We present a density functional theory (DFT) calculation in the generalized gradient approximation to study the possibility for the existence of Jahn-Teller (JT) or pseudo Jahn-Teller (PJT) type local distortions in the La-Ba-Cu-O superconducting system. We performed the calculation and correspondingly group theory classification of the electronic ground state of the CuO$_6^{-10}$ elongated octahedra cluster, immersed in a background simulating the superconductor. Part of the motivation to do this study is that the origin of the apical deformation of the CuO$_6^{-10}$ cluster is not due to a pure JT effect, having therefore a non a priori condition to remove the degeneracy of the electronic ground state of the parent regular octahedron. We present a comparative analysis of the symmetry classified electron spectrum with previously reported results using unrestricted Hartree-Fock calculations (UHF). Both the DFT and UHF calculations produced a non degenerate electronic ground state, not having therefore the necessary condition for a pure JT effect. However, the appearance of a degenerate E$_g$ state near to the highest occupied molecular orbital in the DFT calculation, suggests the possibility for a PJT effect responsible for a local distortion of the oxidized CuO$_6^{-9}$ cluster.

Keywords: Cuprates superconductors; density functional theory; Jahn-Teller effect

1. Introduction

Since the discovery of high $T_c$ superconductivity, the understanding of the mechanism responsible for this novel phenomenon has been one of the most challenging problems in condensed matter physics. To date, it is known to involve the pairing of charge carriers, although the precise nature of these carriers and the mechanism by which the pairing occurs is still an open problem.\textsuperscript{1-4} The evidence that strong electron-phonon interaction in oxides as well as in mixed-valence systems can occur owing to polaron formation, together with the fact that a possible mechanism for...
polaron formation is the Jahn-Teller (JT) effect, where spontaneous lattice distortions remove the degeneracy of the electronic ground state, led to Bednorz and Müller to the discovery of high temperature superconductivity. One reason to suspect the JT effect might play an important role in those systems, is the fact that all superconducting copper oxides have perovskite-like crystal lattices, with Cu$^{2+}$ ions surrounded by O$^{2-}$ ions. One of the most studied system, La-Ba-Cu-O has this particular structure, containing sheets of corner-sharing CuO$_6$ octahedra. The Cu-O planes, where it is believed that superconductivity and charge transport are mostly confined, have an electronic structure, within the ionic model, built up from the 3d$^9$ states of Cu$^{2+}$ and the 2p$^6$ states of O$^{2-}$.

In the insulating parent compound of the La based superconductor La$_2$CuO$_4$, the CuO$_6$ octahedra are elongated, with a Cu-O distance of 1.90 Å within the plane and 2.42 Å perpendicular to it. This distortion, some authors believed, could be at least partly due to a static JT effect. This can be seen from the fact that for the regular octahedron we have the O$_h$ symmetry, with a splitting of the d$^9$ electron states into E$_g$ + T$_{2g}$ irreducible representation (IR). The corresponding decomposition of the ions vibrational modes $Q_k$, according to the IR of the O$_h$ group gives $\Gamma = a_1g + e_g + t_2g + 2t_{1u} + t_{2u}$. The general condition in order to have a JT effect, is that the generalized force between nuclei, defined as the matrix element of the force operator $(-\partial V/\partial Q_k)$, between the total electronic ground state $\psi_i$, transforming respectively as the $\Gamma_k$ and $\Gamma_i$ IR of the corresponding symmetry group, should be different from zero. From general group theory rules, we know that this condition can be fulfilled if $\Gamma^*_i \times \Gamma_k \times \Gamma_i \subset \Gamma_1$ is satisfied (or equivalently $\Gamma^*_i \times \Gamma_i \subset \Gamma_k$), where $\Gamma_1$ is the identity IR. Hence for the regular octahedron having the O$_h$ symmetry group, the JT condition is fulfill, being the $e_g$ and $t_{2g}$ modes the possible JT active modes. Hence in order to have a pure JT effect and as a consequence a completely removal of the electronic degeneracy, the Cu site symmetry should be cubic. This would be precisely the case for an isolated regular CuO$_6$ octahedra. However in the insulating parent compound of the La based superconductor La$_2$CuO$_4$, the Cu site symmetry is far from being cubic. Even if the CuO$_6$ octahedra would be regular, the crystal field would not possess cubic symmetry. It has also been shown (and references cited there), that at least half of the octahedral distortion in the CuO$_6$ cluster can be accounted for, as a consequence of the strongly layered crystal structure and the large ionic interaction. From the above mentioned arguments one would expect that the partially filled electronic E$_g$ state in the regular CuO$_6$ octahedra might only be partly responsible for the CuO$_6$ elongated shape, having therefore a non a priori condition for the complete removal of the electronic degeneracy. As a clear example of an apical distortion where the JT effect does not play any role is when the Cu ion is substituted by Ni, obtaining La$_2$NiO$_4$. This system has the same structure as La$_2$CuO$_4$, but the Ni$^{+2}$ is not a JT ion. There are also in the literature some proposed models where the JT effect plays a definite role in high T$_c$ superconductivity beyond that of producing the static deformation of the CuO$_6$...
Experimental results in Cu K-edge absorption spectroscopy XANES (x-ray absorption near edge structure) and EXAFS\textsuperscript{12} (extended x-ray absorption fine structure) as well as PDF (pair-distribution-function) analysis of neutron powder-diffraction data\textsuperscript{13} have shown the existence of important inhomogeneities in the high-Tc superconductor structures. In particular, the CuO\textsubscript{6} octahedra in La\textsubscript{1.85}Sr\textsubscript{0.15}CuO\textsubscript{4} exhibits local deformations in the apical direction as well as in the planar Cu-O bond length due presumably to changes in the local charge state.\textsuperscript{12} This fact together with the previously mentioned arguments concerning the possible symmetry of the electronic ground state, raises the question as whether this deformation is somewhere connected to a JT or pseudo Jahn-Teller (PJT) kind of distortion. In order to determine whether the JT or PJT effect might play any significant role on the local distortion on the La-Ba-Cu-O system, it is necessary to determine the symmetry properties of the total electronic ground state. Being the condition for a JT that this state must be degenerate. If it is not the case then the possibility of a PJT effect emerges and it is determined by non null matrix elements of the force operator (-\(\partial V/\partial Q_k\)), between the non degenerate ground state and closed excited states. Concerning the PJT effect it has been pointed out\textsuperscript{14} that there are no a priori exceptions for vibronic coupling effects. The presence of electronic degeneracy is just an important special case of vibronic coupling. Bersuker\textsuperscript{15} has introduced a PJT vibronic coupling through the mixing with the \(^1B_{1g}\) excited state to explain a polaron formation mechanism in high T\textsubscript{c} superconductors. It is worth mention that the PJT effect has been some times misinterpreted as a second order correction, and in fact this effect may be very strong, specially when the JT effect is absent. The study of those effects might be relevant in understanding the electron-lattice interaction.

In this paper, we examine the possibility of having a local distortion in the CuO\textsubscript{6} octahedra in La-Ba-Cu-O superconducting system originated by a JT or PJT effect. This is done under the assumption of a CuO\textsubscript{6}--10 cluster model for the superconductor. The CuO\textsubscript{6}--10 cluster is immersed in a set of static charges, located in the proper positions in order to simulate the crystalline background. This background stabilizes the cluster and preserves the point symmetry group. The electronic spectrum is calculated using the density functional theory in the generalized gradient approximation (DFT-GGA), and classified according to the IR of the symmetry group $D_{4h}$.

The paper is organized as follows. In Sec. 2 we introduce the cluster model representing the La-Ba-Cu-O system, and the methods used for the calculation and symmetry classification of the electronic spectrum. In Sec. 3 we present the results and discussion for the spectrum obtained and compared with the results of a unrestricted Hartree-Fock (UHF) calculation, and discussed the possible JT or PJT type of distortions. The conclusions are presented in Sec. 4.
2. Cluster Model

Embedded cluster models are used to describe real systems by treating the cluster electronic structure with some degree of sophistication by using \textit{ab initio} or semi-empirical methods, where as cruder approximations have to be made in order to treat the background used to embed the cluster. The basic philosophy in the use of cluster models is to study essential characteristics of the solid which are primarily determined by local properties that can be simulated by cluster calculations. Its use has been mainly justified by many successful applications including, by example, the La$_2$CuO$_4$ undoped cuprate\textsuperscript{16,17} or the La$_{2-x}$Sr$_x$CuO$_4$ superconductor system.\textsuperscript{18}

In this work we used the cluster model to study the effect of the localized orbital electronic states on the possibility for the existence of Jahn-Teller (JT) or pseudo Jahn-Teller (PJT) type local distortions in the La-Ba-Cu-O superconducting system.

We study the elongated octahedral CuO$_6^{-10}$ cluster immersed in a point charges environment according to the structure of the tetragonal superconductor (La,Ba)$_2$CuO$_4$ with the experimental lattice constants: $a = 3.7873$ Å and $c = 13.2883$ Å and with a Cu-O apex distance of 2.42 Å.\textsuperscript{19} This background simulates the crystalline surrounding.

The necessity to preserve the experimental bond lengths of the cluster, lead us to adjust the background arrangement in order to stabilize the cluster system. The values for the point charges environment were determined by performing a UHF cluster stability analysis.\textsuperscript{20} The first trial of stability calculations was done surrounding the cluster with fixed point charges corresponding to the formal charges values La$^{3+}$, Cu$^{2+}$, O$^{2-}$, and placing O$^{1.1538-}$ at the outer boundary (in a spherical radius of 8 Å ) accumulating 178 charges which neutralize the -10 charge of the cluster. We found this structure unstable in this background. However, if we change the formal charge of the nearest copper atoms in Cu-O planes to Cu$^{1+}$ (value consistent with possible Cu valence states), we recuperate stability with an absolute value for the energy gradient of $2.2 \times 10^{-3}$ a.u. for the oxygen atoms in the plane.

At this stage we did not try to make a full structure optimized calculation.

Recent works dealing with similar cuprate clusters have shown that the use of pseudopotential models for the nearest atoms to the cluster are advantageous in order to prevent an artificial polarization of the oxygen electrons towards the (in other way) bare positive charges.\textsuperscript{17,18,21} In a previously reported work,\textsuperscript{20} we performed an electronic structure calculation for the neutral CuO$_6^{-10}$ cluster embedded in the modified point charges environment using different basis in the HF formalism. Looking at the hybridization of the different wave functions, we do not observe the artificial polarization effect. This is due to the fact that we are using an effective charge of +1 for the nearest Cu atoms on the Cu-O planes . The only case where we note anomalies was in the use of minimal gaussian basis 3-21G, where we got a wrong symmetry for the total wave function. By the addition of a polarization term to the oxygen 3-21G basis, we recuperated the correct wave function symmetry. It
should be mentioned that the point charges substitution by the pseudopotentials does not guarantee the stabilization of the structure without a full relaxation of the cluster. In a DFT structure optimization calculation using bare pseudopotentials, relaxing only the apical length, Pliberšek et al. found a +0.04 Å shift from the correct experimental value for the apical distance Cu-O. Hence, since our main interest is in the analysis of the symmetry properties of the electron spectrum we try as a first model calculation a background with point charges.

When a point charges set is used to simulate the crystalline environment, some small adjustments in the charge values or its positions, or the inclusion of a ghost charges set are made in order to obtain the Madelung potential on the points corresponding to the atoms positions in the cluster. We do not assume this procedure here because the difference between the potential resultant from the number of charges in our model and the Madelung potential becomes rather small. Even more, assuming this procedure, the background symmetry could be changed if some charges are moved from its original positions. In our model we need to preserve the point symmetry of the environment in order to obtain the correct IR’s corresponding to the cluster molecular orbital (MO) and the nature of the vibronic coupling.

In summary, our model consists of a CuO$_6^{-10}$ cluster embedded in an environment formed by point charges placed at the positions of the nearest shell of atoms outside the cluster with the outer shell always being oxygen and the immediate copper atoms in the Cu-O plane with a charge +1. For the present calculation we have surrounded the cluster with 178 fixed point charges corresponding to La$^{3+}$, Cu$^{2+}$, O$^{2-}$, Cu$^{1+}$, and O$^{1.026-}$ at the outer boundary, with a net charge of +10 which neutralized the -10 charge of the cluster. The radius of the outer shell was fixed at 8 Å. In order to consider the possible undesirable basis effects on the electronic spectrum we selected a 4-21G basis with polarization d-components in the oxygens and no diffuse components s or p were added. The additional oxygen d-components privileges the Cu3d-O2p hybridization over the artificial polarization O2p-(Cu$^{1+}$, La$^{3+}$ bare charges). The arrangement selected, guarantees approximately the stability of the cluster, as well as the D$_{4h}$ symmetry properties of the electronic states and small polarization effects.

In a simple ionic model, the molecular levels formed by the 3d$^9$ states of Cu$^{2+}$ hybridized with the 2p$^6$ states of O$^{2-}$ immersed in a D$_{4h}$ crystalline field produce a nondegenerate electronic ground state. The same result is obtained within a quasi-molecular approximation in an extended Hückel model and also in open shell restricted and unrestricted Hartree-Fock (RHF-OS and UHF) calculations for the electronic ground state. This shows that within these approximations we do not find a possibility for pure JT distortions. The question is whether the same symmetry for the total electronic wave function is preserved in an electronic spectra obtained from ab initio calculations where higher electron correlations are taken into account. In order to investigate this situation we have performed a DFT-GGA calculation to determine the electronic ground state for the apical octahedron cluster together with their symmetry classification. This allows us to analyze the possibility
of realization of total degenerate electronic wave function.

The DFT calculation for the electronic ground state was performed using The Cambridge Analytic Derivatives Package CADPAC 6.1 running in a CRAY/YMP-4. This calculation was done using the generalized gradient approximation (GGA) with a 3-21G basis set for Cu and a 4-31G* for O (where * means polarized). The GGA improves the previous commonly used DFT-LDA (local density approximation) incorporating some nonlocal effects to the exchange-correlation functional using the gradient of the electron density. We employed a convergence criterium of $1 \times 10^{-7}$ for the density. The expected value for the spin operator $S^2$ in the ground state, was systematically checked to be $3/4$. The symmetry of the total electronic wave function and hence of the density is guaranteed by the symmetry of the hamiltonian ($D_{4h}$). For the exchange-correlation X-C functionals, the BP86 approximation (Becke exchange and Perdew correlation) was used. We consider a system formed by 87 electrons of the CuO$_6$ octahedron cluster which corresponds to the Cu$^{2+}$ and 6O$^{2-}$ ions. For the calculation, a total of 119 Gaussian base functions were employed, corresponding to 29 for the Cu$^{2+}$ and 15 for each of the six O$^{2-}$.The number of $\alpha$ and $\beta$ occupied states are 44 and 43 respectively, corresponding to the 87 electrons within the cluster. The obtained electronic wave functions were classified according to the IR of the $D_{4h}$ symmetry group using a simple algorithm based on the projection of characters that permits to find the classification according to the IR of a given symmetry group with the application of at most three symmetry operation.

3. Results and Discussion

We have studied within density functional theory in the generalized gradient approximation, the electronic ground state for the CuO$_6$ elongated octahedra cluster. This cluster represent one of the T$_c$ superconductors that have been suggested as a prominent candidate to show the JT effect: La-Ba-Cu-O.

The electronic spectrum for $\alpha$ states in the DFT for the Cu-3-21G plus O-4-21G* basis set in joint to the UHF spectra for Cu-3-21G plus O-3-21G*, O-4-21G* and O-6-31G* is shown in Fig. 1. The HOMO (highest occupied molecular orbital) states correspond, in both UHF and DFT, to a nondegenerate $\alpha$ level whose IR is $4B_{1g}$ giving, after making the product with the $\beta$ electronic wave function, a total orbital nondegenerate electronic ground state wave function whose symmetry is $2B_{1g}$. It should be mentioned that in Ref. 21, although the authors do not explicitly refer to the symmetry of the ground state, it is possible to infer it from their components of the atomic orbitals, corresponding the $2B_{1g}$, which agrees with our result. As can be seen from the spectra, all the HOMO states correspond to nondegenerate $B_{1g}$ states. Also all $\alpha$-LUMO (lowest unoccupied molecular orbital) states are the nondegenerate IR 11$A_{1g}$. It should be noted that the $\alpha$-(HOMO-LUMO) gap is reduced considerably in DFT respect UHF, from 11.02 eV to 2.4 eV for the same basis. This result is consistent with the well known fact that the HF
DF electronic spectrum of the CuO$_6$ and JT distortions in La-Ba-Cu-O. 

- 8E_u
- 11A$_{1g}$ (LUMO)

| Energy (eV) | 13 | 12 | 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 | -1 | -2 | -3 | -4 | -5 |
|-------------|----|----|----|----|---|---|---|---|---|---|---|---|---|---|----|---|---|---|---|
| UHF(3-21G*) | 8E_u
| UHF(4-21G*) | 8E_u
| UHF(6-31G*) | 11A$_{1g}$ (LUMO)
| KS-BP86(4-21G*) |

Fig. 1. DFT electronic spectrum for the $\alpha$ states using the Cu-3-21G plus O-4-21G$^*$ basis set. This is compared with the UHF spectra using the Cu-3-21G plus O-3-21G$^*$, O-4-21G$^*$ and O-6-31G$^*$ basis sets respectively of the CuO$_6$ cluster.

method overestimates the HOMO-LUMO gap in many molecular systems.

In Fig. 2 we show the DFT spectra for $\alpha$ and $\beta$ states and in Table 1 the contributions from the copper 3d and the planar and apical oxygens 2p to the highest occupied KS-BP86 MO's. The LUMO is the $\beta$ state 4B$_{1g}$ located 1.8 eV
Fig. 2. Spin-unrestricted DFT-GGA spectrum for the CuO$_6^{10-}$ cluster using the Cu-3-21G plus O-4-21G$^*$ basis set.

over the HOMO, compared with 1.4 eV reported in Ref. 21. We would like to remark some of the particular features shown in the DFT spectrum. There are two molecular orbital “bands” in the occupied electronic spectrum under the HOMO,
DF electronic spectrum of the CuO$_6^{-10}$ and JT distortions in La-Ba-Cu-O.

Table 1. Square of the copper 3d and the oxygen 2p (planar and apical) expansion coefficients of the highest occupied KS-BP86 MO’s of the CuO$_6^{-10}$ cluster.

| α MO   | $d_{zz}$ | $d_{xz}$ | $d_{xy}$ | $d_{yz}$ | $p_x(p)$ | $p_y(p)$ | $p_z(a)$ | $p_y(a)$ | $p_z(a)$ |
|--------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|
| 4B$_{1g}$ | 0.3546   | 0.1282   | 0.1282   |          | 0.0621   | 0.0011   |           |           |           |
| 3E$_g$(1) | 0.9354   | 0.9354   | 0.0621   | 0.0011   |           |           |           |           |           |
| 3E$_g$(2) | 0.9113   | 0.0432   | 0.0432   | 0.0621   | 0.0011   |           |           |           |           |
| 10A$_{1g}$ | 0.1089   | 0.3313   | 0.0082   | 0.0082   | 0.0638   |           |           |           |           |
| 1A$_{2g}$ | 0.5000   | 0.5000   |           |           |           |           |           |           |           |
| 7E$_u$(1) | 0.9632   | 0.0000   |           |           |           |           |           |           |           |
| 7E$_u$(2) | 0.9632   | 1.0000   |           |           |           |           |           |           |           |
| 1B$_{2u}$ | 0.0267   | 0.0267   | 0.6081   | 0.3649   | 0.3649   |           |           |           |           |
| 2E$_u$(1) | 0.0267   | 0.0267   | 0.6081   | 0.3649   | 0.3649   |           |           |           |           |
| 2E$_u$(2) | 0.0267   | 0.0267   | 0.6081   | 0.3649   | 0.3649   |           |           |           |           |

| β MO   | $d_{zz}$ | $d_{xz}$ | $d_{xy}$ | $d_{yz}$ | $p_x(p)$ | $p_y(p)$ | $p_z(a)$ | $p_y(a)$ | $p_z(a)$ |
|--------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|
| 4B$_{1g}$ | 0.3971   | 0.0831   | 0.0831   | 0.0543   | 0.0012   |           |           |           |           |
| 3E$_g$(1) | 0.9450   | 0.9450   | 0.0543   | 0.0012   |           |           |           |           |           |
| 3E$_g$(2) | 0.9166   | 0.0406   | 0.0406   | 0.0543   | 0.0012   |           |           |           |           |
| 10A$_{1g}$ | 0.1039   | 0.3056   | 0.0100   | 0.0100   | 0.0564   |           |           |           |           |
| 1A$_{2g}$ | 0.5000   | 0.5000   |           |           |           |           |           |           |           |
| 7E$_u$(1) | 0.9692   | 0.0008   |           |           |           |           |           |           |           |
| 7E$_u$(2) | 0.9692   | 0.0008   |           |           |           |           |           |           |           |
| 1B$_{2u}$ | 0.0226   | 0.0226   | 0.6342   | 0.3429   | 0.3429   |           |           |           |           |
| 2E$_u$(1) | 0.0226   | 0.0226   | 0.6342   | 0.3429   | 0.3429   |           |           |           |           |
| 2E$_u$(2) | 0.0226   | 0.0226   | 0.6342   | 0.3429   | 0.3429   |           |           |           |           |

Separated by a 2.9 eV gap. The first band with energy between 0 and -0.91 eV has MO’s with predominantly 3d cooper components: 4B$_{1g}$ (HOMO), 3E$_g$, 2B$_{2g}$, and 10A$_{1g}$. The second band with energy between -3.81 and -5.10 eV include MO’s composed mainly by oxygen 2p components: 1A$_{2g}$, 7E$_u$, 1B$_{2u}$, and 2E$_u$ (Table 1). This feature is not present in the UHF spectrum, where this MO band is mixed. Similar results were obtained in Ref. 21: the first band between 0 and -1.5 eV and the second band between -2.6 and -4.4 eV.

We show in Fig. 3 the predominant d orbitals for the 4B$_{1g}$ (HOMO), 3E$_g$, 2B$_{2g}$, and 10A$_{1g}$ containing the 3d$^9$ states of Cu$^{2+}$. In the HOMO state 4B$_{1g}$, the 3d$_{xz}$ (3d$_{yz}$) state of Cu is hybridized with the 2p$_\sigma$ O orbitals along the Cu-O bond in the x-y plane. This state is occupied only by one α electron and is orbitally nondegenerate. It should be noted however that it is spin degenerate, but since it has a degeneracy of order two in spin, it does not produce a JT deformation. It is basically the same kind of hybridization we got for the UHF wave function, except by a lower contribution from the 2p$_\sigma$ O orbitals. The occupied state nearest to the HOMO, the double degenerate orbital 3E$_g$, could be seen as the result of hybridization of the 3d$_{xz}$ (3d$_{yz}$) states with the p$_x$ and −p$_x$ (p$_y$ and −p$_y$) oxygen orbitals along the apical axis with no contribution of the p$_z$ and −p$_z$ oxygen orbitals along the x (y) axis. The 2B$_{2g}$ orbital becomes the hybridization of the Cu 3d$_{xy}$ state with the p$_\pi$
of the oxygens in the x-y plane (perpendicular to the Cu-O bond). Finally, the 10A₁g orbital is the hybridization of the 3d₃/2₋r₂ state of Cu with the 2pσ states of the oxygens in the apical z axis and with the pₓ, −pₓ, pᵧ and −pᵧ orbitals of the oxygens in the x-y plane along the Cu-O bonds.

Hence, since the electronic ground state is the nondegenerate \(^2\)B₁g state, we can
not have a residual static JT effect in the CuO$_6^{-10}$ cluster. The possibility for a PJT deformation, in this state of oxidation, is low since the HOMO-LUMO gap which is about 2 eV is much greater than the characteristic vibrational energy (20-100 meV). However, in the oxidized CuO$_6^{-9}$ cluster, the spin-singlet $^1A_{1g}$ electronic ground state could be mixed with some near excited states giving non-zero PJT vibronic couplings. Those states could be the spin-singlet (predominantly copper 3d states) $^1E_g$ and/or $^1B_{1g}$. This result is consistent with the assumption made in the model introduced by Bersuker$^{15}$ to explain a polaron formation mechanism in high T$_c$ superconductors. There he assumes a PJT vibronic coupling through the mixing with the $^1B_{1g}$ excited state. Here we have shown that besides the $^1B_{1g}$ excited state, the inclusion of the $^1E_g$ excited state in a PJT vibronic coupling might be also relevant. In the context of the model we have presented in this work, the PJT effect may produce a coupling with the $e_g$ and/or $b_{1g}$ vibrational modes which could be responsible for the local deformations in the superconducting system.

Recent DFT Becke-3-Lee-Yang-Parr band calculations$^{32}$ in the La$_{2-x}$Sr$_x$CuO$_4$ doped system support a highly inhomogeneous hole formation with symmetry $^1A_{1g}$ adjacent to the Sr impurity, giving us additional reliability about our final conclusion.

4. Conclusions

We have performed ab initio calculations in the CuO$_6^{-10}$ elongated octahedra cluster having the symmetry group D$_{4h}$, representing the La-Ba-Cu-O system, to investigate the possibility of having a Jahn-Teller or pseudo Jahn-Teller effect as the origin for the local distortions found in this system. This study has been motivated by the fact that the apical distortion of the CuO$_6$ octahedra in the insulating parent compound of the La based superconductor La$_2$CuO$_4$ is only partially due to a static Jahn-Teller effect, having therefore a non a priori condition to remove all the degeneracy of the electronic ground state of the parent regular octahedron with O$_h$ symmetry.

The DFT-GGA electronic spectrum was compared with the corresponding UHF calculated in a previous work. As a result in both cases, we found that the electronic degenerate states correspond only to intermediate levels, which are fully occupied. The symmetry of the total electronic ground state wave functions being therefore a nondegenerate $^2B_{1g}$ state, ruling out the possibility of a residual static JT effect in the CuO$_6^{-10}$ cluster. It should be noted however, that the DFT electronic spectrum contains a degenerate $3E_g$ state very close to the HOMO $4B_{1g}$ state. This belongs to a first set of filled molecular levels, including the HOMO state, which are spread on a width of the order of 1 eV, and which are characterized by being predominately formed by the 3d states of Cu. This set is separated by a gap of the order of 3 eV from another set of molecular states originated mainly by 2p states of O.

Since the HOMO-LUMO gap (about 2 eV) is much greater than the characteristic vibrational energy (20-100 meV), the possibility for a PJT deformation, in this
state of oxidation is low. However, in the oxidized CuO$_6^{-9}$ cluster, the spin-singlet $^{1}A_g$ electronic ground state could be mixed with some near excited states giving non-zero PJT vibronic couplings. Those states could be the spin-singlet (predominantly copper 3d states) $^{1}E_g$ and/or $^{1}B_{1g}$. We therefore conclude that the PJT effect in the CuO$_6^{-9}$ cluster may produce a coupling with the $e_g$ and/or $b_{1g}$ vibrational modes. This PJT effect could be the responsible for the local distortions observed in the CuO$_6$ octahedra in the La$_{1.35}$Sr$_{0.15}$CuO$_4$ superconductor.

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