Theory of electron distributions and ^{63}Cu and ^{17}O nuclear quadrupole interactions in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$

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Abstract. *Ab initio* unrestricted Hartree-Fock Cluster investigations have been carried out on the electronic structures of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ systems. The results of these investigations provide satisfactory explanations of available ^{63}Cu and ^{17}O nuclear quadrupole interaction data. The electron distributions obtained rule out the presence of Cu^{3+} ions and are supportive of the presence of Cu^{2+} , Cu^{1+} , O^{1-} ions in the O_7 system and Cu^{2+} , Cu^{1+} and O^{2-} in the O_6 system with actual charges departing significantly from the formal charges, especially in the O_7 system, indicating the importance of covalency effects. Suggestions will be made regarding possible sources that can bridge the remaining gap between theoretical and experimental results for the nuclear quadrupole interaction parameters.

Keywords. Electron distribution; nuclear quadrupole interaction; Hartree-Fock clusters.

1. Introduction

A substantial amount of data is now available (see references in Sahoo *et al* 1990; Lütgemier 1988; Mendels and Alloul 1988; Takigawa *et al* 1989; Troger *et al* 1990; Hodges and Sanchez 1990) on the hyperfine properties, especially nuclear quadrupole interactions (NQI), of the copper oxide high T_c systems from nuclear magnetic and nuclear quadrupole resonance, Mössbauer effect and perturbed angular correlation measurements. The understanding of these data from an *ab initio* point of view can provide a valuable assessment of the accuracy of calculated electron distributions which can be helpful in the understanding of the origin of the superconductivity in these systems. The first comprehensive attempts (Adrian 1988) at theoretical understanding of the NQI data have utilized a point ion model for evaluation of the electric field gradient (EFG) tensors at the nuclear sites. From these analyses, information can be derived about the extent of covalency from comparison of the theoretical and experimental values of the EFG and an attempt has been made in the literature (Garcia and Bennemann 1989) to include covalency contributions to the EFG tensor in a semi-empirical manner. The next step in the understanding of the origin of the NQI is to study the electronic structures of the high- T_c systems by *ab initio* procedures and use the calculated electronic structures to explain the observed experimental data. In this article, we shall present the results of our first principle investigations on the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ systems by the unrestricted Hartree-Fock (UHF) cluster procedure (Colburn and Kendrick 1982; Sauer 1989) and the ^{63}Cu and ^{17}O NQI parameters that we have obtained for the sites where experimental data are available (Pennington *et al* 1988; Shimizu *et al* 1988; Takigawa *et al* 1989; Mendels and Alloul 1988; Lütgemier 1988). Our investigations provide both a satisfactory explanation of the available NQI data as well as information on the charge states of the different

copper and oxygen ions. We are also able through our investigations to make a comparison between available X-ray photoemission spectroscopy (XPS) data (Chakraverty *et al* 1988) for the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system and our theoretical predictions.

Section 2 presents the procedure used in this work, including the clusters used in the investigation of the NQI parameters for ^{63}Cu and ^{17}O nuclei. Section 3 presents the results of our investigation and discussion including a comparison between the origins of the EFG tensor in Cu_2O (Stein *et al* 1990) and the present systems. The conclusions from this work are presented in the final section.

2. Procedure

For our electronic structure investigation, we have used the UHF Cluster procedure (Colburn and Kendrick 1982; Sauer 1989) which has been found to yield satisfactory agreement with experiment for the magnetic hyperfine properties of a number of systems involving impurity atoms in semiconductors (see for instance Sahoo *et al* 1983) and NQI tensors in a number of ionic crystal systems (Kelires 1987; Stein *et al* 1990) including ^{63}Cu in cuprous oxide and ^{17}O in corundum. Gaussian basis functions were employed in these investigations, the oxygen basis functions being obtained employing the Watson sphere model (Watson 1958; Kelires 1987) to include the influence of the environmental potential for this rather diffuse ion. For the copper ion we have used extensive variational basis sets (Poirier *et al* 1985) consisting of $10s$, $7p$ and $5d$ primitive Gaussian type functions (GTF) contracted to $4s(6,2,1,1)$, $4p(4,1,1,1)$ and $2d(4,1)$ basis functions.

The geometrical parameters for the clusters employed in our work were taken from crystal structure data (Beno *et al* 1987; Bordett *et al* 1987) in $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$, a unit cell for $\text{YBa}_2\text{Cu}_3\text{O}_7$ being shown in figure 1. The Cu_3O_{12} cluster used in our investigation of the EFG at the $^{63}\text{Cu}(1)$, $^{63}\text{Cu}(2)$ and $^{17}\text{O}(4)$ nuclei involves the atoms A to O in figure 1. These include one chain copper ($\text{Cu}(1)$) A and two planar copper ions ($\text{Cu}(2)$) F and K, two bridging $\text{O}(4)$ ions B and D and other nearest oxygen neighbours C, E, G-J and L-O of O(1), O(2) and O(3) categories of the oxygen ions in the cluster. With this choice, the $\text{Cu}(1)$, $\text{Cu}(2)$ and $\text{O}(4)$ ions each have all their nearest neighbours included in the cluster. For the $\text{YBa}_2\text{Cu}_3\text{O}_6$ system (Beno *et al* 1987; Bordett *et al* 1987), the oxygens O(1) in figure 1 are absent. Correspondingly, the cluster Cu_3O_{12} is replaced by Cu_3O_{10} with the oxygens O(1) removed. For studying the EFG at the ^{17}O nuclei at the O(2) site (which is expected to have an electronic environment very similar to O(3)) for the O_7 system, for which experimental data are also available (Takigawa *et al* 1989), we used a O_7Cu_2 cluster consisting of atoms F-J and P-S in figure 1. This cluster includes a central O(2) ion J with its two nearest planar Cu(2) ion neighbours and all their oxygen nearest neighbours on the plane. Clusters larger than the ones described including all the additional neighbours needed to retain proper symmetry would have been impracticable from a computational point of view. The influence of the ions, outside the finite cluster chosen, on the electronic structure was incorporated by augmenting the Hartree-Fock potential experienced by the electrons in the cluster with the potential from the rest of the lattice, treating the lattice ions as point charges (Colbourn and Kendrick 1982; Sauer 1989; Kelires 1987). The formal charges of +3 and +2 were used for the yttrium and barium ions respectively. For the

Figure 1. Unit cell of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Beno *et al* 1987; Bordett *et al* 1987). The ions A-O are included in the Cu_3O_{12} cluster and F-J and P-S are included in the O_7Cu_2 cluster used for the O_7 system. For the O_6 system, the O(1) ions represented by C and E are absent and are excluded in the Cu_3O_{10} cluster used for this system.

copper and oxygen ions outside the cluster, the charges obtained self-consistently for the ions within the cluster were used.

Using the electronic wavefunctions obtained from the cluster investigations, one can, as in the earlier work (Kelires 1987; Sahoo *et al* 1990; Stein *et al* 1990) in the literature using the cluster procedure, calculate the components V_{ij} of the EFG tensor in any chosen axis system including the contributions from the electrons and nuclear charges within the cluster and the point charges in the lattice outside the cluster. The calculated EFG tensor is then diagonalized to obtain the principal components and principal axes, the component with the largest magnitude being referred to as $V_{Z'Z'}$, Z' being the Z -direction in the principal axis system, the X' and Y' principal axes being chosen according to the convention $|V_{Z'Z'}| > |V_{Y'Y'}| > |V_{X'X'}|$. The asymmetry parameter η is given by $(V_{X'X'} - V_{Y'Y'})/V_{Z'Z'}$ and is representative of the departure from axial symmetry.

It should be remarked that since the core electrons are included in the electronic structure calculation and the contribution to the non-central potential produced inside the cluster by the point charges on the lattice outside the cluster have also been included (Kelires 1987), Sternheimer antishielding effects (Sternheimer 1986) associated with the contributions from the valence electrons, nuclear charges within the cluster and external charges are all implicitly incorporated through the electronic contribution. There is thus no need for the use of any Sternheimer antishielding parameters (Sternheimer 1986; Das and Schmidt 1986) in the theory.

3. Results and discussion

The electronic wavefunctions obtained for the Cu_3O_{12} and Cu_3O_{10} clusters simulating the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ systems respectively can be used together with the Mulliken approximation (Daudel *et al* 1983) to obtain the effective charges on the copper and oxygen ions in these systems. The charges obtained for the $\text{YBa}_2\text{Cu}_3\text{O}_7$ system are:

$$\begin{aligned} {}^5\text{Cu}(1) &= 1.49, {}^5\text{Cu}(2) = 1.86, {}^5\text{O}(1) = -1.87, \\ {}^5\text{O}(2) &= -1.94, {}^5\text{O}(3) = -1.95, {}^5\text{O}(4) = -1.28, \end{aligned} \quad (1)$$

and for the $\text{YBa}_2\text{Cu}_3\text{O}_6$ system:

$$\begin{aligned} {}^5\text{Cu}(1) &= 0.94, {}^5\text{Cu}(2) = 1.93 \\ {}^5\text{O}(2) &= -1.98, {}^5\text{O}(3) = -1.98, {}^5\text{O}(4) = -1.99 \end{aligned} \quad (2)$$

The charges in (1) effectively support the assignments of formal charges of +2 and +1 for Cu(2) and Cu(1); -2 for O(1), O(2) and O(3) and -1 for O(4). The charges in (2) for the $\text{YBa}_2\text{Cu}_3\text{O}_6$ system support the assignment of +2 for Cu(2) and +1 for Cu(1) and -2 for O(2), O(3) and O(4). The sizeable departures of the charges on Cu(1) and O(4) from the formal charges +1 and -1 in equation (1) for $\text{YBa}_2\text{Cu}_3\text{O}_7$ suggest significant covalent bonding between the two ions. The relative closeness of the charges on Cu(1) and O(4) to 1 and -2 suggest weaker covalent bonding between these two ions in the O_6 system as compared to O_7 . However, the analysis of the EFG at the ^{63}Cu nucleus in the related system, Cu_2O has indicated (Stein *et al* 1990) that even though the formal charges on Cu and O ions in the latter system are close to +1 and -2, there is still significant covalent bonding between them. The same remark could be made about the O_6 system, although the covalent bonding is expected to be weaker than in the O_7 system. An important feature of our results is the lack of evidence for Cu^{3+} ion in keeping with current ideas (Hass 1989). The magnitudes of the Cu(1) 2p-like and O(4) 1s-like molecular orbital energies are 967 eV and 551 eV for the O_7 system, close to the observed ionization energies (Chakraverty *et al* 1988) of 933 eV and 533 eV respectively from XPS measurements, lending qualitative support to our calculated one-electron energies and charge distributions. The highest occupied energy levels were found to have oxygen 2p-like character supporting the expectation in the literature (Hass 1989) that holes in these systems are likely to be located in oxygen-like orbitals. Also the covalent bonding between the Cu(1) ion and its two nearest neighbour O(4) ions indicates that the O(4)-Cu(1)-O(4) system can act as a single unit for superexchange interaction between the two Cu(2) ions directly above and below this unit in figure 1 for the antiferromagnetism (Tranquada *et al* 1988; Rossat-Mignot *et al* 1988) observed in $\text{YBa}_2\text{Cu}_3\text{O}_6$.

We shall next discuss our results for the NQI parameters for the ^{63}Cu and ^{17}O nuclei for which experimental results are currently available. These are presented in tables 1 and 2 along with the experimental data.

The important features of the experimental data on ^{63}Cu for the O_7 system are the smaller e^2qQ for the chain $^{63}\text{Cu}(1)$ nuclei as compared to the planar ones $^{63}\text{Cu}(2)$ and the large departure from axial symmetry for the $^{63}\text{Cu}(1)$. For the O_6 system the order of e^2qQ is reversed, that for the chain $^{63}\text{Cu}(1)$ nuclei being larger than that for the planar. As regards the ^{17}O nuclei in the O_7 system, the e^2qQ for the $^{17}\text{O}(2)$ nuclei in figure 1,

Table 1. Nuclear quadrupole interaction parameters in $\text{YBa}_2\text{Cu}_3\text{O}_7$

Nucleus	Theory		Experiment	
	e^2qQ	η	$ e^2qQ $	η
$^{63}\text{Cu}(1)$	57.3 MHz	0.30	38.4 MHz ^a	1.00 ^a
$^{63}\text{Cu}(2)$	96.7 MHz	0.04	62.9 MHz ^a	0.02 ^a
$^{17}\text{O}(4)$	-10.4 MHz	0.20	7.3 MHz ^b	0.32 ^b
$^{17}\text{O}(2)$	-8.0 MHz	0.27	6.6 MHz ^b	0.22 ^b

^aPennington *et al* (1988); Shimizu *et al* (1988)^bTakigawa *et al* (1989)**Table 2.** Nuclear quadrupole interaction parameters in $\text{YBa}_2\text{Cu}_3\text{O}_6$

Nucleus	Theory		Experiment	
	e^2qQ	η	$ e^2qQ $	η
$^{63}\text{Cu}(1)$	132.4 MHz	0.00	60.4 MHz ^c	0.00 ^c
$^{63}\text{Cu}(2)$	98.2 MHz	0.00	46.4 MHz ^d	0.00 ^d

^cLütgemier (1988);^dMendels and Alloul (1988)

which are nearly identical with those for the other oxygen neighbours of the planar Cu(2), are somewhat smaller than those for the chain $^{17}\text{O}(4)$. The asymmetry parameters η of both these sets of nuclei are substantial, although much smaller than the value close to unity for the chain $^{63}\text{Cu}(1)$. No ^{17}O NQI parameters are available for the O_6 system. In using our calculated EFG parameters q to obtain the quadrupole coupling constants e^2qQ , we have employed the values (Schaefer *et al* 1969) $Q(^{17}\text{O}) = -0.0257$ barns and $Q(^{63}\text{Cu}) = -0.18$ barns (Stein *et al* 1990).

Considering first the results for the O_7 system, the trend in the calculated e^2qQ in going from $^{63}\text{Cu}(2)$ to $^{63}\text{Cu}(1)$ is seen from table 1 to be in agreement with experiment, the e^2qQ for $^{63}\text{Cu}(2)$ being substantially larger than that for $^{63}\text{Cu}(1)$ for both theory and experiment. The same is seen to be the case for the ^{17}O nuclei, the $^{17}\text{O}(4)$ coupling constant being larger in magnitude than that for $^{17}\text{O}(2)$. The calculated magnitudes of the quadrupole coupling constants are also in reasonable agreement with experimental values, the experimental values for the $^{63}\text{Cu}(1)$, $^{63}\text{Cu}(2)$ and $^{17}\text{O}(4)$ nuclei being about 30% lower than theory. The difference between experiment and theory for $^{17}\text{O}(2)$ is somewhat less, the experimental value being about 18% lower than theory. The quadrupole coupling constants have been obtained by the nuclear quadrupole resonance technique with which the signs are difficult to determine. So the signs of the experimental coupling constants are not available to compare with theory. The EFG at the $^{63}\text{Cu}(2)$ nuclei is found to be nearly axially symmetric with the asymmetry parameter η being only 0.04, in agreement with the experimental situation. The electronic environment around $^{63}\text{Cu}(1)$ is on the other hand rather asymmetric with η having the much larger value of 0.3 but still significantly smaller than the experimental

value near unity. The EFG tensors associated with the $^{17}\text{O}(4)$ and $^{17}\text{O}(2)$ nuclei can be seen from table 1 to depart significantly from axial symmetry, there being good agreement between the asymmetry parameters from theory and experiment in both cases.

For the O_6 system, table 2 indicates that the trend of significant decrease observed experimentally in the e^2qQ for ^{63}Cu nuclei in going from $\text{Cu}(1)$ to $\text{Cu}(2)$, the reverse of that in O_7 , is explained by our theoretical results. The NQI tensors are found in both cases to be axially symmetric, in agreement with experiment. The axial symmetry is a result of the absence of the $\text{O}(1)$ ion neighbours that $\text{Cu}(1)$ has in the O_7 system (figure 1). For $^{63}\text{Cu}(2)$, the environment is again axially symmetric because the ions $\text{O}(2)$ and $\text{O}(3)$ are located (Beno *et al* 1987; Bordett *et al* 1987) at equal distances from $\text{Cu}(2)$ in the O_6 system. The calculated magnitudes of e^2qQ however now differ somewhat more from experiment than in the case of O_7 system, the experimental values being about 50% of the theoretical results. The experimental trend of a strong increase in the e^2qQ for $^{63}\text{Cu}(1)$ in going from the O_7 to the O_6 system is also seen from tables 1 and 2 to be explained by the theoretical results. For $^{63}\text{Cu}(2)$ on the other hand, the theoretical values of e^2qQ are seen from tables 1 and 2 to be nearly equal in the O_7 and O_6 systems while experimentally there is a significant decrease in going from the former to the latter. A part of the reason for this difference between theoretical and experimental trends could be the somewhat larger difference between theory and experiment in the O_6 system as compared to the O_7 , as remarked earlier.

Thus, Hartree-Fock cluster calculations explain a number of the important features of the experimental data in the O_7 and O_6 systems including most of the trends within the individual systems as well as between the two. The remaining differences between theory and experiment are the overestimations in the magnitudes of e^2qQ compared to experiment, the smaller though sizeable calculated η for $^{63}\text{Cu}(1)$ in the O_7 system as compared to experiment and the nearly equal calculated values of e^2qQ for $^{63}\text{Cu}(2)$ in both the O_7 and O_6 systems, although the experimental data suggest a significant decrease.

There are a number of possible sources that could lead to a bridging of the remaining differences with experiment. One of these is perhaps the influence of many-body effects (Rodgers *et al* 1973; Guo *et al* 1988). The Hartree-Fock procedure used here is a purely one-electron approach and there is evidence from atomic calculations regarding the important influence of many-body correlation effects on the magnetic hyperfine constant. Thus, many-body effects are found (Dougherty *et al* 1990) to contribute about 25% of the observed magnetic hyperfine field at the ^{63}Cu nucleus in copper atom in the ground ^2S state. While many-body effects may not be as pronounced for nuclear quadrupole interaction, it is important to attempt to incorporate such effects in future calculations on the O_6 and O_7 systems, which is admittedly a difficult problem due to the large numbers of electrons and atoms involved in the cluster we have used. A second possibility is the role of spin-orbit effects, which can influence the anisotropy of the electron distribution around the ^{63}Cu nucleus and thus influence the EFG tensor. Such effects have been shown (Roy *et al* 1983) to be important for the NQI of ^{57}mFe in a number of hemoglobin derivatives and should also be examined in the future. A third possible source is perhaps the need for larger variational basis sets for obtaining the molecular orbitals in the Hartree-Fock cluster calculation. We have used the largest basis sets that can be conveniently used with the computing facilities we have employed, but we are exploring further techniques to enhance the sizes of the basis sets.

A fourth possible source is the influence of the multipole electrostatic moments on the lattice ions (Das and Dick 1962; Sharma and Das 1965; Quigley and Das 1968) outside the cluster on the potential experienced by the electrons within the cluster and on the direct contribution of these ions to the EFG at the nuclei under study. Lastly, and what we feel may be the most likely source, is the interaction between the electrons in the clusters we have used and those on the Y^{3+} and Ba^{2+} ions (figure 1) which have been handled in the present work as point charges. There seems to be some evidence for this from a consideration of the NQI (Stein *et al* 1990) for ^{63}Cu in Cu_2O . In the latter system, the two oxygen nearest neighbours are similarly located around copper in a linear array as in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ system. However, a Hartree-Fock calculation of the present type leads to much better agreement with experiment for the $e^2 qQ$, the theoretical value being (Stein *et al* 1990) 62.3 MHz as compared to the experimental magnitude of 52.04 MHz. This suggests that the different environments of the copper atom and its oxygen neighbours involving the Y^{3+} and Ba^{2+} ions may be exerting significant influences on the electron distributions around the $^{63}\text{Cu}(1)$ nucleus in the 1:2:3 copper oxide systems.

4. Conclusion

In summary it is hoped that in addition to allowing an understanding of the factors that contribute to the NQI in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$, the information regarding the nature of the electron distributions and effective charges obtained from the present Hartree-Fock cluster calculations will be useful in the interpretation of other electronic properties of these systems and in quantitative analyses of the mechanisms contributing to the high temperature superconductivity in this class of systems. It will be helpful to attempt to include in the future some of the sources that we have listed as being possible significant contributors to the NQI and which could possibly bridge the remaining differences between theory and experiment for the NQI, especially the influence of interactions between the electrons on the Y^{3+} and Ba^{2+} ions and the copper and oxygen ions in these systems.

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