

Electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics at the MP2 electron correlation level

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Received 3 June 1998, in final form 1 September 1998

Abstract. The electronic structure of the superconducting ground state of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics is calculated at the MP2 electron correlation level using the self-consistent embedded-cluster method. The $[\text{Cu}_3\text{O}_{12}]^{14-}$ quantum cluster is embedded in a finite array of point charges which produce the correct value of the Madelung potential at each cluster site. The results obtained reveal the strong influence of electron correlation effects on the charge distribution. The coupling between chains and planes is found to be essentially ionic while covalent bonding is predominant within both chains and planes. The symmetry of the holes on oxygens in the CuO_2 planes is $2p\sigma$ in accordance with nuclear magnetic resonance and x-ray absorption experiments. A partially unoccupied state associated with the orbitals $3d_{z^2-y^2}$ and $3d_{x^2}$ is found to be present on the copper ions. The unpaired spin is located on the Cu1 atom in the chains; in the CuO_2 planes, the hypothetical Zhang–Rice singlet is indicated.

1. Introduction

In spite of there having been extensive experimental and theoretical study of high- T_c superconductivity (HTSC) carried out in the last decade, we still do not have a rigorous microscopic theory of this phenomenon. In the past few years, some interesting conceptions and theories have been published (see [1–8]), but for creating a quantitative theory which could connect the physical properties and chemical composition of the HTSC ceramics with the value of the transition temperature, a more detailed knowledge of the electronic structures and their related properties is needed.

The electronic structures of the HTSC ceramics have been studied by a variety of methods (see Pickett's review [9] and references [10–30]), which range from the band approach (the first publications were by Mattheiss [10] and Freeman with collaborators [11]) to the embedded-cluster method (ECM) [15, 19, 21, 24–28]. It is well known that the effects of the unusually strong localization in oxides of transition metals make the task of performing electronic structure calculations very difficult [31]. As was revealed in spectroscopic experiments using different techniques (x-ray and ultraviolet photoemission [32], electron energy-loss spectroscopy [33], polarization-dependent x-ray absorption spectroscopy [34]), in copper oxide ceramics both copper 3d electrons and holes are localized, the latter mainly at the oxygen sites. There is a strong and to a great extent covalent coupling between Cu and O atoms in the lattice. Now there is much evidence that the electron correlation plays an extremely important role in copper oxide materials; see the review by Brenig [35]. Band-structure calculations based

on the one-electron approach, therefore, cannot be a good approximation for studying the electronic structure of copper oxide ceramics. More sophisticated and precise band calculations [23, 29, 30] can represent many spectroscopic features of the HTSC ceramics. However, to reveal the peculiarities of the electronic structure responsible for the HTSC phenomenon, precise band calculations must be supplemented by calculations of local configurations at the electron correlation level. The most appropriate approach for this is the ECM; see [36–38]. Although we must keep in mind that the ECM approach, due to the lack of periodic conditions, underestimates the degree of metallic character of the systems studied, this approach also cannot take into account charge- or spin-density fluctuations which occur at intermediate length scales. Different methodologies of the ECM are distinguished according to two general aspects:

- (a) The precision of the computational method used for the quantum mechanical description of the cluster.
- (b) The embedding scheme used for coupling the cluster to the environment which must represent an infinite crystal.

It is well established that in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics, the small changes of oxygen concentration, which preserve the crystal structure, can completely destroy the superconductivity [2]. So, the yttrium ceramics provide a very convenient basis for a comparative study of SC and non-SC ceramics. Below, we give a brief review of the results of previous calculations for yttrium ceramics based on the ECM.

In studies by Goodman *et al* [19] and Kaplan *et al* [24, 25], the calculations for the embedded quantum clusters, representing the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics (with different values of x), were made by the discrete variation method in the local density approximation (LDA). Although in these studies many interesting results were obtained, it is necessary to keep in mind that the LDA has restricted applicability to cuprate oxides; e.g. it does not describe correctly the magnetic properties [39] and gives an inadequate description of anisotropic effects [40, 41]. Therefore, comparative *ab initio* calculations in the framework of the Hartree–Fock approximation are desirable.

Such calculations with a precise self-consistent account taken of the crystal surroundings were performed by—at least—four scientific groups: Baetzold [15], Das with co-workers [21, 22], Winter *et al* [27] and Ladik with co-workers [28]. Winter *et al* [27] performed cluster calculations by the restricted Hartree–Fock (RHF) method, so they did not take into account the electron correlation. The other three groups used the unrestricted Hartree–Fock (UHF) method for cluster calculations which allows electron correlation to some extent. The strongly covalent C–O bonding in planes and chains was revealed (in accordance with results obtained in references [19, 24, 25]). For covalent systems, the precision of the calculations depends upon the extent to which the electron correlation is taken into account. Thus, it is important to take into account the electron correlation beyond the UHF method.

Precise quantum cluster calculations of the electronic structures of HTSC ceramics were performed in references [12, 16, 20]. Guo *et al* [12] used the generalized valence bond method; Martin and Saxe [16] and Yamamoto *et al* [20] performed calculations at the configuration interaction level. But in these studies the calculations were carried out for isolated clusters; the second aspect of the ECM scheme—see above—was not fulfilled. The influence of the crystal surroundings may change the results obtained considerably (see table 3, later).

Thus, to the best of our knowledge, there is a lack of embedded-cluster studies on the yttrium ceramics in which both aspects of the ECM were taken into account with sufficient precision. In this paper, we attempt to fill this gap, and present the results of cluster electronic structure calculations at the UHF and the Møller–Plesset levels for $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics with

a self-consistent account taken of the infinite-crystal surroundings of the quantum cluster; these calculations, where the lattice is considered as a static lattice, correspond to overdoped ceramics. The Gaussian basis set employed is larger than those used in previous cluster calculations [15, 19, 21, 28]. The results obtained in this study reveal the strong influence of the electron correlation effect on the charge distribution and the orbital population of Cu and O atoms. The unpaired spin is located in chains on Cu1. In CuO_2 planes, the covalent bonding leads to spin coupling: the so-called Zhang–Rice singlet [42].

The paper is organized in the following way. Section 2 describes the methodology of our study. We give the results and discussion in section 3, and provide a summary in section 4.

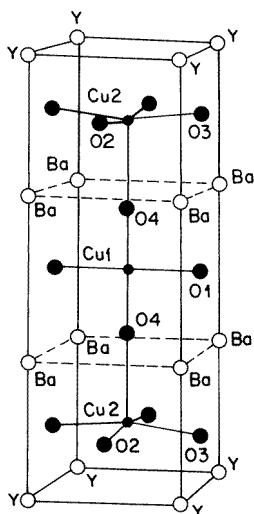


Figure 1. The quantum cluster Cu_3O_{12} (black circles) embedded into a unit cell.

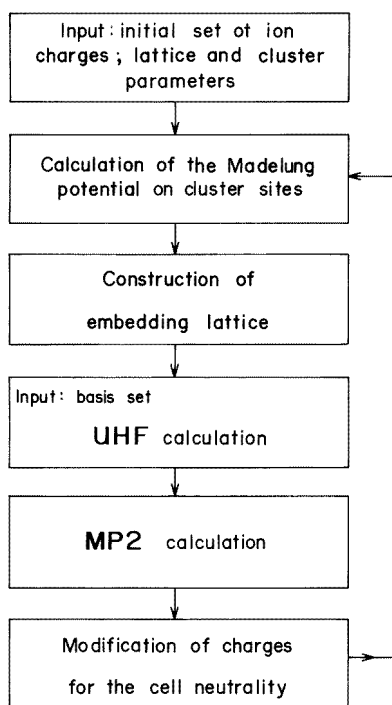


Figure 2. The iteration cycle in the self-consistent charge calculation.

2. Methodology

The cluster considered to calculate the electronic structure of the superconducting $YBa_2Cu_3O_7$ ceramic is represented in figure 1. With this choice, the ions Cu1, Cu2 and O4 each have all of their nearest neighbours included in the cluster. The interionic distances are taken from Jorgensen *et al* [43]. In order to simulate the Madelung potential produced by the infinite crystal lattice, the cluster is located in a finite array of background charges. This array of charges is built taking into account the symmetry elements of the crystal (space group $Pmmm$). The charges of the outermost ions are adjusted in order to provide the correct value of the Madelung potential at each cluster site as well as the electrical neutrality of the set: cluster plus background charges. This is achieved by using a procedure originally proposed by Kelires and Das [44, 21]. To a shell of n_i equal exterior charges q_i which creates at the site j a

potential $V_i(j)$ is associated a charge scaling factor f_i such that the Madelung potential at the site j due to the infinite crystal, $V_M(j)$, is equal to the potential of each shell of scaled charges plus that created by the whole set of charges minus those included in the shells, denoted as $V_q(j)$. If the Madelung potential of the infinite lattice has to be reproduced at k cluster sites, the following system of linear equations (similar to that in reference [45]) has to be solved for the scaling factors f_i :

$$\begin{aligned} f_1 V_1(1) + f_2 V_2(1) + \cdots + f_{k+1} V_{k+1}(1) + V_q(1) &= V_M(1) \\ f_1 V_1(2) + f_2 V_2(2) + \cdots + f_{k+1} V_{k+1}(2) + V_q(2) &= V_M(2) \\ \vdots & \\ f_1 V_1(k) + f_2 V_2(k) + \cdots + f_{k+1} V_{k+1}(k) + V_q(k) &= V_M(k) \\ f_1 n_1 q_1 + f_2 n_2 q_2 + \cdots + f_{k+1} n_{k+1} q_{k+1} + Q &= 0. \end{aligned} \tag{1}$$

The last equation is associated with the electrical neutrality of the whole set of charges, Q being the net charge of the charge array not included in the scaled shells. The Madelung potential at cluster sites j , $V_M(j)$, is calculated separately by the Ewald method. In our case there are six different sites in the cluster considered.

Several attempts with various groups of seven shells were carried out in order to obtain scaling factors associated with a background self-energy that was as small as possible. In table 3—see later—we present the Madelung potential values at the cluster sites calculated with the self-consistent set of charges found in the second order of the Møller–Plesset perturbation theory (MP2). Our finite charge array reproduces the Madelung potential values of the infinite crystal with a precision better than 10^{-9} au which is the precision of the Madelung potential calculation. We used two charge arrays with 5083 and 475 charges, respectively. The latter was found preferable because it gives smaller values of the scaling factors and background self-energy.

Generally, the charges of cluster ions obtained after a calculation at the MP2 level differ from those of the background ions, and the unit cell associated with these new ionic charges is not neutral. In order to achieve consistency between the cluster and the background charges, a series of calculations have been performed where the charges obtained as a result of a calculation are taken as the background charges of the next calculation; at each step, the ionic charges are modified in order to ensure the electrical neutrality of the unit cell. In this modification procedure we used two parameters: the cation charge variation (Δq_c) and the anion charge variation (Δq_a) which were determined from a set of two equations expressing the unit-cell neutrality and the fact that the cluster charge must be preserved and be an integer. The flow chart of this procedure is shown in figure 2.

The background charges were introduced as solvent charges in the *Gaussian 94* program [46]. The *ab initio* calculations were done using the UHF method with the triply split valence basis set 6-311G. In this basis set, each inner-shell atomic orbital is represented by a single function written in terms of six primitive Gaussians. Three basis functions are employed to describe each valence shell orbital; one is contracted, and each of the other two consists of one primitive Gaussian. The electron correlation was then included through the second order of MP2. We did not use pseudopotentials; the core electrons were directly included in all of our *ab initio* calculations. To calculate the charge distribution we used Mulliken population analysis along with the natural bond orbital (NBO) option provided by the program.

It is clear that the size of our system imposes limitations on the size of the basis set that can be used. As was proved in [47], the 6-311G basis set which was used yields reliable results, comparable to those obtained with larger basis sets in other systems. So we are confident that the observed behaviour would not change if a larger basis set was used.

We found many convergence problems for this system. In particular the UHF procedure frequently converges to a solution with a very high S^2 -value, indicating a large contamination of the solution by excited states. Only solutions with negligible spin contamination were considered. To achieve consistency between the cluster and background charges we used the *Gaussian 94* program repeatedly, taking as the initial guess the solution of the previous iteration; see figure 2.

Table 1. The influence of the electron correlation on ion charges for three initial charge sets (the UHF and MP2 results are obtained at the first iteration).

$[Cu_3O_{12}]^q$	Cu1	Cu2	O1	O2	O3	O4	Ba	Y
Baetzold [15], $q = -16$	2.00	2.00	-1.80	-1.90	-1.90	-1.80	2.00	3.00
UHF	1.39	1.37	-1.64	-1.71	-1.73	-1.54	2.00	3.00
MP2	0.97	0.62	-1.48	-1.58	-1.55	-1.48	2.00	3.00
Li <i>et al</i> [28], $q = -15$	1.61	1.78	-1.37	-1.80	-1.80	-1.61	2.00	2.63
UHF	1.49	1.76	-1.66	-1.69	-1.70	-1.57	2.00	2.63
MP2	0.84	1.14	-1.53	-1.54	-1.54	-1.37	2.00	2.63
Gupta–Gupta [13], $q = -14$	1.55	1.64	-1.61	-1.51	-1.55	-1.65	1.81	2.58
UHF	1.50	1.72	-1.74	-1.70	-1.72	-1.57	1.81	2.58
MP2	1.20	1.17	-1.12	-1.55	-1.57	-1.39	1.81	2.58

Table 2. The iterative self-consistent charge calculation at the MP2 level starting from the Gupta–Gupta [13] charge set with fixed charges on Ba and Y atoms.

	Cu1	Cu2	O1	O2	O3	O4	Ba	Y
Gupta–Gupta [13]	1.55	1.64	-1.61	-1.51	-1.55	-1.65	1.81	2.58
MP2 ₁	1.20	1.17	-1.12	-1.55	-1.57	-1.39		
MP2 ₂	0.95	1.11	-1.44	-1.51	-1.50	-1.13		
MP2 ₃	1.07	1.10	-1.28	-1.52	-1.53	-1.25		
MP2 ₄	1.02	1.10	-1.37	-1.51	-1.52	-1.18		
MP2 ₅	1.04	1.10	-1.33	-1.52	-1.52	-1.21		
Modified set providing cell neutrality ^a	1.07	1.13	-1.30	-1.49	-1.49	-1.18	1.84	2.61

^a In this particular case, the requirement of constancy of the cluster charge was removed.

3. Results and discussion

In all of our calculations, the importance of including the electron correlation beyond the UHF level was revealed. We carried out calculations for three different initial charge sets obtained by three groups. As follows from table 1, the charges calculated at the MP2 level differ considerably from those calculated at the UHF level for all three sets used. The changes are greater for copper ions than for oxygen ions, although they are still non-negligible in the latter case. In the self-consistent charge calculation (see the block scheme in figure 2), the final charge distribution must not depend on the initial charge set. We performed such calculations using the Gupta–Gupta [13] initial charge set. Only five iterations were needed for obtaining the self-consistent charge set with an error less than $0.03 e$; see table 2.

Table 3. The influence of the background on the charge and spin distributions in the cluster $[\text{Cu}_2\text{O}_{12}]^{14-}$ calculated at the MP2 level, in au.

	Isolated cluster		Cluster in crystal		Madelung potential
	Charge	Spin	Charge	Spin	On cluster sites
Cu1	0.96	0.81	1.04	0.80	-0.508
Cu2	0.68	0.05	1.10	0.00	-0.646
O1	-1.52	0.03	-1.33	0.05	0.515
O2	-1.50	0.00	-1.52	0.00	0.537
O3	-1.48	0.00	-1.52	0.00	0.538
O4	-0.68	0.02	-1.21	0.05	0.471

Next we assess the role of the embedding lattice. In table 3, the self-consistent charge and spin distributions, calculated at the MP2 level for the isolated cluster $[\text{Cu}_3\text{O}_{12}]^{14-}$ and for the same cluster embedded in the lattice, are presented. The influence of the crystal field on the spin distribution is very small, in contrast with that on the charge distribution. The large changes take place for the Cu2, O4 and O1 ions in the quantum cluster. On the other hand, the charges on Cu1, O2 and O3 ions undergo small changes.

Table 4. Self-consistent spin and charge distributions at the UHF and MP2 levels.

	Spin		Charge							
			Average		Diagonal values		Valence orbital population			
	UHF	MP2	UHF	MP2	UHF	MP2	UHF	MP2		
Cu1	0.89	0.80	+1.42	+1.04	+1.57	+1.18	$4s^{0.33}$	$3d^{9.04}$	$4s^{0.56}$	$3d^{9.05}$
Cu2	0.00	0.00	+1.69	+1.10	+2.06	+1.40	$4s^{0.35}$	$3d^{8.74}$	$4s^{0.38}$	$3d^{9.33}$
O1	0.02	0.05	-1.36	-1.33	-1.31	-1.30	$2s^{1.98}$	$2p^{5.41}$	$2s^{1.95}$	$2p^{5.34}$
O2	0.00	0.00	-1.67	-1.52	-1.59	-1.43	$2s^{1.97}$	$2p^{5.75}$	$2s^{1.95}$	$2p^{5.52}$
O3	0.00	0.00	-1.67	-1.52	-1.60	-1.43	$2s^{1.97}$	$2p^{5.75}$	$2s^{1.96}$	$2p^{5.52}$
O4	0.04	0.05	-1.36	-1.21	-1.30	-1.15	$2s^{1.96}$	$2p^{5.43}$	$2s^{1.94}$	$2p^{5.24}$

The self-consistent spin and charge distributions calculated at the UHF and MP2 levels are presented in table 4. Even at the UHF level, we do not have the formal valence values for an ionic crystal: +2 for copper and -2 for oxygen. This is a well-known result: the bonding in copper oxides has a mixed covalent-ionic character. The calculation at the MP2 level leads to a further reduction of the absolute values of the charges on copper and oxygen ions. This decrease is the consequence of accounting more precisely for the electron correlation in the MP2 approach. Its influence is more important for copper charges than for oxygen ones. Its influence is smallest on the O1 charge, where the change is only 2%; for O2 it is 9% and for O4 it is 11%. Much greater changes are observed for copper ions: 26.8% for the Cu1 charge and 34.9% for the Cu2 charge. The greater extent of taking into account the electron correlation causes the further change of the occupation orbital numbers of the 4s and 3d copper shells. The 4s copper electrons are involved in the covalent bonding with the 2p oxygen electrons (according to the MP2 results, the 4s Cu2 electrons are more involved than the 4s Cu1 electrons).

The average charge on ions in table 4 is calculated in the framework of the Mulliken population analysis, according to which the charges on atom-atom bonds (or on lines connected to different atom pairs) are divided into two equal parts and added to the diagonal values of

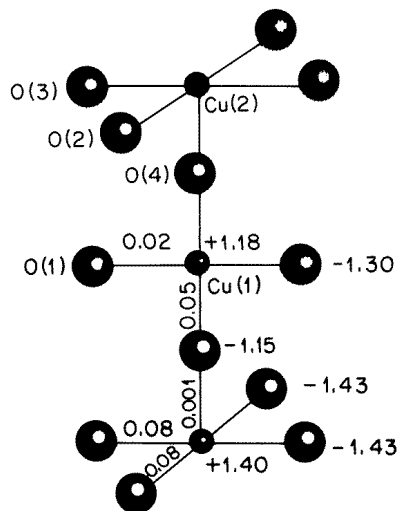


Figure 3. The charge distribution obtained at the MP2 level.

the charge matrix. The diagonal values are also presented in table 4 and figure 3. The charges on bonds are exhibited in figure 3; they are given as fractions of the electron charge, so their values are negative. The largest values of the electron density are indicated on the Cu–O bonds in planes and on the Cu1–O4 bond. The value of the electron density on the Cu1–O1 bond is smaller. The latter reflects the relative weakness of this bond. As follows from experimental data, the deoxygenation occurs in chains: in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ ceramics the oxygen O1 is absent.

Thus, the covalent bonding is stronger in planes and between the chain copper, Cu1, and the apex oxygen, O4. The small value of the electron density on the line Cu2–O4, $0.0006 e$, indicates that the coupling between chains and planes is essentially ionic. The suggestion [48] that covalent bonding can also occur through O–O interactions does not agree with our calculation because the charge on the line O4–O1 is very small, $0.0017 e$, and becomes even smaller on the lines O4–O2 and O4–O3: $0.0005 e$ and $0.0004 e$, respectively. According to table 4, there are no unpaired spins in planes. This supports the surmise [42] that due to a strong Cu–O hybridization, all spins in the CuO_2 planes are coupled (the so-called Zhang–Rice singlet). Our results indicate that unpaired spin is located in chains on Cu1. In the previous ECM calculations [21, 28] at the UHF level, the unpaired spin was indicated to be in planes on Cu2. The reasons for this contradiction are not clear, because in our calculations the location of unpaired spin is the same for both the UHF and MP2 approaches. Note that the location of the unpaired spin is found to be very sensitive to the spin contamination in the UHF calculations. In our case, we found that the value of S^2 in a cluster may differ from 0.75 only in the third digit for a physically correct result; even a value of 0.76 for S^2 leads to the location of the unpaired spin elsewhere in the cluster.

The electron paramagnetic resonance experiments on the yttrium ceramics, on the other hand, are ambiguous. In the study by Murrieta *et al* [49], the EPR signal of $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples was interpreted as a superposition of two different lines attributed to Cu1 and Cu2 sites. In some other studies of yttrium ceramics, the EPR signal was not detected or was attributed to an impurity phase [50]. Thus, further, more refined EPR experiments are needed to confirm the location of the unpaired spin in the cluster.

Finally, we turn to the symmetry of the holes on oxygen and copper ions. This problem has

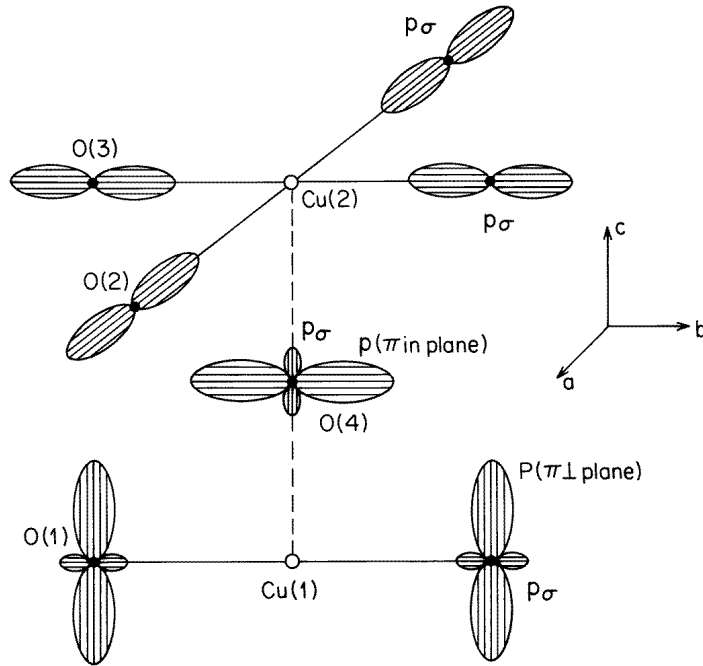


Figure 4. The symmetry of holes on oxygens.

a long history. In the early band calculations [10, 11], $2p\sigma$ symmetry of the holes on oxygen ions was obtained, while, in the more precise generalized bond calculations made by Guo *et al* [12], but without taking into account a crystal surrounding, $2p\pi$ symmetry of the holes on oxygen ions was reported. The symmetry of holes and its relation with the superconducting properties were studied in a model Hamiltonian formalism by Di Castro *et al* [51]. In the X_α ECM calculations for $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics in the Madelung potential field [24, 25], $2p\sigma$ symmetry of the holes on oxygen ions in planes was obtained. In the present more precise calculation, we confirmed this result: as follows from figure 4, the holes on plane oxygen ions have $2p\sigma$ symmetry. This is in agreement with NMR experiments [52, 53] and recent x-ray absorption spectroscopy [34] studies. We also revealed that the symmetry of the holes on O1 and O4 has predominantly $2p\pi$ character; or more precisely: $0.45\ 2p\pi + 0.14\ 2p\sigma$ on O1 and $0.56\ 2p\pi + 0.21\ 2p\sigma$ on O4. On the Cu1 ion there is a partially unoccupied state associated with the orbitals $3d_{z^2-y^2}$ which is favourable to the covalent bonding with the O4 and O1 atoms. For the Cu2 ion the symmetry of unoccupied orbitals has a mixed character: $0.17\ 3d_{z^2-y^2} + 0.46\ 3d_{x^2}$.

It is instructive to study the influence of the Madelung field on the symmetry of the holes. As follows from our calculation for an isolated cluster at the MP2 level, the Madelung field has very little influence on the symmetry of holes on the Cu1 and Cu2 ions. The symmetry of holes on the O1 and O4 ions is changed: for the O1 in the absence of the Madelung field, the $2p\pi$ contribution is diminished to less than half; for the O4 there is a sharp increase of the $2p\pi$ contribution. For an isolated cluster, the holes on the oxygens O2 and O3 still have $2p\sigma$ symmetry as in the Madelung field, although some contribution from the $2p\pi$ state appears. Thus, the crystal field makes the $2p\sigma$ symmetry of the holes on the oxygens in planes more pronounced.

4. Conclusions

As follows from our study, both aspects of the embedded-quantum-cluster approach are found to be important for electronic structure calculations of the ground-state electron structure of superconducting Y ceramics. Analysis of the charge distribution in the quantum cluster reveals that the Madelung field has a great influence on the Cu2, O4 and O1 ions, while the inclusion of the electron correlation has more effect on both Cu1 and Cu2 ions.

The chemical bond in the $YBa_2Cu_3O_7$ crystal has a mixed covalent–ionic nature, as expected. The covalent binding is more predominant in the CuO_2 planes and between the Cu1 and O4 than in the chains, while the coupling between the CuO_2 planes and chains has essentially an ionic character. The calculated symmetry of the holes on the planar oxygens is $2p\sigma$ in accordance with recent experimental results. It is found that the crystal field makes the $2p\sigma$ symmetry of the holes on the planar oxygens more pronounced, comparing with an isolated cluster. A partially unoccupied state associated with the orbitals $3d_{z^2-y^2}$ and $3d_{x^2}$ is found to be present on the copper ions. Our results confirm the existence in the CuO_2 planes of the so-called Zhang–Rice singlet [42], and the unpaired spin is predicted to be on Cu1 in chains.

Acknowledgments

We are grateful to R C Baetzold and J Ladik for helpful discussions and useful references and to S Shrinivas for sending some unpublished material from her thesis. This work was supported by DGAPA-UNAM, Project IN 108697.

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