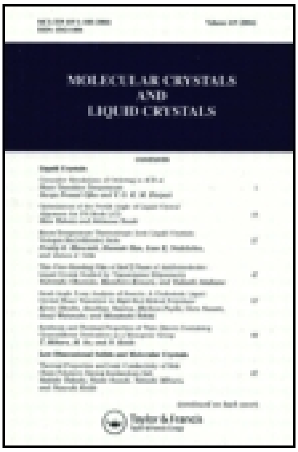

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Edward A. Boudreaux [a] & Eric Baxter [a]
[a] Department of Chemistry, University of New Orleans, New Orleans, Louisiana, U.S.A.

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MO CALCULATIONS ON EXTENDED CLUSTERS OF $YBa_2Cu_3O_7$

EDWARD A. BOUDREAUX AND ERIC BAXTER
Department of Chemistry, University of New Orleans
New Orleans, Louisiana, U.S.A.

Abstract Molecular orbital studies of the electronic structure and bonding in $Y Ba_2 Cu_8O_{26}^+$ and $Ba_2Cu_8O_{26}^-$ clusters of the high Tc superconductor, $YBa_2Cu_3O_7$, have been carried out. The results show a distribution of single electrons and pairs over all occupied M.O.s. The single electrons are localized over O and Cu atoms in an approximate ratio of 19/4 respectively. An antiferromagnetic coupling of all spins to produce an open shell singlet state is anticipated.

INTRODUCTION

Molecular orbital calculations via the S.C.-M.E.H.-M.O. method[1-5] have previously been reported on the high Tc superconductor $YBa_2Cu_3O_7$, in which one Cu_4O_{14} and one Cu_4O_{16} cluster were taken to represent respectively a verticle stack and a horizontal sheet within the unit cell structure of the orthorhombic crystal.[6] A similar study of the $YBa_2Cu_8O_{26}^+$ cluster was also reported on in its initial phases of completion.[7]

The two most essential features derived from these studies are: 1) there are enough major differences between the calculated electronic structures of small vs extended clusters, to render interpertation from small cluster calculations (ab initio or otherwise) questionable; 2) there does not appear to be any rationale for differentiating Cu(II) and Cu(III) formal valence states. In fact, the calculated net charges on all Cu atoms are relatively low (~0.3 to 0.6) and the total d orbital populations are the order of 9.7 - 9.8 and 9.9 in small and extended clusters respectively. This suggests that the formal Cu valence is close to (I), which is also in agreement with ab initio calculations on a $Ba_4Cu_2O_7^+$ cluster[8]. An analysis of spin pairing energies in $YBa_2Cu_8O_{26}^+$, suggests that the magnetic spin states and the probable superconducting mechanism arises from decoupling of single-electron, antiferromagnetically coupled, M.O. levels.[7] This in complete agreement with recent magnetic susceptibility data.[9,10]

In this report, the electronic structures of both $Y Ba_2Cu_8O_{26}^+$ and

$Ba_2Cu_8O_{26}^-$, as indedpendent and coupled clusters, are presented.

METHOD OF CALCULATION

The development and applications of the S.C.-M.E.H.-M.O. procedure have already been presented in detail elsewhere,[1-5] hence only the salient features and highlights of the method will be stated here.

The only resemblance that this method bears to the usual Extended Hückel (EH-MO) method is the general format of the one-electron hamiltonian. There are no scaling parameters and all multicenter molecular integrals are approximated systematically. Löwdin orthogonalization is employed in calculating orbital populations and charges. Either non-relativistic or quasi-relativistic atomic wave functions and orbital energies are obtained from independent HF-SCF calculations, with or without configuration interaction, as required. Calculated one-electron M.O. eigenvalues are systematically adjusted for spin-pairing, spin-orbit and electrostatic splitting effects. A stablizing potential buffer is applied to compensate for the physically realistic charge neutralization present in the environment of ionized molecules and ionic clusters. The calculations are carreid out iteratively with a simultaneous three-fold convergence on population, charge and total energy. There are, in principle, no restrictions as to types and numbers of atoms; however, in its present format the program is limited to 50 atoms and 190 m_l orbitals.

For calculations on the $Y\ Ba_2\ Cu_8O_{26}^+$ and $Ba_2Cu_{82}O_6^-$ clusters the following overlap-matched STO's were employed: Cu 3d, 4s, 4p; O 2p; Ba 6s and Y 4d, 5s. It was found from earlier calculations that the O 2s orbital contributes only a very small amount (~2-3 per cent) to the total bonding.[6] Orbital energy data were derived from HF-SCF A.O. calculations on all feasible configurations of; Cu^- thru Cu^{3+}; O^{2-} thru O^+; Ba^o thru Ba^{2+} and Y^o thru Y^{3+}.

Since there is only moderate spin orbit coupling in these systems, the non-relativistic form of the average spin-pairing energy equation was used.[1]

$$\overline{E}_{sp} = 1/2 \sum_{uv} C_{uv}^2 D_{uv} \ [<\overline{S}_{uv}(\overline{S}_{uv} + 1) - S_u(S_u + 1) - S_v(S_v + 1)]$$

where C_{uv} are the Löwdin coefficients of the uth and vth AOs in each LCAO-MO, D_{uv} is the AO spin-pairing-parameter defined in terms of Slater-Condon repulsion parameters, S_u and S_v are the net electron spins in the uth and vth AOs, and $<\bar{S}_{uv}(\bar{S}_{uv}+1)>$ is the effective average spin given by

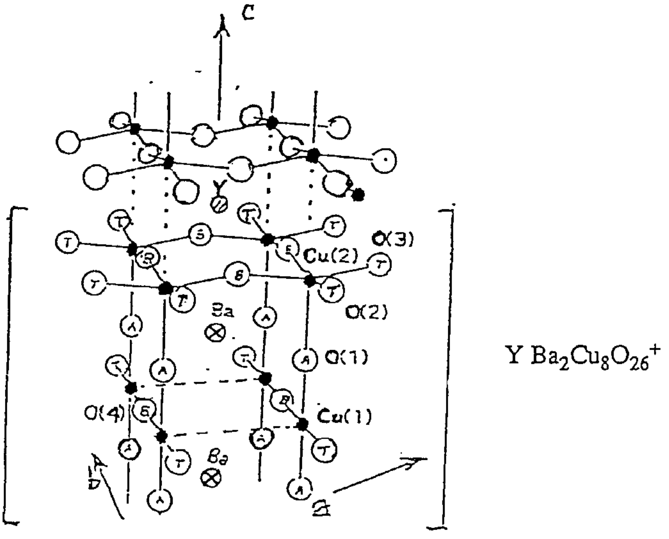
$$<\bar{S}_{uv}(\bar{S}_{uv}+1)> = \frac{P_{uv}(P_{uv}+2)}{4} - \left(\frac{2\ell_{uv}+1}{2\ell_{uv}+1}\right)\frac{P_{uv}(P_{uv}-1)}{2}$$

where P_{uv} are the calculated Löwdin populations and ℓ_{uv} the orbital quantum numbers of the uth and vth AOs.

X-ray structural data were taken from that reported by Torardi and co-workers.[11] The specific structural features pertinent to the cluster calculations are depicted in Figure 1. $Cu_{(1)}$ is in an axially contracted four-fold coordination site of D_{2h} symmetry, while $Cu_{(2)}$ is in an axially elongated five-fold coordination site of disotorted C_{4v} symmetry. The Y atom is in an eight-fold square antiprismatic coordination, with an average Y-O bond distance of 2.39 Å. Ba is effectively ten-fold coordinated with five different Ba-O distances varying by ±0.2Å. The average Ba-O bond distance is taken to be 2.90Å. These same data were used for both $Y\,Ba_2CuO_{26}^{+}$ and $Ba_2\,Cu_8O_{26}^{-}$ clusters, hereafter referred to as C(I) and C(II) respectively. In the coupled-cluster arrangement C(II) is stacked above C(I).

RESULTS AND DISCUSSION

Pertinent atomic charges and A.O. populations are presented in Table I for C(I) and C(II) clusters. It is also interesting that Ba atoms have little higher positive charges in C(II) than in C(I), in spite of the fact that C(II) has a net negative charge. Thus all the increase in negative charge of C(II) over C(I) resides on the O atoms. The top layer of C(I) bears a net charge of -1.187esu while the bottom layer of C(II) has a -1.175esu charge. Both of these charges are counter-balanced by the +1.060 charge on Y (see Fig. 1). Thus there is a small imbalance between the two charged regions, so that a small flow of negative charge from C(II) to C(I) via the Y ion, would be indicated. While it is not expected that this would be a major contributor to the superconductivity mechanism, it still provides some small effect. In fact, it is well known that the observed resistivity along the C axis of the Y $Ba_2Cu_3O_7$ unit cell is some 10^3 times greater than that in the directions of the a,b axes.



Oxygens: A = Axial

B = Bridge

T = Terminal

Chain: Cu(1), O(1), O(4)

Layer: Cu(2), O(2), O(3)

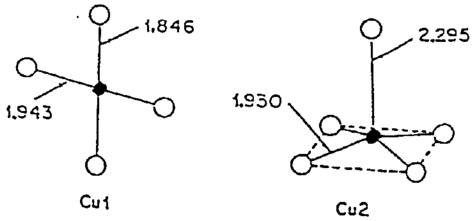


Figure 1. Y $Ba_2Cu_3O_7$ local unit cell structure

Table I. Populations and charges.

Cluster	Atom	Charge							
			3d	4s	4p	2p	4d	5s	6s
C(I)	Cu(C)	0.311	9.854	0.430	0.405	--	--	--	--
	Cu(L)	0.296	9.868	0.433	0.405	--	--	--	--
	(C)O(Ax-br.)	-0.328	--	--	--	4.328	--	--	--
	(C)O(Eq-br.)	-0.417	--	--	--	4.417	--	--	--
	(L)O(br.)	-0.366	--	--	--	4.360	--	--	--
	Y	1.060	--	--	--	--	1.795	0.146	--
	Ba(C)	1.900	--	--	--	--	--	--	0.100
	Ba(L)	1.931	--	--	--	--	--	--	0.069
C(II)	Cu(C)	0.403	9.897	0.406	0.297	--	--	--	--
	Cu(L)	0.433	9.903	0.386	0.279	--	--	--	--
	(C)O(Ax-br.)	-0.403	--	--	--	4.404	--	--	--
	(C)O(Eq-br.)	-0.501	--	--	--	4.500	--	--	--
	(L)O(br)	-0.372	--	--	--	4.328	--	--	--
	Ba(C)	1.934	--	--	--	--	--	--	0.066
	Ba(L)	1.944	--	--	--	--	--	--	0.056

(C)* = chain; (L) = layer; (AX) = axial; (Eq) = equitorial; (br) = bridge

The pertinent electronic structural data calculated for C(I) and C(II) clusters are presented in Tables II and III. The C(I) cluster has 198 electrons distributed over 116 M.O.s. The HOMO (116) has one electron and is primarily O, 2p characters from the chains. The LUMO (117), only 0.03 eV higher, is also O, 2p but from both and layers. M.O.s 115-56 are primarily O, 2p with $\leq$ 15% Cu character. These orbitals contains 35 pairs and 25 single electrons. M.O.s 55 and 47 each contain one electron and are mainly O, 2p; but the former has ~ 11% Y, 4d and the latter ~ 10% Y, 4d, 0.5% Y, 5s and 0.8% Ba, 6s character. M.O.s 54 - 48 and 46 - 41 are doubly occupied and 41 is the LOMO of the O band. This orbital is 5.539 eV higher than 40, the HOMO of the Cu, 3d band. M.O.s 40 - 1 contain 6 single electrons and 34 pairs.

The results for the C(II) cluster are similar to those of C(I), but naturally lack the features of the Y contributions. Also, the HOMO does not have as much Cu character as does C(I), and the HOMO - LUMO separation is 3.5 times greater. Of the 197 total electrons, the O,2p band contains 27 singles and 48 pairs while the Cu,3d band contains 6 singles and 34 pairs.

The criterion for determining whether an M.O. is singularly or doubly occupied, is based on the following procedure. The differences in energies (with $\bar{E}_{sp}$ substracted out), ΔE_o, between singularly occupied adjacent M.O.s are compared to the differences of their respective $\bar{E}_{sp}$, $\Delta \bar{E}_{sp}$; if $\Delta E_o > \Delta \bar{E}_{sp}$ the lower orbital is assigned two spin-paired electrons, but if $\Delta E_o < \Delta \bar{E}_{sp}$ then only one electron is assigned to the lower orbital. This procedure is continued systematically until enough M.O.s to accomodate all available electrons have been assigned either single electrons or pairs.

It then remains to be determined whether the singularly occupied orbitals form a set of open shell singlets (anti-ferromagnetic coupling) or not (ferromagnetic coupling). This is accomplished by comparing energy differences between these successive one-electron levels, ΔE_1, to the magnitude of the effective two-electron coupling constant, J_{ab}. If $\Delta E_1 > J_{ab}$, the adjacent spins are paired; if not, they remain unpaired. Recent magnetic susceptibility data[12] suggests that $J_{ab} \simeq 10^3$ cm^{-1}. While it is true that multidimensional magnetic coupling is possible in any multi electron spin system, it is not unreasonable to assume, as a first approximatation, that these molecular cluster systems can be reduced to systematic, pair-wise coupling.

Thus, the 12 single electrons in the Cu bands of C(I) and C(II) can enter into pair-wise coupling. Similarly, the 28 electrons in the O band of C(I) can be involved in pair-wise coupling; however, the C(II) cluster provides 28 of the 29 electrons in the O band to partake of pair-wise coupling. The net result for the C(I) - C(II) united cluster is that six coupled pairs are involved in the Cu bands and 28 coupled pairs in the O bands. Furthermore, it can be shown that the calculated Cu, J_{dd} is one third the magnitude of O, J_{pp}.[13] Since the observed J_{ab} reflects the averaged of all the couplings, the pair-wise couplings can be assigned; 250 cm^{-1}/6, Cu pairs = 42 cm^{-1}/Cu pair and 750 cm^{-1}/28, O pairs = 27 cm^{-1}/O pair. When these values are assigned to the electrons in the appropriate M.O.s, it is found that $\Delta E_1 >$ J_{ab}/ pair for all the singularly occupied levels. This results in 34 antiferromagnetically coupled, pairs plus uncoupled spin over both C(I) and C(II) clusters. The pair in the HOMO of C(II) will be readily decoupled under the perturbation of the single spin in the HOMO of C(I), since $J_{ab} < \Delta E$. Thus these three spins are allowed to couple antiferromagnetic, so as to complete the coupling mechanism between C(I) and C(II) clusters. Perhaps these are the electrons to be initially decoupled at T > Tc, where the superconductor makes a transition from the diamagnetic to the paramagnetic state.

Table II. Energies, electron distributions and A.O. Character in C(I).

M.O.	E (eV)	Electrons	Per cent A.O. Character*
117	-20.856	0	(C) Cu, $3d_z^2 = \underline{6.2}$, $3d_{x2-y2}$
(LUMO)			$= \underline{1.8}$, $4P_z = \underline{0.5}$; (L) Cu, $3d_z^2 = \underline{0.4}$, $4p_z = \underline{1.1}$;
			(C) O 2p = $\underline{49.8}$; (L)O,2p = $\underline{39.0}$.
116	-20.886	1 single	(C) Cu, (same as LUMO); (L)
(HOMO)			Cu, $4p_z = \underline{1.4}$; (C) O (Ax.), 2p = $\underline{49.3}$; (C) O (Eq.),
			2p = $\underline{35.3}$; (L) O(T), 2p = $\underline{3.3}$.
115	-21.866	35 pairs	Cu, 3d, 4s, 4p $\underline{15}$; O, 2p ≥ $\underline{85}$.
↓	↓	+	
56	-25.705	25singles	
55	-25.830	1 single +	Cu, 3d = $\underline{1.2}$ 4s = $\underline{1.3}$, 4p = $\underline{1.8}$; (C)(L) O(br), 2p = $\underline{27}$;
↓	↓	7 pairs	O, 2p = $\underline{57.8}$; Y, $4d_{x2-y2} = \underline{10.9}$.
47	-26.689	1 single	Cu, 3d = $\underline{3.0}$; 4p = $\underline{4.7}$; O, 2p = $\underline{81.4}$; Y, $4d_{z2} = \underline{9.6}$, 5s
			= 0.5; Ba, 6s = $\underline{0.8}$.
46	-26.857	6 pairs	Cu, 3d=$\underline{1.5}$, 4s=$\underline{10.6}$, 4p=$\underline{3.5}$; $\underline{83.8;}$
↓	↓	↓	Y, 5s = $\underline{0.6}$. (#43-Y, $4d_{xz} = \underline{11.8}$)
41	-28.288		(L) Cu, $3d_{z2} = \underline{3.0}$; 4s = $\underline{17.7}$; (L)O(br), 2p =
			$\underline{59.7}$; (C)O(br); 2p ≐ $\underline{12.7}$; Y, $4d_{xy} = \underline{6.9}$.
40	-33.827	6 singles	(C) Cu, 3d ≥ $\underline{95}$; O, 2p ≤ $\underline{5}$.
↓	↓	↓	(#39-35; (L) Cu, 3d)
35	-34.318	+	
34	-34.544	34 pairs	(same as #40 - 35)
↓		↓	
1	-35.716		

*(C)=chains; (L)=layers; (T) = terminal; (br)=bridges; (Ax)=axial; Eq.=Equitorial.

Table III. Energies, electron distributions and A.O. Character in C(II).

M.O.	E (eV)	Electrons	Per cent A.O. Character*
116 (LUMO)	-17.372	0	(C)Cu,3d$_{z}^{2}$ = 4.4, 4p$_{z}$ = 1.0; O, 2p = 94.6
115 (HOMO)	-17.478	1 pair	(C,L)Cu, 3dσ = 3.1, 4s = 1.2; O, 2p = 95.7
114	-18.191	29singles	
↓		+	Cu, 4s = 19.2 to 6.4; O, 2p = 80.8 to 99.6
42	-22.928	46 pairs	
41	-22.962	1 pair	(C,L)CU, 4s = 20.8; O, 2p = 79.2.
40	-31.708	1single	(L)Cu,3dσ = 99.4; O, 2p = 0.6
39	-31.724	5singles	(C,L)Cu, 3d≥ 97; (C,L)O, 2p ≤ 3.
↓		+	
1	-32.797	34 pairs	

*(C) = chains; (L) = layers;

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