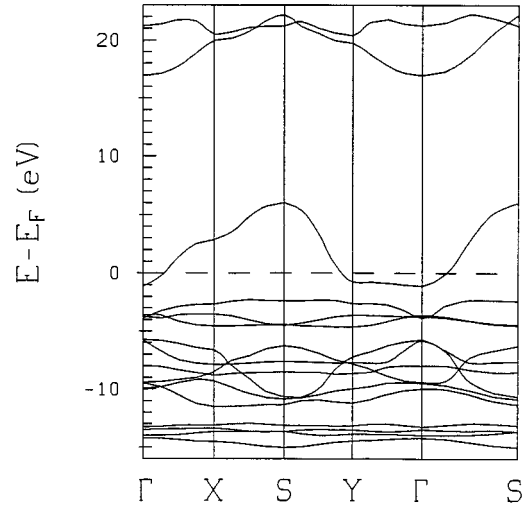


FIG. 4. HF band structure of one CuO<sub>2</sub> planelike layer along high symmetry lines of the irreducible Brillouin zone.

method used is based on theoretical developments of Suhai<sup>34</sup> and of Liegener, Ladik, and Vračko.<sup>35</sup> The Dyson equation

$$\mathbf{G}(\omega) = \mathbf{G}_0(\omega) + \mathbf{G}_0(\omega)\mathbf{\Sigma}(\omega)\mathbf{G}(\omega) \quad (5)$$

can be taken as our starting point.  $\mathbf{\Sigma}$  is the self-energy, which was considered in our calculation up to second order of the Møller-Plesset MBPT.<sup>36</sup>  $\mathbf{G}(\omega)$  is the Green's matrix for the corrected system, whereas  $\mathbf{G}_0(\omega)$  belongs to the unperturbed HF Hamiltonian. Using the relation

$$\mathbf{G}_0(\omega) = (\omega \cdot \mathbf{1} - \boldsymbol{\epsilon})^{-1}. \quad (6)$$

( $\boldsymbol{\epsilon}$  is a diagonal matrix containing the HF band energies) and applying the diagonal approximation<sup>37</sup> one can derive the scalar inverse Dyson equation<sup>38</sup>

$$\omega_I = \epsilon_I + \Sigma_{II}^{(2)}(\omega_I). \quad (7)$$

$\omega_I$  denotes the quasiparticle band energy and  $\epsilon_I$  the corresponding HF energy value.  $I \equiv (i, \mathbf{k}_i)$  is a composite index

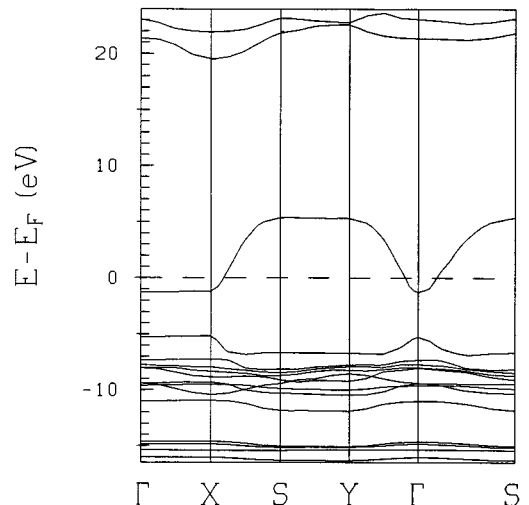


FIG. 5. HF band structure corresponding to the chain unit calculated in a mutually consistent way with the plane region.

referring to both a band and a  $k$  index. The self-energy term  $\Sigma_{\Pi}^{(2)}(\omega_l)$  up to second order is given by

$$\begin{aligned} \Sigma_{\Pi}^{(2)}(\omega_l) = & \sum_{K,L,M} V_{IKLM} (2V_{IKLM}^* - V_{IKML}^*) \delta_{\mathbf{k}_k, \mathbf{k}_l + \mathbf{k}_m - \mathbf{k}_i} \\ & \times \lim_{\eta \rightarrow 0} \left[ \frac{n_K \bar{n}_L \bar{n}_M}{\omega_l + \epsilon_K - \epsilon_L - \epsilon_M + i\eta} \right. \\ & \left. + \frac{\bar{n}_K n_L n_M}{\omega_l + \epsilon_K - \epsilon_L - \epsilon_M - i\eta} \right]. \end{aligned} \quad (8)$$

The summation is restricted by the Kronecker  $\delta$  and by occupation numbers  $n_j$  ( $n_j=1$  for an occupied state and  $n_j=0$  in the unoccupied case,  $\bar{n}_j=1-n_j$ ). The two-electron integral  $V_{IKLM}$  is defined through

$$V_{IKLM} = \langle \phi_I(1) \phi_K(2) | r_{12}^{-1} | \phi_L(1) \phi_M(2) \rangle \quad (9)$$

containing HF crystal orbitals  $\phi_j$  which correspond to the HF energy eigenvalues  $\epsilon_j$ . Solving Eq. (7) iteratively<sup>39</sup> we obtain the correlation corrected energy values  $\omega_l$ . The whole procedure is very time consuming, especially the calculation of the two-electron integrals  $V_{IKLM}$  which includes the so-called four-index transformation [every  $\phi_j$  is a linear combination of many atomic orbital (AO) basis set functions]. The computational effort was diminished with the help of the following methods.

(1) Implementing a suitable loop structure the  $N^8$  algorithm for calculating  $\Sigma_{II}^{(2)}$  was transformed into an  $N^5$  routine.<sup>39</sup>

(2) Taking into account translation and permutation symmetry, the number of AO integrals could be reduced definitely.

(3) Symmetry characteristics of  $\mathbf{k}$  points in the irreducible Brillouin zone were used to remove redundant two-electron integrals  $V_{IKLM}$ .

These improvements made it possible to correct our HF energy values for correlation. It could be argued that this time-consuming procedure should be done in every cycle of our method described in the previous section (see also Fig. 2). Fortunately the mutually consistent treatment depends only on fixed and calculated charge values which are already well described by the HF theory.<sup>40</sup>

A comparison of the correlation corrected band structures (given in Figs. 6 and 7) to the HF results reveals the following characteristics: The width of the partially filled band is reduced from 7.2 to 4.5 eV in the plane (PL) case and from 6.7 to 4.2 eV in the chain calculation (CH). As expected, also the band gap decreases (PL: 10.8 eV  $\rightarrow$  7.0 eV; CH: 14.2 eV  $\rightarrow$  10.3 eV). In both cases the intermediate valence region is shifted closer to the Fermi level (PL: [-11.6 eV; -3.2 eV]  $\rightarrow$  [-8.0 eV; -0.2 eV]; CH: [-12 eV; -5.1 eV]  $\rightarrow$  [-8.2 eV; -1.4 eV]). Remarkably, the highest fully occupied chainlike band changes (in contrast to all other bands) its curvature completely through correlation corrections.

The gaps above and below the intermediate valence region vanish nearly completely. Only in the chain case remains a greater energy difference of 1.7 eV (previously 2.5 eV) to the lowest valence region (the four flat bands, which are also shifted remarkably to lower binding energies).

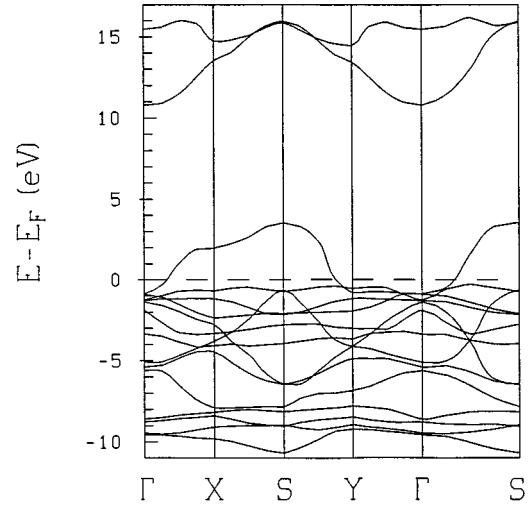


FIG. 6. Band structure of the *plane* subunit after implementation of correlation corrections. The energy range of the valence region and the band gap were reduced definitely in comparison to Fig. 4.

#### IV. COMPARISON TO OTHER CALCULATIONS

We compare our results to LDF band structures and DOS, which take into account the whole 3D system. The unoccupied bands have to be excluded, because for those energy regions no LDF results could be found in the literature. This may be due to the fact that the correctness of these methods for unoccupied bands is not generally accepted. All other features of our plots are compared to the band structure given by Hirao *et al.*<sup>11</sup> Figure 1 in the cited reference shows a 2D cut of their 3D energy band results at  $k_z=0$ . It contains, besides three (two plane- and one chain-derived) partially filled bands, 33 occupied bands within an energy region of 8 eV below the Fermi level. Their calculation has used the mixed DF pseudopotential-valence basis method and the results fit best to ours. The comparison to other LDF computations<sup>12-16</sup> shows also a rather good agreement but on a more qualitative level.

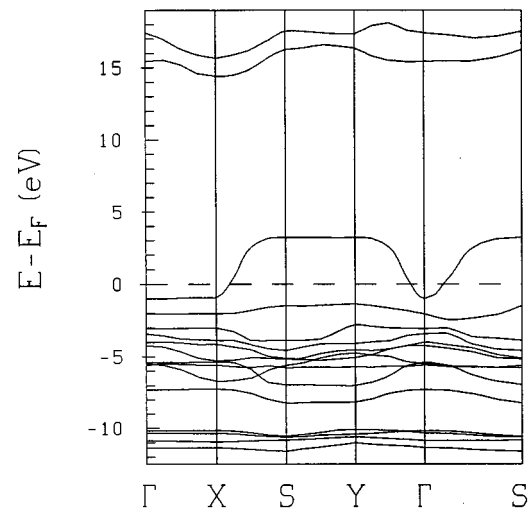


FIG. 7. Correlation corrected energy band structure of the *chain* region, using the same Green's-function method as in the planelike case (the corresponding HF bands are given in Fig. 5).

In every case the valence region is strongly dominated by  $\text{Cu}3d$  and  $\text{O}2p$  derived bands, whereas the Y and Ba states (which cannot be reproduced by our method) do contribute distinctively just below approximately  $-13$  eV and in the unoccupied regions close to the partially filled bands.<sup>41</sup> Naturally these characteristics support the validity of our results within the valence energy regions.

To perform the comparison, the number of bands and  $\text{O}(4)$  atoms has to be considered adequately. The 14 valence bands (including the band crossing the Fermi level) of each plane or chain layer calculation have to be compared with the 36 bands of Fig. 1 in Ref. 11. The complete elementary cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  contains one chain and two plane cells, but only two  $\text{O}(4)$  atoms. Therefore we double the number of bands in Fig. 6 and add the chain-derived ones, which leads to 42 bands. Subtracting the six bands corresponding to the  $2p$  orbitals of the two doubly counted  $\text{O}(4)$  atoms we obtain also 36 bands. With the help of this procedure a comparison becomes possible.

Inspecting the three partially filled bands we get quite good agreement to the curvature and the points of Fermi level crossings. The two plane-derived bands of Hirao *et al.* having its maximum at  $S$  correspond to our partially filled band in Fig. 6. One of their bands crosses the Fermi level nearly exactly at the same points as in our case. The same feature—even more precisely—can be detected by a look at the partially filled chainlike band. In Fig. 7 this band shows nearly no dispersion along  $S$  and  $Y$ , whereas in the LDF case the influence of the plane bands leads to a lowering of energy around the  $S$  point. Kim and Ihm<sup>16</sup> insist on avoided crossing between  $S$  and  $Y$ , which cannot be reproduced by our approach. Interestingly the band structure in Ref. 16 for a 2D cut at  $k_z = \pi/c$  corresponds much better (in respect to Fermi level crossings, curvature and the lack of avoided crossing) to our results as the cut at  $k_z = 0$ .

Returning to our figures and the results given by Hirao *et al.*,<sup>11</sup> we detect in our case a greater energy shift for the band containing the Fermi level (plane case) around  $X$ . Furthermore, our partially filled bands cover an energy range, which is more than 1 eV broader than in the LDF case.<sup>11</sup>

The next comparison refers to the chain-derived occupied band lying very close to the Fermi level in Fig. 1 of Ref. 11. Our corresponding band shows the same shape but at much larger distance to  $E_F$ . Taking in Ref. 11 at point  $S$  a look at higher binding energies we come to planelike bands which lie nearly in the same energy region as in our corresponding plot (Fig. 6). Therefore we should transfer the intermediate valence region of our chain-layer calculation with about 1.4 eV to lower binding energies to obtain the sequence of bands proposed by LDF calculations. This necessary shift may be due to the effect of the unshared apical oxygens belonging to the planes and chains, respectively, in our model (which compensates this effect possibly through the change of the charge transfer due to the use of the mutually consistent treatment). Furthermore we should not forget that we have too many bands [due to the too many  $\text{O}(4)$  atoms], which influence this energy region containing hybridized  $\text{O}2p$  bands.

Continuing our comparison we come to very good agreement at the lower end of the intermediate valence region, whereas in between qualitatively similar curvature character-

istics around  $S$  and  $\Gamma$  can be detected. The last two bands in Fig. 1 of Ref. 11 correspond in nearly every respect to the fifth (counted from below) of our plane calculation. The same may be stated for the fifth chain-derived band in Fig. 7 which is to be identified with the third band of the LDF plot. The energy ranges of our intermediate valence bands are in good correspondence, too.

It is interesting to point out that the remaining lowest-lying four bands in each of our plots have no counterpart in any of the LDF calculations we have found in the literature. Because having 36 bands (as discussed above) these approaches have all their  $\text{Cu}3d$  contributions already in the intermediate valence region. In comparison, to experiment<sup>42</sup> we find good agreement to our flat  $\text{Cu}3d$  bands region. The  $\text{Cu}3d$  satellite around  $-9.4$  eV detected with resonant photoemission studies lies exactly in the energy region of the four plane-derived bands. The corresponding ones of the chain calculation may be identified as lying slightly above another  $\text{Cu}3d$  satellite around  $-12$  eV.

Let us turn our attention to the comparisons of the DOS. The plots corresponding to our corrected band-structure calculations are given in Fig. 8 (chain cell) and in Fig. 9 (plane cell). Unfortunately in Ref. 11 no projected DOS is given. Therefore we use the results of the *ab initio* pseudopotential plane-wave calculation of Ref. 16 for the comparison. Figure 7 of this reference contains the projected DOS for all copper and oxygen atoms in the energy regions under consideration.

Looking at our chainlike DOS (Fig. 8), peaks (a)–(d) correspond (after an energy shift of 1.0 to 1.4 eV) to the four  $\text{Cu}(1)$  peaks and two  $\text{O}(4)$  ones between  $-5$  and  $-2$  eV in Fig. 7(b) of Ref. 16. The higher-energy region differs more strongly. This is due to two facts: The agreement to the band structures in Ref. 16 is not as good as to the calculated values in Ref. 11 for this energy region. Furthermore the demanded energy shift of 1.4 eV (see above) cannot be expected to be exactly the same everywhere within the intermediate valence zone.

Coming to the plane-derived DOS (Fig. 9), our strong peak lying close to  $E_F$  has no counterpart in Ref. 16. The reason may be found again in the different dispersions of the corresponding bands. At higher binding energies the correspondence improves. Peaks (a)–(c) in Fig. 9 may be identified with the three highest values between  $-4$  eV and  $-1$  eV in the  $\text{Cu}(2)$  DOS plot of the LDF calculation.<sup>16</sup>

The energy region closer to the lower end of the intermediate valence region of the plane-derived DOS shows good agreement, too. The more expressed peak structure in our case is due to the fact that we had to include the apical  $\text{O}(4)$  atom, which leads to characteristic DOS contributions in this energy region.

Finally we should mention that the peaks in our plots at the lower end of the negative energy scale are derived from the flat  $\text{Cu}3d$  bands which could not be found in any paper using LDF methods.

## V. CONCLUSION

We developed a method to enable theoretical statements about the electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The comparison of our results with LDF computations showed in many respects good agreement for the Fermi level crossings, the

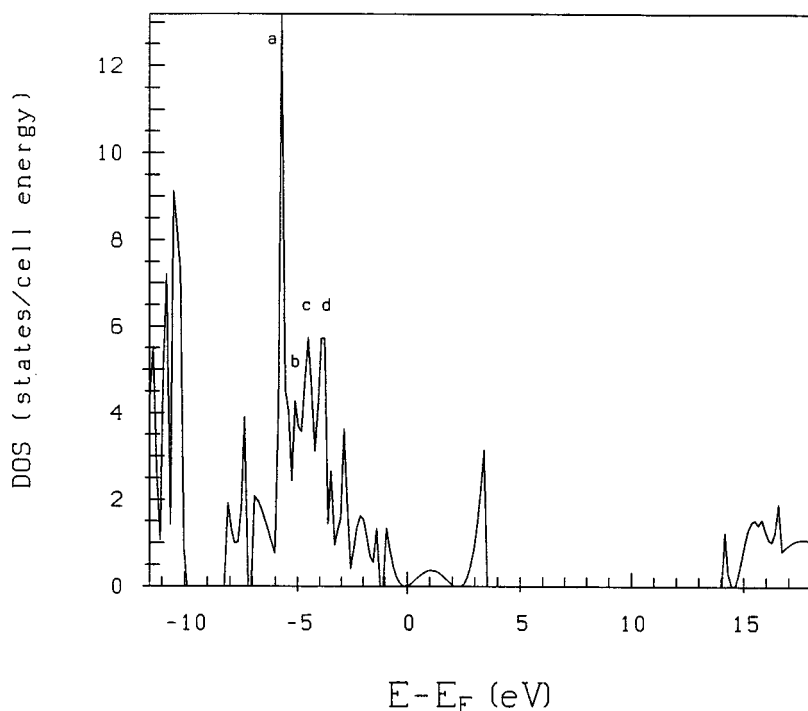


FIG. 8. The DOS of the *chainlike* region (corresponding to Fig. 7), which covers a greater energy range in comparison to the plane case.

partially filled bands and in the intermediate valence zone. The LDF results, on the other hand, agree rather well with photoelectron spectra in the case of “123.”<sup>17-19</sup> Therefore, we conclude that our correlation corrected band structures give a rather good description of the filled bands. Furthermore, neither the chain nor the plane cell could be handled without including the apical oxygen atoms. It is an important link influencing both subunits and should be taken into account in the search for mechanisms of high- $T_c$  superconductivity. Low-lying, flat, and Cu3d-dominated energy bands may play an important role for approaches based on exci-

tonic coupling.<sup>33</sup> Therefore, it is interesting that we could compute those bands in contrast to LDF calculations and in agreement with experimental observations.<sup>42</sup> It is also interesting to note that these bands are more flat in the “123” case, than in the case of  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ,<sup>22</sup> making the Cu3d electrons belonging to these bands more localized and therefore more strongly polarizable. Assuming a polarization (excitonic) mechanism of high- $T_c$  superconductivity in cuprates this could explain the larger  $T_c$  in “123” than in the “214” system.

Last, but not least, in contrast to the LDF computations

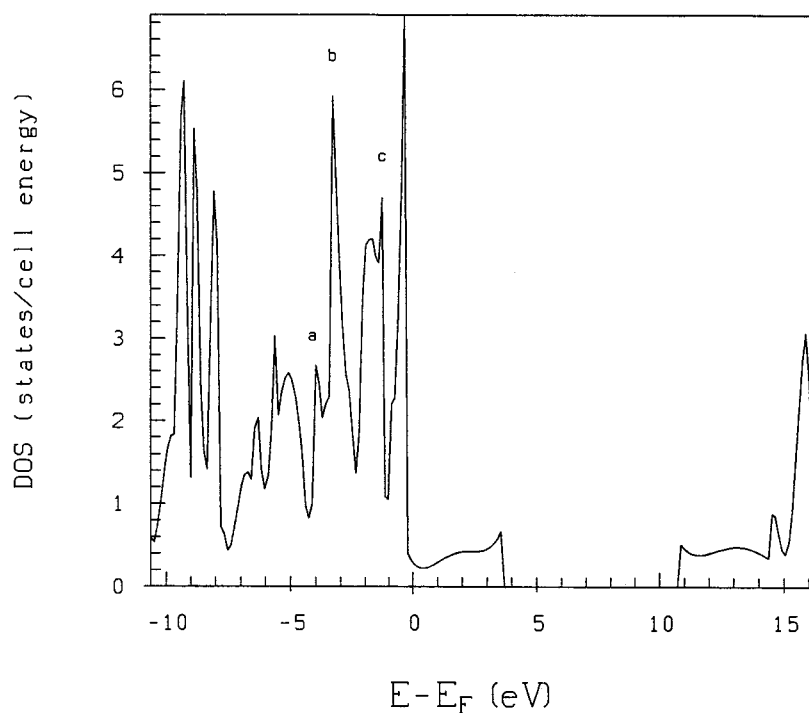


FIG. 9. The DOS referring to our *plane* cell. This plot corresponds to the correlation corrected bands given in Fig. 6.

we were able to calculate also mutually consistent and correlation corrected CuO<sub>2</sub> planelike and Cu-O chainlike unfilled bands. These will be used to subsequent exciton bands calculations to look more thoroughly at the proposed exciton mechanism<sup>3-5</sup> of high- $T_c$  superconductivity, calculating the effective potential,  $T_c$ , the superconducting gap and finally the coherence length.

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