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On the distribution of intrinsic holes in cuprates

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Abstract

First-principles density functional calculations on the La_2CuO_4 crystal, simulated by using the $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$ cluster, have been analysed to reveal that the Cu 4s orbital is occupied by about 0.5 electrons. Since this may have important consequences on the method of calculation of the intrinsic hole distribution in cuprates, a study of the frontier orbitals has been made. It is concluded that the Cu 4s occupancy is a direct result of a charge transfer from the oxygen anions but does not involve the hole. It is a clear illustration that the hole distribution cannot always be estimated from the charge density distribution alone. 60% of the hole remains on the copper while the rest is spread evenly about the planar oxygen atoms.

1. Introduction

Progress towards understanding the design of cuprate systems which promote high temperature superconductivity remains slow. There is a multi-pronged attack from both the experimentalist and theorist which are not always cooperative. The theoretical methods, which investigate the electronic structure of these materials, range from band structure [1, 2] and supercell approaches which account for dopants [3, 4] to cluster calculations [5–11], but are largely complementary in their areas of success.

The main motivation for this work comes from band structure calculations on $\text{YBa}_2\text{Cu}_3\text{O}_7$ which implied that the Cu 4s orbital may be significantly occupied with 0.2 [6] and 0.25 [12] electrons. Although we have done calculations on this material we decided to concentrate on La_2CuO_4 since the higher symmetry is more conducive to a satisfactory qualitative explanation. Our first objective was to confirm whether the 4s orbital is significantly occupied, and to do this we chose to use cluster calculations since orbital populations are easily obtained. Secondly, if a significant occupancy of the 4s is reproduced, we will attempt to construct a qualitative bonding diagram to understand how the charge transfer arises and hence decide if the partially

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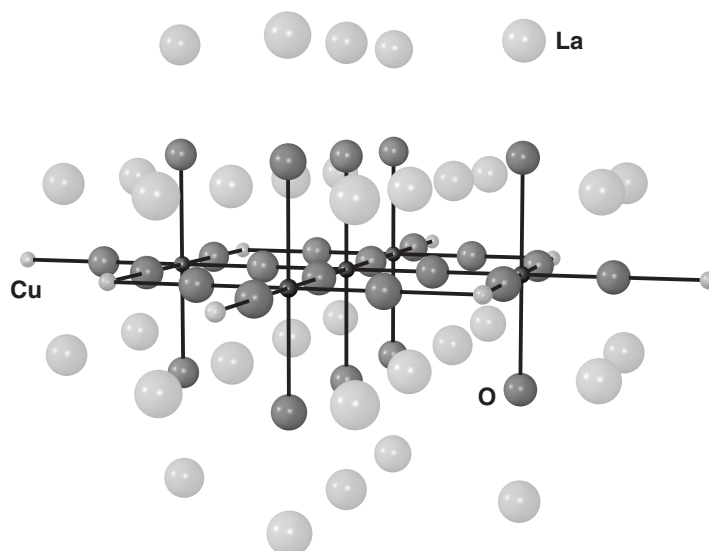


Figure 1. The $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$ cluster.

occupied 4s orbital could be important when determining the hole distribution and whether it has any role in superconductivity.

The Cu 4s orbital plays an important role for the (contact) on-site hyperfine field and the hyperfine field transferred from neighbouring copper ions. These quantities contribute substantially to the local fields at the copper nucleus which can be measured by nuclear magnetic resonance. We therefore also present details of the calculated spin densities.

2. Clusters and theoretical methods

A cluster is a contiguous symmetrical selection of ions extracted from a crystal with the same geometric structure. Target ions, that is, ions whose properties are to be calculated as accurately as possible, are normally chosen to be at or very near the cluster centre. To minimise edge effects at least the nearest neighbours of the target ions are added to form the core of the cluster; these are treated most accurately using first-principles all-electron methods. To further minimise edge effects the next shell of ions which surround the core cluster are represented by pseudopotential functions in the first-principles calculations. The remainder of the cluster (≈ 2000 ions) is replaced by point charges; some of the more remote charges are adjusted so that the target ions experience the correct Madelung potential. For clarity these clusters are labelled X/Y where X is the chemical formula of the core cluster and Y the formula of the ions represented by pseudopotential functions. In this work we have studied La_2CuO_4 (tetragonal structure with space group $I4/mmm$, [13]) with parameters $a = b = 3.77 \text{ \AA}$ and $c = 13.18 \text{ \AA}$, represented by the cluster $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$, and shown in figure 1.

All cluster calculations use the spin-polarised density functional method as implemented in the Gaussian 98 software package [14] choosing the 6-311G basis set, the exchange functional of Becke [15] and the correlational functional of Lee *et al* [16] (corresponding to the BLYP keyword in Gaussian 98). Further details can be found in [10, 11] where we have already presented details of electric field gradient (EFG) properties which agree well with the available experimental data.

Table 1. Mulliken charges (ρ_c), CDM charges $\bar{\rho}_c = \rho_c - \text{overlap terms}$, and Mulliken spin densities (ρ_{spin}) for the atoms in La_2CuO_4 for the $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$ cluster for various multiplicities M . The averages of the charges for $M = 4$ and 6 , denoted by av, are only given to two decimal places.

	M	Cu	O _p	O _a	$\rho(2)$	$\rho(3)$
ρ_c	4	1.133	-1.627	-1.940	-2.122	-0.001
ρ_c	6	1.179	-1.660	-1.939	-2.141	-0.018
ρ_c	av	1.16	-1.64	-1.94	-2.13	-0.01
$\bar{\rho}_c$	4	1.312	-1.671	-1.932	-2.030	0.106
$\bar{\rho}_c$	6	1.348	-1.718	-1.931	-2.088	0.050
$\bar{\rho}_c$	av	1.33	-1.70	-1.93	-2.06	0.08
ρ_{spin}	4	0.263	-0.025	-0.012	0.212	0.187
ρ_{spin}	6	0.674	0.136	0.013	0.946	0.972

We have extended these calculations by performing a Mulliken population analysis [17] to divide the total electron density among the various atoms and then among the orbitals on those atoms.

3. Results

The $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$ cluster has five unpaired electrons leading to a choice of possible multiplicities, $M = 2, 4$ or 6 . ($M = 6$ corresponds to a ‘ferromagnetic’ alignment of the spins, whereas $M = 4$ leads to an ‘antiferromagnetic’ alignment.) In table 1 we list the total atom charge for the *central* copper and neighbouring oxygen atoms in La_2CuO_4 for only $M = 4$ and 6 ; the $M = 2$ multiplicity is not considered since it has the highest energy and additionally the spin distribution is inappropriate for this cluster geometry. There are 5 Cu atoms and 26 oxygen atoms in the cluster but we select only those atoms at the centre of the cluster for consideration. Those atoms close to the periphery of the cluster are not accounted for since these will include effects expected from the cluster edge.

In table 1 we use the symbols $\rho(2)$ and $\rho(3)$, which are defined as follows.

$$\rho(2) = \rho(\text{Cu}) + 2\rho(\text{O}_p) \quad (1)$$

and

$$\rho(3) = \rho(2) + 2\rho(\text{O}_a) + 2\rho(\text{La}) \quad (2)$$

where ρ is either ρ_c , the Mulliken charge, or ρ_{spin} , the spin density. O_p and O_a are planar and apical oxygens respectively. $\rho_c(\text{La}) = 3$ is the ionic charge and $\rho_s(\text{La}) = 0$ is the spin density on La^{3+} . The notations $\rho(2)$ and $\rho(3)$ point to the fact that the former accounts for charges confined to the two-dimensional CuO_2 -plane while the latter also comprises the out-of-plane atoms and is representative for the charge in three dimensions. In addition we have also listed charge densities, $\bar{\rho}_c$, which are derived solely from the diagonal elements from the charge density matrix (CDM), and differ from the Mulliken charge densities in that all overlap contributions have been neglected. The relation between these quantities is discussed in the appendix. The quantities denoted by av are the averages of the charges resulting from multiplicities $M = 4$ and 6 . We have not averaged the spin densities since, as expected, they change significantly for different spin multiplicities.

In tables 2 and 3 we present the corresponding Mulliken partial populations for the orbitals of copper and the two types of oxygen. In table 3 we have used $2p_{\parallel}$ to represent the $2p$ planar oxygen orbital whose axis lies parallel to the line connecting that oxygen atom to copper.

Table 2. Partial Mulliken populations ($p(\text{Cu})$) and partial CDM populations $\bar{p}(\text{Cu}) = p(\text{Cu}) - \text{overlap terms}$, of the atomic orbitals of the central copper atom in LaCuO_4 for the $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$ cluster for $M = 4$ and 6 . $M = \text{av}$ is the average of the values for $M = 4$ and 6 . The p_{spin} are the corresponding partial Mulliken spin density populations.

	M	4s	$3d_{3z^2-r^2}$	$3d_{x^2-y^2}$	$3d_{xy}$	$3d_{yz}$	$3d_{xz}$
$p(\text{Cu})$	4	0.491	1.917	1.430	1.993	1.993	1.993
$p(\text{Cu})$	6	0.497	1.913	1.378	1.993	1.994	1.994
$p(\text{Cu})$	av	0.49	1.92	1.40	1.99	1.99	1.99
$\bar{p}(\text{Cu})$	4	0.339	1.904	1.384	2.000	1.996	1.996
$\bar{p}(\text{Cu})$	6	0.338	1.901	1.350	2.001	1.996	1.996
$\bar{p}(\text{Cu})$	av	0.34	1.90	1.37	2.00	2.00	2.00
$p_{\text{spin}}(\text{Cu})$	4	0.031	0.015	-0.312	0.001	0.001	-0.001
$p_{\text{spin}}(\text{Cu})$	6	0.027	0.025	0.620	0.000	0.000	0.000

Table 3. Partial Mulliken populations ($p(\text{O})$) and partial CDM populations $\bar{p}(\text{O}) = p(\text{O}) - \text{overlap terms}$, of the atomic orbitals of the central oxygen atoms in LaCuO_4 for the $\text{Cu}_5\text{O}_{26}/\text{Cu}_8\text{La}_{34}$ cluster for $M = 4$ and 6 . $M = \text{av}$ is the average of the values for $M = 4$ and 6 . The p_{spin} are the corresponding partial Mulliken spin density populations.

	M	O(p)				O(a)			
		2s	$2p_{\parallel}$	$2p_{\perp}$	$2p_z$	2s	$2p_x$	$2p_y$	$2p_z$
$p(\text{O})$	4	1.963	1.662	1.998	2.003	2.000	1.997	1.997	1.946
$p(\text{O})$	6	1.959	1.701	1.996	2.002	2.000	1.996	1.996	1.944
$p(\text{O})$	av	1.96	1.68	2.00	2.00	2.00	2.00	2.00	1.95
$\bar{p}(\text{O})$	4	2.018	1.604	2.037	2.013	2.007	1.996	1.996	1.933
$\bar{p}(\text{O})$	6	2.006	1.663	2.037	2.012	2.007	1.996	1.996	1.932
$\bar{p}(\text{O})$	av	2.01	1.63	2.04	2.01	2.01	2.00	2.00	1.93
$p_{\text{spin}}(\text{O})$	4	0.001	0.024	0.000	0.001	0.000	0.001	0.001	0.012
$p_{\text{spin}}(\text{O})$	6	0.007	0.127	0.002	-0.000	0.000	0.000	0.000	0.012

$2p_{\perp}$ is at right angles to $2p_{\parallel}$. If $2p_{\parallel}$ corresponds to a $2p_x$ orbital then $2p_{\perp}$ is a $2p_y$ orbital and vice versa.

4. Discussion

4.1. Simple ionic approach

The $M = 4$ spin state is lowest in energy and corresponds to the four spin-down electrons being distributed on the four exterior copper atoms of the cluster and one spin-up electron on the central copper atom, coinciding with the model of long-range antiferromagnetism observed for La_2CuO_4 . However, clusters are not ideally suited to studying long-range effects and the spin distribution calculated is not entirely correct. The spin-up electron strongly pairs up with the four spin-down electrons, probably in a more extreme manner than occurs in the crystal because the peripheral spin-down electrons have only one neighbour with a spin-up electron instead of four. In the crystal the *magnitude* of the spin density on each copper is the same although half are positive and half are negative. So there is a possibility that the spin-up density on the central copper in the cluster has been unreasonably reduced. On the other hand the $M = 6$ spin state places spin-up electrons on all coppers and probably overestimates the spin densities since pairing is now completely excluded. This is well illustrated in table 1,

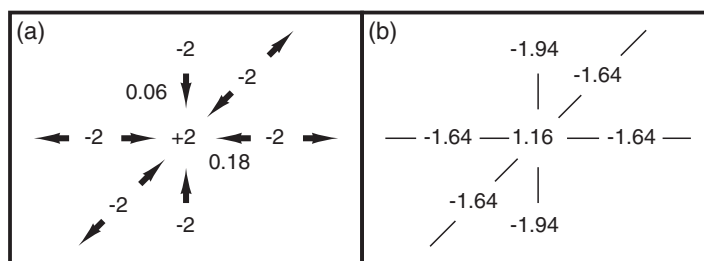


Figure 2. (a) A simplistic model, showing the charge transfer of 0.84 electrons from oxygen anions (-2) to a copper cation ($+2$) as a result of covalent bonding. The charge transfers pointing away from the planar oxygen anions are to other planar copper cations which are not shown. The resulting Mulliken charges are shown in (b).

where the spin density (ρ_s) on copper is much higher for $M = 6$ than 4. Note the change of sign on the neighbouring oxygen ions showing domination of the spin-down electrons for $M = 4$. Hence we are reluctant to use the spin densities in tables 1–3 to estimate the hole distribution. However, the charge densities are far less sensitive to the choice of spin state and we will use the averaged values for convenience.

The total electron density distribution is an observable and its accuracy can in principle be tested experimentally. However, it is otherwise rather intractable to use for qualitative models. A long established procedure is to partition the density in terms of atomic orbitals so that the behaviour can be associated with the properties of a small number of atoms. Although atomic orbitals do not strictly exist in molecules it is possible to identify functions centred on nuclei which possess all the characteristics (number of nodal surfaces and angular properties) which correspond to hydrogen-like atomic orbitals. For example in these calculations we can identify a function in the molecular orbitals which is spherically symmetric about the central copper nucleus with three spherical nodal surfaces corresponding to a 4s hydrogen-like orbital. The most commonly used method of achieving this partition is the Mulliken population analysis [17]. The procedure is clearly defined and accounts for the whole electron population although there is some concern how the overlap densities are apportioned to the individual basis orbitals [18] (see the appendix). To obviate the concerns we also list the appropriate diagonal elements of the CDM which are the CDM populations (or Mulliken charge populations *without* the overlap contributions) $\bar{p}(\text{Cu})$ and $\bar{p}(\text{O})$ in tables 2 and 3 which, when collected together, lead to $\bar{\rho}_c$ in table 1.

When each atom is represented by the ions La^{3+} , Cu^{2+} and O^{2-} and the ionic charge replaces the Mulliken charge, $\rho(3)$ (see equation (2)) corresponds to the formula La_2CuO_4 and is zero. Therefore in the limit of an infinitely large cluster, the charge $\rho(3)$ should be zero. For our clusters $\rho_c(3)$ (table 1) is very close to zero and even $\hat{\rho}_c(3)$ is missing only a small negative charge.

The simplistic ionic model of the crystal relies on the ions Cu^{2+} , O^{2-} and La^{3+} , the only hole in the electronic configuration being localised on $\text{Cu}^{2+}(3d^9)$. The Mulliken charges (ρ_c in table 1) suggests that 0.84 electrons are transferred to the oxygen atoms (figure 2). The CDM data reduces this to 0.67 holes. These results should be viewed with extreme caution if we continue to associate partial occupancy of orbital with holes. For example using the Mulliken population data in tables 2 and 3 the hole is distributed 60% in the Cu $3d_{x^2-y^2}$ copper orbital, 9% in $3d_{3z^2-r^2}$ copper orbital, 64% in the four planar oxygens $2p_{\parallel}$ orbitals and 10% in the two apical oxygen $2p_z$ orbitals, which is clearly nonsense.

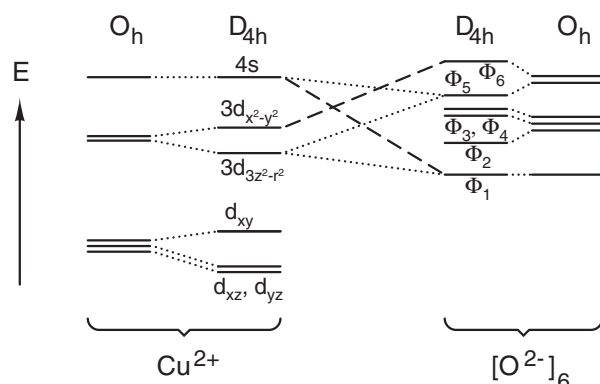


Figure 3. The interaction of the atomic orbitals of copper with the symmetry combinations of the surrounding oxygen hybrid orbitals. The dashed lines indicate the primary interactions which remain even in O_h symmetry. The secondary (smaller) interactions are shown by dotted lines. Bonding and anti-bonding combinations of the orbitals of the primary interactions explain the occupancy of the 4s orbital and the transfer of the hole from the $3d_{x^2-y^2}$ orbital to oxygens (Φ_6 only).

The inadequacy of this approach is further exposed by the observation that the 4s orbital is significantly populated by 0.49 electrons (Mulliken) or 0.34 electrons (CDM). The latter is expected to be smaller but the observation seems real and requires an explanation, which is provided in the next section (section 4.2).

4.2. A qualitative molecular orbital study

In order to proceed further we need to construct a molecular orbital energy diagram of the copper ion and its six nearest neighbour oxygen ions which leaves little room for doubt and explains the charge transfer observed. As is normal in similar circumstances we concentrate only on the frontier orbitals, the highest occupied, and at least for copper the lowest unoccupied, orbitals of the interacting ions. There is no difficulty with the Cu^{2+} ion since the qualitative orbital energy diagram has remained unchanged now for many years (see for example [19]), and is shown on the left-hand side of figure 3 for O_h and D_{4h} symmetry. Note that we have added the copper 4s orbital, the lowest energy unoccupied orbital.

In table 3 only the four planar oxygen $2p_{\parallel}$ orbitals and the two apical oxygen $2p_z$ orbitals have significantly reduced populations from complete occupancy, which indicates that only these oxygen frontier orbitals are significantly involved in bonding. We define each of these 2p orbitals in such a way that the phases of the lobes pointing towards the central copper atom are the same. Fortunately in O_h symmetry we can form six symmetry adapted orbitals easily. Let the symmetry adapted orbitals be represented by Φ and the 2p orbitals by ϕ so that

$$\Phi = U\phi$$

where U is a unitary 6×6 matrix. The moduli of the non-zero elements of each row of the matrix are all identical, so we only require the sign of these elements. These are given in figure 4 for each Φ . The energies increase as a function of the number of nodal planes in each selection. Φ_1 has no nodal planes, Φ_2 , Φ_3 , Φ_4 have one nodal plane and Φ_5 , Φ_6 have two nodal planes. These are drawn on the extreme right of figure 3, and also show, immediately to the left, how the degeneracies are lifted for D_{4h} symmetry. Only the $4s(a_{1g})$ and $3d_{x^2-y^2}(b_{1g})$ orbitals on the copper are available for bonding since these are not completely occupied.

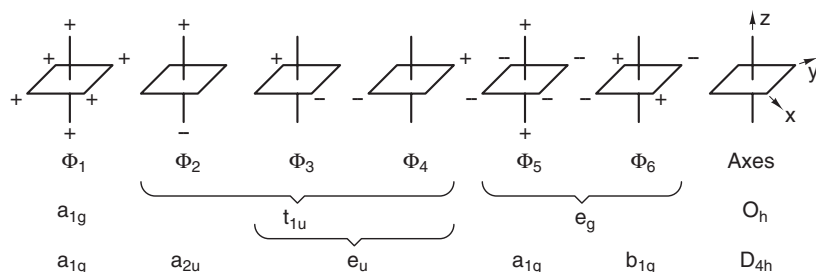


Figure 4. The signs of the orbital coefficients for the various combinations of hybrid orbitals of the oxygen atoms. The absence of a sign indicates a zero coefficient. The hybrid orbitals are defined such that the phases pointing towards the copper atom have all the same sign.

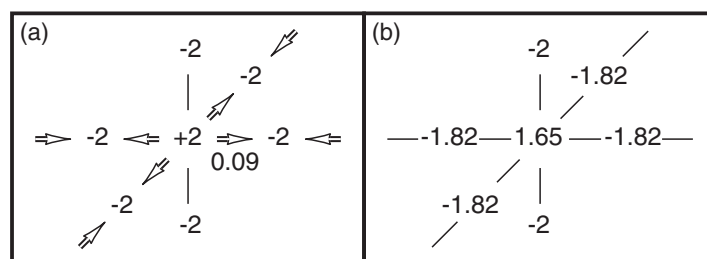


Figure 5. (a) A simplistic model showing the transfer of 0.0875 holes from the copper cation to each of the planar oxygen anions arising from the bonding involving the Cu $3d_{x^2-y^2}$ orbital and the oxygen valence orbitals. The corresponding Mulliken charges resulting from the hole transfer is given in (b).

All the oxygen Φ orbitals are completely occupied and can only interact, if allowed by symmetry, by donating electrons into vacant or partially occupied orbitals on copper. The only interactions in O_h symmetry are $4s-\Phi_1$ and $3d_{x^2-y^2}-\Phi_6$. These are also allowed in D_{4h} symmetry and are regarded as being the dominant interactions. Secondary additional interactions arising from the reduction in symmetry to D_{4h} are $4s-\Phi_5$, $3d_{3z^2-r^2}-\Phi_5$ and $3d_{3z^2-r^2}-\Phi_1$.

Since the hole, from the ionic model, originates from the $3d_{x^2-y^2}$ copper orbital there is *only one* interaction involving the hole: $3d_{x^2-y^2}-\Phi_6$. This uniquely restricts the transfer from the copper to the planar oxygen $2p_{\parallel}$ orbitals (see the definition of Φ_6 in figure 4).

The Mulliken population analysis clearly indicates that 40% of the hole has been transferred to the planar oxygens (see figure 5 for more detail), and none by this mechanism to the axial oxygens, leaving 60% on the copper. The CDM analysis is very similar, and unambiguously places 63% of the hole remains on copper, the rest being evenly distributed on the adjacent planar oxygens. Since a hole transfer is accompanied by an electron charge transfer in the opposite direction we conclude that of the 0.84 electrons (Mulliken) transferred from the oxygens to copper, 0.40 electrons have been accounted for by the hole transfer. The remaining 0.44 electrons almost correspond exactly to the Mulliken $4s$ orbital population of 0.49 electrons which can be associated with the dominant $4s-\Phi_1$ interaction. The discrepancy of 0.05 electrons can be attributed to the secondary interactions which also involve the $3d_{3z^2-r^2}$ orbital. The CDM data are very similar. The 0.67 electrons transferred from the oxygens to copper can largely be associated with the hole transfer of 0.37 electrons and the $4s$ population of 0.34 electrons. Again secondary interactions will have a small influence but not on the hole transfer.

4.3. Further observations

The slight spin preference ($p_{\text{spin}}(\text{Cu})(4s) = 0.03$) could be interpreted as arising from a spin polarization stemming from the unpaired electron in the $3d_{x^2-y^2}-\Phi_6$ anti-bonding orbital, rather than a direct involvement in the hole transfer. However, the effect on the hyperfine coupling constant is disproportionately large. The resultant spin in the 4s polarizes the electrons in the 3s and to a minor extent in the 2s and 1s orbitals. The on-site contact hyperfine field is negative ($-1.78 a_{\text{B}}^{-3}$) but there exists a positive field that is transferred from nearest neighbour copper ions ($+0.71 a_{\text{B}}^{-3}$). A detailed analysis of these calculated spin transfers has been given [20, 21]. Here, we first note that the theoretical results are in very good agreement with the values derived from the NMR data [22, 23]. We further note that Pavarini *et al* [24] have emphasized the importance of the 4s orbital in intralayer hopping.

The hole distribution, which is predominantly centred on the $3d_{x^2-y^2}$ orbital on copper, should sensitively affect the EFG at the copper nucleus (see [20]) since this property is dependent on the $1/r^3$ function. However, it is the $\bar{\rho}_{\text{c}}(3d_{x^2-y^2})$ value rather than $\rho_{\text{c}}(3d_{x^2-y^2})$ which is important since the overlap terms make only a relatively small contribution.

Finally we note that for the $M = 6$ spin state the Mulliken spin density in the $3d_{x^2-y^2}$ implies that 62% of the hole remains on copper in agreement with the 60% derived from the Mulliken charge densities with the help of the MO diagram.

5. Conclusions

The relatively high symmetry (D_{4h}) of the immediate oxygen anion environment of copper cations, represented by the distorted octahedral cluster CuO_6^{10-} in La_2CuO_4 , enables the hole distribution to be uniquely and unambiguously associated with the Cu $3d_{x^2-y^2}$ orbital and the symmetry-adapted oxygen orbital Φ_6 from a qualitative molecular orbital energy diagram. The diagram also allows for the participation of the formerly unoccupied Cu 4s orbital to receive electrons directly from two doubly occupied oxygen orbitals without spin preference. It should now be clear that analysis of charge alone cannot determine the hole distribution. These results are in agreement with, and provide an explanation for, the Cu 4s orbital population from both previous band structure and current cluster calculations.

Although the spin density in the Cu 4s orbital is calculated to be very small (0.03) its contribution to the NMR contact field is very important [10, 11].

Acknowledgments

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Appendix

If \mathbf{R} is the CDM of our system and \mathbf{S} is the overlap matrix of the basis orbitals the total number of electrons (or negative charge) is simply $\text{Tr}(\mathbf{RS})$. Each term in this sum involves one of the overlap integrals which involves either one or two nuclear centres. Fortunately every term involving a reference to two nuclear centres is duplicated in the sum and the neatest solution is to assign one term to each centre. This is equivalent to the negative charge density calculated by the Mulliken [17] population analysis. This neat solution has been criticised [18] since it shares the overlap density in situations which are clearly highly polarised. However, negative

overlap densities are also possible and the physical picture is blurred and there is no consensus on which should be the best procedure to follow. It is convenient to insist that the basis orbitals on each centre are orthonormal so that the diagonal elements of \mathbf{S} are all unity. If we now ignore all off-diagonal elements of \mathbf{S} we obtain the unit matrix. This means that $\text{Tr}(\mathbf{RS}) = \text{Tr}(\mathbf{R})$, the sum of the diagonal elements of the CDM, every term now referring just to one centre. These are now called the CDM charges. Unfortunately removing the overlap controversy now means that the total negative charge is incorrect. However, if the Mulliken charges and the CDM charges give the same unambiguous interpretation of the qualitative molecular orbital energy diagram described here we can be sure that the controversy of the overlap densities is not important here.

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