Theory of the location and associated hyperfine properties of the positive muon in La_2CuO_4

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(Received 30 August 1993; revised manuscript received 18 November 1993)

The location of the positive muon, used as a tool for probing the magnetic properties of high-T_c systems, is investigated for La_2CuO_4. Our calculations, using the unrestricted Hartree-Fock cluster procedure, indicate that the muon is located in the a-c plane, at a distance of 1.08 Å from the apical oxygen, with the μ^+-O(a) direction making an angle of 25° with the O(a)-Cu direction. The magnitude and direction of the hyperfine field at the equilibrium position are determined. Our results, which are in reasonable agreement with μSR data in powdered samples and single crystals, show the importance of including the local contact and dipolar contributions to the hyperfine field associated with the unpaired spin distribution in the neighborhood of the muon. Possible additional factors that could lead to a bridging of the remaining quantitative differences with experimental hyperfine data will be discussed.

I. INTRODUCTION

The hyperfine properties of high-T_c copper-oxide systems have been studied by a number of different techniques including nuclear magnetic resonance,[1] Mössbauer effect,[2] perturbed angular correlation,[3] and muon spin rotation[4] (μSR). The hyperfine properties at the various nuclear sites in the LaCuO and the YBaCuO systems have been studied by first-principles Hartree-Fock cluster procedure[5] and by the linearized augmented plane-wave band-structure procedure.[6] The combined application of the theoretical and experimental methods has provided a great deal of information about the nature of the electronic structures of these systems. The study of the hyperfine properties of the muon by the μSR technique,[4] in addition to providing information about the electronic structure, also provides information about the magnetic ordering in these systems. An important aspect of the muon as a probe is its interstitial position in the system, since the muon is particularly sensitive to the local magnetic fields present and the fluctuations therein. The knowledge of the interstitial position of the muon and the associated hyperfine field can be useful for the analysis of the magnetic ordering and the magnetic moments at the various ionic sites. This fact has been used to demonstrate the existence of long-range antiferromagnetic (AFM) ordering[7,8] in both the one- and two-layer copper-oxide systems. Further, there appears to be some uncertainty regarding the coexistence of magnetism and superconductivity. For example, in $La_{2-x}Sr_xCuO_4$, two earlier measurements, one with a single crystal[7] and the other with a polycrystalline sample[9] have indicated a coexistence of superconductivity and magnetism, while another experiment on a polycrystalline sample[10] has shown no evidence for it. Recently, however, μSR measurements using a high-quality single crystal[11] has confirmed this coexistence, as have Mössbauer measurements[12] using ^{57}Fe and ^{119}Sn probes. In view of this important role of the muon, it is essential to have a definitive knowledge of the position of the muon in high-T_c systems. In the past, the net hyperfine field in the AFM state has been considered[13,14] to arise from the point dipoles at the copper-ion sites, and this has been used to determine the muon position. More recently,[15] relaxation data in the paramagnetic state of La_2CuO_4 have been combined with second moments of the field distributions at the muon due to the nuclear moments in the lattice, in order to locate the likely position of the muon. Theoretical investigations of the position of the muon in La_2CuO_4 have involved using a superposition of potentials around the ions, to make an approximation to the potential seen by the muon,[16] as well as using an embedded-atom–effective-medium approximation[17] and looking for a minimum in the energy.

In the present work, we attempt to determine a possible stable site for the muon, using the first-principles unrestricted Hartree-Fock (UHF) procedure.[5] This procedure has been successfully applied for the study of the locations and hyperfine properties of impurity atoms at the surface[18] and in the bulk[19] of semiconductors. This method has also been applied successfully to study the hyperfine properties of ionic crystals[20] and more recently, high-T_c superconductors.[5] Our investigation of the interstitial position of the muon in La_2CuO_4 involves a search for the minimum in the total energy of the clusters associated with the muon. We calculate the hyperfine field at the muon site thus obtained by combining the different contributions to the net hyperfine field from the contact field and local, in addition to the distant, dipolar fields used in the earlier analyses.[13,14] The local contribu-

tions are found to significantly influence the total hyperfine field.

II. PROCEDURE

Earlier investigations of the position of the muon in La_2CuO_4 have used various methods and approximations for determining the position of the positive muon. An earlier investigation used results of zero-field μSR experiments[14] on powder samples of La_2CuO_4 for the hyperfine field and assuming only dipolar field contributions to this field, calculated the muon position at (0.253,0.0,0.162) in units of tetragonal lattice parameters[21,22] with origin at the copper ion (Fig. 1). This position, which assumes a typical μ^+-O bond length of 1 Å, a typical O-H bond distance, is indicated as position H in Fig. 1. Another calculation,[16] this one a numerical calculation of the potential using charge distributions on the ions and finding the minimum in the interaction energy of the muon and the host ions, finds the muon position at (0.34,0.0,0.25). This position, in the vicinity of the apical oxygen, denoted by S in Fig. 1, gives a μ^+-O(a) distance of 1.57 Å. A third calculation[17] uses a method based on the embedded-atom–effective medium[22] procedure. This calculation obtains a site (0.5,0.0,0.096) denoted by M in Fig. 1, in the vicinity of the planar oxygen, with the μ^+-O(p) distance at 1.27 Å. Recent μSR experiments[15] and the analysis of the relaxation rates and their anisotropy in single-crystal paramagnetic $La_{2-x}Sr_xCuO_4$ (for $x=0.0$, 0.05, and 0.14) have led to three likely sites for the muon, the first time such site determination has been made without using the hyperfine field. The positions found for the muon are based on a comparison of the magnetic-field distributions calculated from μSR relaxation data for different angles of incidence. The three sites obtained are (0.2,0.0,0.15), (0.225,0.0,0.225), and (0.225,0.225,0.263) corresponding to μ^+-O(a) distances of 0.879, 1.008, and 1.592 Å, respectively. The first two of these positions are in the ac plane and are denoted by $T1$ and $T2$ in Fig. 1, while the third one, $T3$, is out of this plane.

The aim of our investigation is to determine both the position of the positive muon and the hyperfine field at this position by the first-principles UHF cluster procedure. A global search for the minimum in energy for the muon site in the La_2CuO_4 unit cell would be computationally prohibitive, so the regions in which the search for the minimum in energy was to be performed were narrowed down. The first step towards doing this was to work with a tetragonal unit cell rather than the orthorhombic phase in which the μSR experiments are performed. However, since the difference in the lattice parameters a and b in the orthorhombic phase is of the order of 1% of the lattice parameters, we feel justified in making this approximation. Next, we follow the suggestion from the previous investigations[14–17] that the muon is most probably located in the a-c plane, and limit our search to the a-c plane. Further, the muon seems to favor a site in the close vicinity of one of the two oxygens, apical or planar, and at a distance close to the typical bond distance[23] of the O-H covalent bond. With these considerations in mind, we search the area around the two inequivalent oxygen sites, and study the variation in the energies with respect to the varying position of the muon. For the apical oxygen, we first fix the μ^+-O(a) distance at 1 Å and vary the μ^+-O(a)-Cu angle (denoted by θ) to scan for the minimum in energy. For the planar oxygen, we again fix the μ^+-O(p) distance at 1 Å and vary the μ^+-O(p)-Cu angle (denoted by ϕ) and look for a minimum in the energy.

To study the variation in total energy, with θ, in the vicinity of the apical oxygen, we use the 17-atom cluster $CuLa_5O_{10}\mu$ shown in Fig. 2 with the atoms that make up

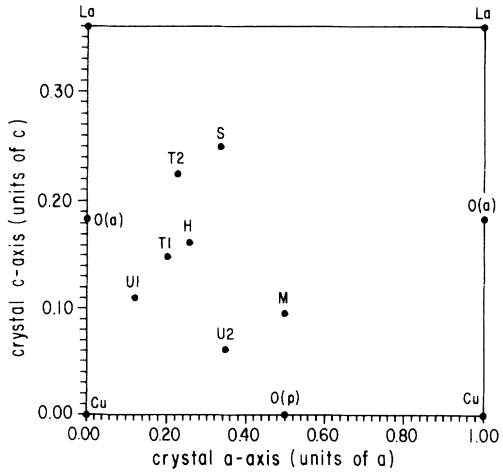

FIG. 1. Positions of μ^+ on the a-c side face of the unit cell determined in earlier work (Refs. 14–17) and in the present work.

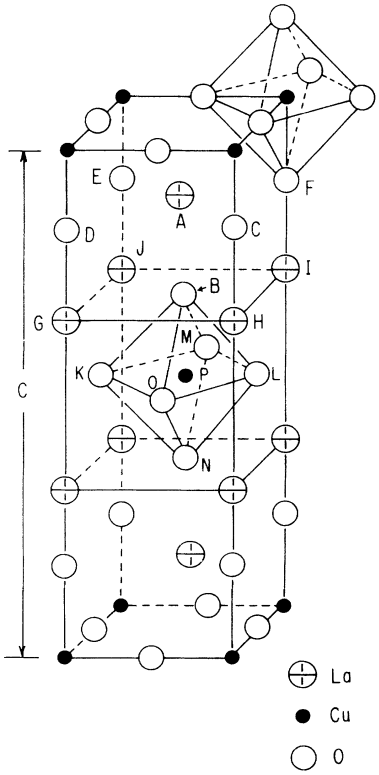

FIG. 2. The 18-atom cluster $CuLa_5O_{10}\mu$ used to study the total energy for the muon near the apical oxygen. The Cu, La, and O ions included in the cluster are labeled A through P.

the cluster labeled A-P. For the muon in the vicinity of the planar oxygen, we use an 18-atom cluster $Cu_2La_4O_{11}\mu$ with the host atoms labeled A-Q in Fig. 3. The muon and its neighboring host ions are then embedded in a sizable array of point charges, the host ions being Cu^{2+}, La^{3+}, and O^{2-}. In previous calculations[5] we have found that the effect of changing the formal charges to those obtained after self-consistency has been reached has very little effect on the hyperfine properties of interest here. With the effect of the rest of the surrounding point charges included, this calculation can be effectively regarded as involving the interaction of the positive muon with the infinite lattice.

The Cu, O, and μ basis sets[24,25] we have used are ones that have given satisfactory results for nuclear hyperfine interactions in other high-T_c systems. A 533/53/5 contracted Gaussian-type orbital[24] (CGTO) is used for the Cu, and an optimized[26] 44/4 CGTO one for the negatively charged oxygen ions. The basis set for the muon[24] has three primitives contracted to a 1s CGTO. Further, the influence of the core electrons in La is approximated by pseudopotentials,[27] and the valence electrons by a 3/3/3 CGTO.

Once the position of minimum energy has been obtained, we next attempt to find the net hyperfine field at this site. The hyperfine field at the muon site in AFM La_2CuO_4 arises from three sources: the Fermi contact field, the local dipolar field, and the distant dipolar field. The Fermi contact and the local dipolar fields are associated with the cluster itself and arise from the local unpaired spin density in the vicinity of the positive muon.

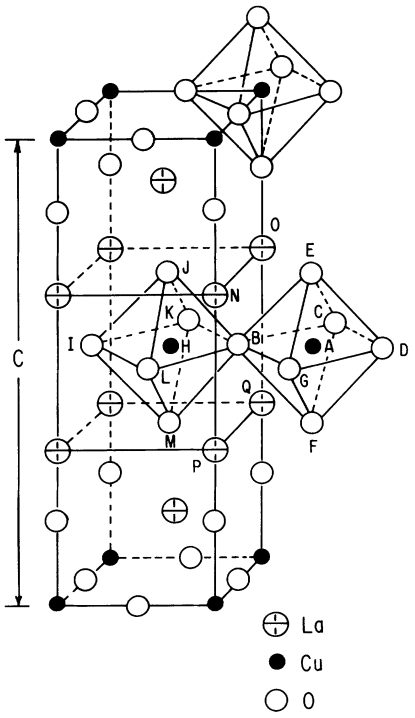

FIG. 3. The 18-atom cluster $Cu_2La_4O_{11}\mu$ used to study the total energy for the muon near the apical oxygen. The Cu, La, and O ions included in the cluster are labeled A through Q.

This unpaired spin density comes from the unpaired spin on the Cu ion and its exchange polarization effect on the paired spin orbitals included in the UHF calculation. The Fermi contact hyperfine constant A_c and the components of the dipolar hyperfine tensor $\mathcal{B}$ in MHz for a nucleus can be expressed as follows in terms of the UHF wave functions of the cluster:

$$A_c=\frac{2\times10^{-6}}{3S}\gamma_e\gamma_M\hbar^2a_0^{-3}\left\{\sum_\nu|\psi_\nu(r_N)|^2+\sum_\mu\{|\psi_{\mu\uparrow}(r_N)|^2-|\psi_{\mu\downarrow}(r_N)|^2\}\right\}, \quad (1)$$

$$B_{ij}^{\rm loc}=\frac{10^{-6}}{4\pi S}\gamma_e\gamma_M\hbar^2a_0^{-3}\left\{\sum_\nu\langle\psi_\nu|\hat{O}_{ij}|\psi_\nu\rangle+\sum\{\langle\psi_{\mu\uparrow}|\hat{O}_{ij}|\psi_{\mu\uparrow}\rangle-\langle\psi_{\mu\uparrow}|\hat{O}_{ij}|\psi_{\mu\downarrow}\rangle\}\right\}, \quad (2)$$

where

$$\hat{O}_{ij}=(3r_ir_j-r^2\delta_{ij})/r^5$$

with r_i and r_j referring to the ith and jth $(i,j=x,y,z)$ components of the position vector $\mathbf{r}$ of an electron with respect to the nucleus at which the hyperfine interaction is being studied as origin. Molecular orbitals denoted by the symbol ψ_ν represent states ν that have unpaired spins and for the paired spin states μ, $\psi_{\mu A}$ and $\psi_{\mu B}$ refer to the molecular orbitals with opposite spins. The net spin of the electrons in the system is S which is $\frac{1}{2}$ for the cluster chosen and γ_e and γ_M the gyromagnetic ratios of the electron and muon, respectively.

The distant dipolar contribution is given by

$$B_{ij}^{\rm dist}=\frac{10^{-6}}{4\pi S}\gamma_e\gamma_M\hbar^2a_0^{-3}\sum_N g_N(3R_{Ni}R_{Nj}-R_N^2\delta_{ij})/R_N^5, \quad (3)$$

where $g_N\gamma_e\hbar$ refers to the magnetic moment at the Nth Cu^{2+}-ion site outside the cluster with radius vector R_N referred to the nucleus under consideration. One should also include the contribution from the nuclear moments at the lattice sites, but it is relatively negligible in effect when electronic moments are present because of the very small sizes of the nuclear moments. The conversion term in going from the hyperfine constant A in MHz to the net hyperfine field B in G is given by[28] $A=[\mu B/IJ(2\pi\hbar)]\times10^{-6}$, the latter often being used in literature, especially in μSR (μ in the conversion factor referring to the muon magnetic moment $\frac{1}{2}\gamma_M\hbar$).

III. RESULTS AND DISCUSSION

Figure 4 shows the total energy obtained from our UHF calculations using the $CuLa_5O_{10}\mu$ cluster for μ^+ at

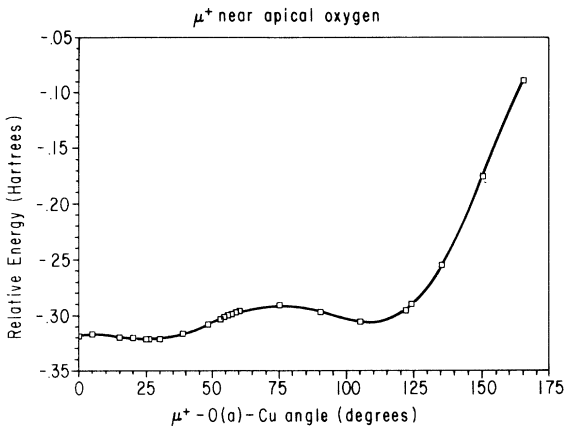

FIG. 4. Variation of energy of the $CuLa_5O_{10}\mu$ cluster with the μ^+-O(a)-Cu angle from our UHF investigation. The zero of the energy is chosen arbitrarily, only the differences in energies between different parts of the curve being important.

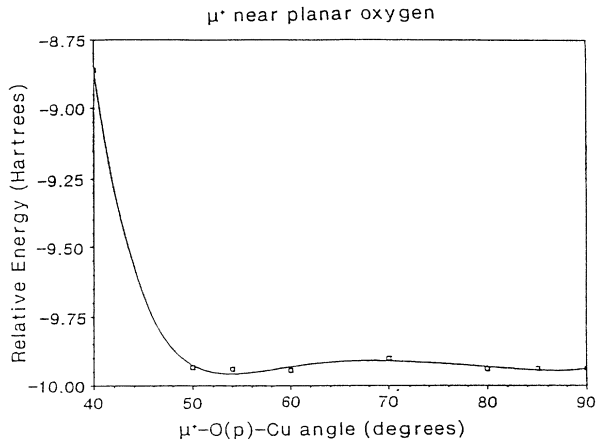

FIG. 5. Variation of energy of the $Cu_2La_4O_{11}\mu$ cluster with the μ^+-O(p)-Cu angle from our UHF investigation. The zero of the energy is chosen arbitrarily, only the differences in energies between different parts of the curve being important.

a distance of 1 Å from the apical oxygen, as a function of θ, the μ^+-O(a)-Cu angle. The zero of the energy scale is chosen arbitrarily and only the differences in energy between different parts of the curve are important. The angle $\theta=0$ corresponds to μ^+ being located on the c axis between the O(a) and the Cu ions. The energy curve in the figure shows three local minima at 0°, 25°, and 110° in the range $0<\theta<165°$. The total energy is, however, lowest for $\theta=25°$. A similar study for ϕ, the μ^+-O(p)-Cu angle (Fig. 5), shows a minimum in the total energy for $\phi=55°$. To compare the two minima which were obtained using different clusters, we took the same $Cu_2La_4O_{11}\mu^+$ cluster used for the study of the muon sites near the planar oxygen, and used it in an UHF calculation with the muon located at a μ^+-O(a)-Cu angle of 25° and a distance of 1 Å from the apical oxygen. This site was lower in energy by 0.72 eV than the site at $\phi=55°$ near the planar oxygen. Further investigations carried out for this site at a μ^+-O(a)-Cu angle of 25° included studying the variation of the total energy with the μ^+-O(a) distance and studying if any minima existed for the muon displaced to points outside the a-c plane. Our investigations showed a minimum corresponding to a μ^+-O separation of 1.08 Å and the energy increase in going out of the a-c plane showed that μ^+ is most likely to be located on the a-c face of the unit cell. This position is marked $U1$ in Fig. 1, while $U2$ represents the position $\phi=55°$ in the vicinity of the planar oxygen. We have also calculated[29] by the first-principles Hartree-Fock procedure the energies for the various sites obtained from earlier investigations. These energies, including that for $U2$, are listed relative to $U1$ in Table I. The energies for M and $T3$ were found to be higher than $U2$. It was found thus that our position $U1$ is the lowest one in energy and represents the most likely stable site for the positive muon.

We now examine the hyperfine field H_{hyp} at the muon site obtained by our energy minimization. The isotropic contact hyperfine constant and the dipolar hyperfine tensor are associated with the Fermi contact and electron-nuclear dipolar interactions between the nuclear and electron spins.[30] Once the isotropic and dipolar hyperfine parameters are obtained, they can be related to the hyperfine field at the muon site.[29] In addition, the antiferromagnetically ordered magnetic moments on the surrounding Cu ions contribute to the distant dipolar fields. Using the electronic wave functions obtained from our UHF calculations, we evaluate the contact hyperfine field and the local dipolar field given by Eqs. (1) and (2). Our cluster contains a Cu^{+2} ion and therefore the corresponding dipolar field is due to the local contribution as well as the contribution from the magnetic moment at the nearest Cu^{+2} neighbor of μ^+. The spin density at μ^+ was found from our calculation to be -2.02×10^{-5} atomic units. This can be converted to the isotropic hyperfine constant A in the spin Hamiltonian term $A\mathbf{I}\cdot\mathbf{S}$ using the conversion factor of 52.461×10^4 to go from MHz to G. Our calculations give us a contact field of -10.6 G, or $(-7.5,-7.5,0.0)$ G since the electron spin is oriented in the $\langle 110\rangle$ direction, as indicated by neutron-diffraction experiments.[31] The dipolar tensor in atomic units was calculated taking the electron spins along the crystal c axis and was found to be

$$\mathcal{B}=\begin{bmatrix} -2398.8 & -31.6 & 2313.0 \\ -31.6 & -2884.5 & -101.4 \\ 2313.0 & -101.4 & 5283.3 \end{bmatrix}\times10^{-5}. \quad (4)$$

TABLE I. Energy differences between the various sites in Fig. 1.

Site	Energy (eV)
$U1$	0.00
$U2$	0.72
H	0.83
S	2.95
$T1$	1.73
$T2$	0.72

The components of $\mathcal{B}$ in Eq. (3) can be expressed in G using[19] the conversion factor 6.262×10^4. The dipolar tensor $\mathcal{B}$ was transformed to correspond to the magnetic moment along the $\langle 110\rangle$ direction using the relations[32]

$$H_x=-[\lambda_x B_{xx}+\lambda_y B_{xy}+\lambda_z B_{xz}]\,,$$
$$H_y=-[\lambda_x B_{xy}+\lambda_y B_{yy}+\lambda_z B_{zy}]\,, \quad (5)$$
$$H_z=-[\lambda_x B_{xz}+\lambda_y B_{yz}+\lambda_z B_{zz}]\,,$$

where λ_x, λ_y, and λ_z refer to the direction cosines of the spins on the copper ions with respect to the crystal axes. The components of the local dipolar field at μ^+ were found from Eqs. (3) and (4) by assuming the spin at the Cu^{2+} ion in the cluster to be a point dipole of $1\mu_B$ and subtracting the contribution of $(-1048.2,-1291.2,979.2)$ due to the Cu^{2+} ion inside the cluster from the total dipolar field of the cluster. The x, y, and z components of the local dipolar field thus calculated at the site of the muon were determined to be 258.0, 371.2, and -305.8 G, respectively. The contribution from the antiferromagnetically ordered point dipoles of $1\mu_B$ from the rest of the lattice was evaluated by a point dipole summation carried out over $10\times10\times10$ unit cells. This contribution was found to be $(-62.6,-15.8,51.2)$ G. We apply a 50% reduction for all the contributions since neutron-diffraction experiments[31] attribute a magnetic moment of about $0.5\mu_B$ to Cu rather than $1.0\mu_B$. Adding up the contributions from the local contact field, the local dipolar field, the contribution due to the Cu^{2+} ion within the cluster and the distant dipoles outside the cluster, we get a net hyperfine field of magnitude 1004.9 G, the x, y, and z components being $(-559.2,-657.3,515.3)$ G. Our calculations thus give a result for the magnitude of the hyperfine field that is about twice as large as that observed from μSR experiments.[13,8] Preliminary results of recent μSR measurements[33] using single-crystal $La_{2-x}Sr_xCuO_4$ samples confirm the earlier measured strength[13,8] of the hyperfine field, and give, for the first time, its direction, namely $\theta=65°\pm5°$ and $\phi=28°\pm8°$, where θ and ϕ are the polar and azimuthal angles. This result is to be compared with the direction of the hyperfine field specified by $\theta=59°$ and $\phi=49.6°$ from our results for the components of the hyperfine field. Both results are given with the Cartesian x,y,z axes taken to coincide with the tetragonal a,b,c crystal axes. In attempting to bridge the quantitative differences between the calculated hyperfine field and experiment, especially its magnitude, one of the main sources that appears to be important is the influence of lattice relaxation effects associated with the presence of the muon. This is because an outward movement of the neighboring copper ions would reduce the distant dipolar contribution significantly. Additionally, such relaxation effects could, in principle, also influence the position of the muon obtained through energy minimization. While, an investigation of lattice relaxation effects is expected to be rather time consuming because of the size of the cluster involved, it is one of the important directions of improvement that should be explored in the future. It should also be mentioned that lattice relaxation effects would also influence the hyperfine fields at the other positions besides the equilibrium position and hence the conclusions regarding the muon site obtained from mapping of the hyperfine field. Additionally the magnetic field at the muon site from the nuclear moments in the lattice would be influenced by lattice distortion in the presence of the muon which would also affect the determination of muon position from zero-field μSR relaxation measurements.

Our first-principles calculation thus leads to an O(a)-μ^+ distance of 1.08 Å, close to the O-H distance in free molecules, in satisfactory agreement with that from zero-field single-crystal relaxation measurements[33] while other theoretical investigations[16,17] lead to larger distances. The results of our hyperfine field calculations are also in reasonable agreement with experimental results for the magnitude and direction of the hyperfine field and emphasize the importance of including the local contributions to the contact and dipolar components of the hyperfine field.

IV. CONCLUSION

In conclusion, our calculations have provided a good overall understanding of the various factors that contribute to the position of μ^+ and the hyperfine field at its site in La_2CuO_4. There are, however, some remaining quantitative differences between our calculations and the hyperfine field obtained from μSR experiments. Among the possible factors that could bridge these differences would be the use of larger basis sets in the molecular orbital calculation and the inclusion of lattice relaxation of the host ions due to the presence of the μ^+. These improvements are expected to be rather time consuming, but should be attempted in the future to add to our understanding of the nature of the environment of the muon in high-T_c materials and through this enhance to our understanding of the electronic and magnetic aspects of high-T_c systems.

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