Nuclear magnetic resonance chemical shifts and paramagnetic field modifications in La$_2$CuO$_4$

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The electronic structure of La$_2$CuO$_4$ has been investigated using first-principles cluster calculations and the chemical shieldings at the copper nucleus have been determined with several state-of-the-art quantum chemical methods. We have also calculated the copper shieldings for CuCl, which is often used as a reference substance for copper nuclear magnetic resonance shifts measurements, and found an appreciable paramagnetic contribution in agreement with precise measurements. The calculated chemical shift at the copper nucleus in La$_2$CuO$_4$ for an applied field parallel to the CuO$_2$ planes is generally smaller than, but still in reasonable agreement with, the values derived from experiment with the assumption that the spin susceptibility vanishes at zero temperature. For the field perpendicular to the planes, the quantum chemical result is substantially smaller than the experimental data but in accord with a perturbation theoretical estimate. Inconsistencies in previous representations and interpretations of the copper magnetic shift data are pointed out and corrected.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy has provided a large amount of data on static and dynamic properties of high-temperature superconducting cuprates. The microscopic electronic properties are reflected in the NMR spectra through the magnetic hyperfine interactions. Thus, valuable information on the dynamics of low-energetic spin excitations can be gained from the analysis of the temperature dependence of the nuclear spin-lattice relaxation rates at various nuclei. The static spin susceptibility can be probed by measurements of the magnetic shifts. With an applied magnetic field the NMR resonance frequency of a particular nuclear isotope species $k$ is shifted with respect to the frequency of the same nucleus in a specified reference substance by an amount that is proportional to the applied field. There are two distinct contributions to the tensor components ($i = x, y, z$) of these magnetic shifts,

$$kK^{ii}(T) = kK^{ii}_L + kK^{ii}_S(T).$$

(1)

Here $kK^{ii}_L$ is the temperature-independent chemical shift and $kK^{ii}_S(T)$ is the spin shift that is proportional to the static spin susceptibility. The latter quantity is of fundamental importance for the understanding of the normal and superconducting state.

NMR shift measurements thus provide unique information about the spin susceptibility if the contribution of the chemical shift can be determined separately. Pairing of the charge carriers in the superconducting state reduces the spin susceptibility and hence $kK^{ii}_L$. The temperature dependence of this reduction is expected to be different for different pairing symmetries but if it is assumed that the spin susceptibility vanishes completely at $T = 0$, the resulting shift $kK^{ii}(T = 0)$ can be identified with the chemical shift $kK^{ii}_L$.

The temperature dependences of the magnetic shifts have been measured for the copper sites in YBa$_2$Cu$_3$O$_7$ by Takigawa et al.$^2$ and, with an improved method, by Barrett et al.$^3$. For the Cu(2) sites in the CuO$_2$ planes, the component $63K^{xx}(T)$ measured with the applied field parallel to the planes is temperature independent in the normal state but declines at the superconducting transition temperature $T_c$ from a value of 0.58% down to 0.28% at the lowest measured temperatures.$^4$ In contrast, the magnetic shift component $63K^{zz}$ measured with the field perpendicular to the planes was found to be 1.28% independent of temperature. Within the experimental error, the same behavior of $63K^{zz}$ was then also observed for YBa$_2$Cu$_3$O$_{6.63}$ (Ref. 5) and for La$_{2-x}$Sr$_x$CuO$_4$ (Ref. 6) with various doping concentrations $x$. This temperature independence of $63K^{zz}$ has been explained by assuming that in YBa$_2$Cu$_3$O$_{7-\delta}$ and La$_{2-x}$Sr$_x$CuO$_4$ there is a coincidental cancellation between the on-site hyperfine field at the Cu nucleus, $A^{zz}$, and 4$B$, the transferred fields from the four nearest-neighbor copper ions. This cancellation gives rise to a vanishing spin shift, leaving as sole contribution to $63K^{zz}$ the temperature-independent chemical shift $63K^{zz}_L$.

In YBa$_2$Cu$_3$O$_{6.63}$ and La$_{2-x}$Sr$_x$CuO$_4$, the decline of $63K^{xx}(T)$ with decreasing temperature begins already at temperatures higher than $T_c$. The values found at the lowest temperatures, however, were again around 0.28%. Moreover, the magnetic shifts at the planar oxygen sites$^3$ vary with temperature, in general, in the same manner as $63K^{xx}(T)$. Furthermore, $63K^{zz} = 1.335\%$ has been measured$^7$ at $T = 505$ K in the paramagnetic phase of the insulator YBa$_2$Cu$_3$O$_6$.

From all these early observations$^8$ it was thus concluded that the chemical shifts $63K^{ii}_L$ for the coppers in the CuO$_2$ planes are virtually independent of the specific cuprate material and of the doping level with values of about $63K^{zz}_L = 1.25\%$ and $63K^{xx}_L = 0.28\%$ and an anisotropy ratio of $63K^{zz}/63K^{xx} = 4.5$.

Theoretical explanations of the copper chemical shifts advocated the perturbation theoretical expression$^9$ for an isolated Cu$^{2+}$ ion which predicts
\[ {^63K_L^{2s,2p}} = 4 \mu_B^2 (r^{-3}) s \sum_n \frac{|\langle n|L^i|0\rangle|}{\Delta_n^4}. \]  

The ground state \( |0\rangle \) was assumed to consist of a full 3d shell apart from a singly occupied 3d,2\( z^2 \) atomic orbital (AO) (raised in energy by the tetragonal crystal field splitting). \( \Delta_n = E_n - E_0 \) is the excitation energy from an occupied 3d,2\( z^2 \) to the singly occupied 3d,2\( z^2 \) AO and \( (r^{-3}) s \) is the average value of \( r^{-3} \) of the 3d AO’s. [Note that in Eq. (2) we have introduced the notation \( {^63K_L^{2s,2p}} \) for reasons to be given later.] Since the square of the matrix element of the angular momentum operator \( L^i \) in Eq. (2) is four times that of \( L^2 \), this formula was used \(^{10,3,11} \) to explain the large anisotropy of the copper chemical shift of \(^{63}Cu\). A much simpler theoretical approach is needed, we present here a theoretical approach to the copper chemical shifts.

Previously, we have calculated the local electronic structure in La\(_2\)CuO\(_4\) and YBa\(_2\)Cu\(_3\)O\(_7\) using extended \textit{ab initio} cluster calculations.\(^{12,13} \) In the present work we report on detailed calculations of the chemical shifts in La\(_2\)CuO\(_4\) which is proposed to be a prototype of the cuprates. To this end, the chemical shielding tensors have been determined with several state-of-the-art quantum chemical methods. Special care was devoted to check the influence of the cluster size, the quality of the basis sets used for the description of the AO’s, and the gauge invariance of the method employed to describe the shielding contributions.

Similar calculations of the chemical shieldings have been performed for CuCl, the most commonly used reference substance for solid-state copper NMR. They revealed that this substance is far from being purely diamagnetic. As a consequence, the use of Eq. (2), as outlined above, to explain the anisotropy of the copper chemical shift of \( ^{63}K_L^{2s,2p} \) = 4.5 needs careful revision. We will also demonstrate that the model of an isolated Cu\(^{2+}\) ion for the calculation of the copper chemical shifts in La\(_2\)CuO\(_4\) is too simplistic.

In Sec. II the computational details and the chosen clusters are discussed. To avoid any ambiguities we outline in Sec. III A first some general aspects of chemical shieldings and their calculation. In Sec. III B we discuss the relation between the chemical shieldings and the various shifts measured in solid-state physics NMR. The results of the calculations of the copper shieldings in CuCl and La\(_2\)CuO\(_4\) are presented in Secs. III C and III D, respectively. Section IV is devoted to the discussion of the results and to a comparison with experiments and previous theoretical estimates. The summary and the conclusions are in Sec. V.

**II. CLUSTER CALCULATIONS AND COMPUTATIONAL DETAILS**

In cluster calculations the solid is approximated using an embedding method, where all electrons in the core of the cluster are treated as accurately as possible using first-principles all-electron methods. The core is surrounded by basis-free pseudopotentials and, further distant, point charges at the atomic sites representing the lattice. Such cluster models have been applied previously and have been found to provide good results for the electric-field gradients and magnetic hyperfine coupling parameters both in La\(_2\)CuO\(_4\) and YBa\(_2\)Cu\(_3\)O\(_7\) (Refs. 12 and 13). The calculations were done in the framework of spin-polarized density-functional theory using Becke’s exchange functional\(^{14,15} \) and the correlation functional of Lee, Yang, and Parr.\(^6 \) For the calculations of the chemical shieldings in La\(_2\)CuO\(_4\) we constructed a series of three clusters of different size to estimate the influence of finite-size effects. The smallest cluster (Cu\(_6\))\(^{10-}\) consists of a copper atom surrounded by four planar and two apical oxygen atoms. As a further development of our work\(^{12,13} \) the core of the cluster was surrounded by a much larger shell of atoms represented by pseudopotentials providing an improved embedding.

The second cluster, (Cu\(_5\)O\(_{11}\))\(^{18-}\), comprises two copper atoms and their nearest planar and apical oxygen neighbors. Calculations for both the spin singlet (\( M = 1 \)) and triplet (\( M = 3 \)) state were performed.

The largest cluster (see Fig. 1) is (Cu\(_5\)O\(_{26}\))\(^{12-}\), surrounded by 157 pseudopotentials. Symmetric spin configurations are obtained with \( M = 6 \) ("ferromagnetic" arrangement with all spins parallel) and \( M = 4 \) ("antiferromagnetic" with the central copper spin density opposite to that at the four other copper atoms). The latter configuration is about 150 meV lower in energy.

For the calculation of the chemical shieldings in the reference substance CuCl a (CuCl\(_4\))\(^{3-}\) cluster consisting of a copper atom and its four nearest chlorine neighbors was constructed (see Sec. III C). It was surrounded by 83 pseudopotentials and point charges at the respective lattice sites. Calculations for a larger cluster representative of CuCl are currently impossible since such an extension would comprise at least twelve additional copper atoms. The chemical shieldings obtained with the CuCl\(_4\) cluster, however, compare very well with experimental results.

Various basis sets have been used. Basis set A is the standard 6-311G basis set in which the radial part of the Cu 3d
AO is described by three different Gaussian functions.\textsuperscript{17}

It is customary in quantum chemistry to check the change of the chemical shielding (and any other quantity) as a function of the basis set size. We followed this procedure by adding both polarization and diffuse functions.\textsuperscript{17} When adding polarization functions no significant change in the chemical shieldings was observed. Therefore we report here only the results obtained when adding diffuse functions. For the basis sets 6-311+\textit{G} (\textit{B}), 6-311+\textit{G}(2d,p) (\textit{C}), and 6-311+\textit{G}(3d,3p) (\textit{D}), progressively more diffuse basis functions with up to \textit{f}-type symmetry have been added.

Some characteristic features of the different clusters and basis sets are collected in Table I.

### Table I. A collection of various characteristics for our clusters.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>(N_a)</th>
<th>(N_e)</th>
<th>(N_{pp})</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO(_6)</td>
<td>7</td>
<td>87</td>
<td>96</td>
<td>117</td>
<td>153</td>
<td>227</td>
<td>264</td>
</tr>
<tr>
<td>Cu(_2)O(_1)</td>
<td>13</td>
<td>164</td>
<td>73</td>
<td>221</td>
<td>289</td>
<td>427</td>
<td>496</td>
</tr>
<tr>
<td>Cu(_5)O(_26)</td>
<td>31</td>
<td>395</td>
<td>157</td>
<td>533</td>
<td>697</td>
<td>1027</td>
<td>1192</td>
</tr>
<tr>
<td>CuCl(_4)</td>
<td>5</td>
<td>100</td>
<td>83</td>
<td>123</td>
<td>151</td>
<td>205</td>
<td>232</td>
</tr>
</tbody>
</table>

The first row gives the cluster name, \(N_e\), number of atoms with a full basis set; \(N_{pp}\), number of electrons; \(N_{pp}\), number of pseudopotentials. The columns with headings \(A\), \(B\), \(C\), and \(D\) indicate the number of basis functions for the corresponding basis sets.

### III. CHEMICAL SHIELDINGS, CHEMICAL SHIFTS, AND PARAMAGNETIC MODIFICATIONS

#### A. Chemical shieldings and methods of calculation

The chemical shielding tensors are defined by

\[
\sigma^k = -\frac{\Delta H}{H}, \tag{3}
\]

where \(H\) is the applied external magnetic field that induces currents in the electronic system and \(\Delta H\) is the additional field at the nucleus \(k\) that is in turn generated by these currents.\textsuperscript{18}

The chemical shieldings thus refer to the bare nucleus. They can be separated into diamagnetic and paramagnetic contributions,

\[
k\sigma = k\sigma_d + k\sigma_p. \tag{4}
\]

This separation, however, is depending on the gauge. Whenever in the following we mention diamagnetic and paramagnetic contributions, we explicitly refer to the gauge

\[
\nabla k^2 = \frac{1}{2}H \times (\vec{r} - \vec{R}), \tag{5}
\]

where \(\vec{R}\) denotes the position of the nucleus under consideration.

Chemical shielding constants are an excellent measure of the local electronic structure around a nucleus. Therefore, NMR provides a “fingerprint” for the characterization of a molecule. In chemistry, structure identification from experimental NMR patterns together with quantum chemical NMR calculations became a standard method\textsuperscript{19} in the late 1990’s. A large number of methods have been developed for the calculation of chemical shieldings. We have used four standard methods, all of which are implemented in the GAUSSIAN98 program package.\textsuperscript{20} These methods are: (1) single gauge origin (SGO), (2) continuous set of gauge transformations (CSGT), (3) individual gauges for atoms in molecules (IGAIM), and (4) gauge-including atomic orbitals (GIAO).

They mainly differ (see Refs. 21–23) in the choice of the gauge origin.

The implementation of the four methods into GAUSSIAN98 is qualitatively different. Methods (1)–(3) are implemented by direct use of Biot-Savart’s law, thus calculating the induced magnetic field in terms of the induced current density. Diamagnetic and paramagnetic contributions are not distinguished directly and are not accessible for technical reasons. In the case of GIAO, they have to be calculated separately within the molecular-orbital picture. Each method shows advantages and disadvantages depending on the particular molecule to be calculated or the quality of the basis set. Ultimately, of course, all methods should provide the same results if the quality of the basis set is sufficiently high.

The common practice, therefore, is to employ several different methods along with different basis sets of increasing quality and investigate how the results for the various quantities converge. Here, we follow this strategy and note that the seemingly technical difficulties are connected with the basic physical fact that an applied magnetic field attempts to induce ring currents around the individual nuclei. The AO basis sets must be flexible enough to account for a proper description of these currents. Besides these series of tests on the methods and basis set sizes, the approach of the cluster method requires an additional study of the calculated quantities with respect to the cluster size.

The most sophisticated of the NMR methods in quantum chemistry is the GIAO ansatz, where each atomic orbital has its own local gauge origin placed on its center. However, the implementation is suffering from several inaccuracies and implementation errors, for example, the missing orthogonalization of the perturbed wave function with the surrounding pseudopotentials.\textsuperscript{24} This leads to spurious results when our two largest cluster models are calculated using diffuse basis functions and therefore we do not include GIAO results in the forthcoming discussion (Secs. III C and III D). In addition, all results obtained with the IGAIM method are so close to those calculated with CSGT that only the latter will be given.

With all four methods and the four basis sets \(A\), \(B\), \(C\), and \(D\) the diamagnetic shielding for Cu and Cu\(^{+}\) was calculated to be \((2400\pm 4)\) ppm. For Cu\(^2\)\(^+\) ions in a tetragonal crystal field simulated by charged pseudopotentials, a CuCl molecule, a CuCl\(_2\) cluster, and in the cluster CuO\(_6\) we found the same value for \(\sigma_d\) with anisotropic deviations of about 20 ppm. Since in the context of copper NMR in cuprates differences in the order of 20 ppm are irrelevant, we will use the value \(\sigma_d = 2400\) ppm for the interpretation of our results later. In this respect, it is noteworthy that in 1941, Lamb\textsuperscript{25} calculated diamagnetic shieldings for various atoms with a value of \(\sigma_d = 2388\) ppm for copper.
For oxygen in H$_2$O, an isotropic value of $^{17}\sigma_d = 390$ ppm resulted. At variance, for the oxygen in the Cu$_2$O$_{11}$ cluster we calculated the isotropic part to be $^{17}\sigma_d = 450$ ppm. In both cases, the anisotropies were in the range of about 10 ppm.

### B. Resonance shifts in solid-state physics NMR

In the literature on solid-state physics NMR there is no general consensus about the terminology of the various contributions to the resonance shifts. Since this may easily lead to incorrect interpretations, we summarize the essential aspects and define our notation in the present subsection.

In 1949, Knight$^{25}$ observed that with the same value of the applied field, the NMR frequency of nuclei in metals occurred at higher resonance frequencies than in insulating salts of the corresponding metal. This effect which is due to the interaction of the conduction electrons with the nucleus (Pauli paramagnetism) was then referred to as “Knight shift.” The same notation, however, is sometimes used for other shifts as well. We prefer, therefore, to restrict the notion of “shift” to differences of properties measured at the nucleus $k$ in the target (t) substance and the corresponding one in the auxiliary reference (r) substance. We use the symbolic notation $(t-r)$ for these shifts.

The magnetic shift $K$ is thus defined by

$$kK(t-r) = \frac{k\nu(t) - k\nu(r)}{k\nu(r)}.$$  

Here, $k\nu(t)$ is the NMR frequency of the nuclear species $k$ in the target substance and $k\nu(r)$ the frequency of the nucleus in the reference substance measured in the same magnetic field.

The contributions to the diagonal components of the tensor in Eq. (1) then are

$$kK_{ii}(t-r) = k\sigma_{ii}^d(t) + kK_{ii}^s(t-r),$$

where $kK_{ii}^s(t-r)$ are the chemical shifts and $k\sigma_{ii}^d(t)$ the spin contributions to the change in the field at the nucleus of the target substance, provided that there are no contributions of conduction electrons in the reference substance. In many cases the spin contributions dominate. For copper in cuprates, however, the chemical shifts are of similar magnitude and the following systematic identification of terms is necessary.

The chemical shifts are related to the chemical shieldings defined above (Sec. III A) by

$$kK_{ii}(t-r) = k\sigma_{ii}^d(r) - k\sigma_{ii}^d(t) 1 + k\sigma_{ii}^d(r) \approx k\sigma_{ii}^d(r) - k\sigma_{ii}^d(t)$$

or, with the separation of $\sigma$ into diamagnetic and paramagnetic parts, by

$$kK_{ii}^s(t-r) = k\sigma_{ii}^d(r) + k\sigma_{ii}^p(r) - k\sigma_{ii}^d(t) - k\sigma_{ii}^p(t).$$

Under the condition that one can ignore the differences between $k\sigma_{ii}^d(r)$ and $k\sigma_{ii}^d(t)$, the chemical shifts then comprise only paramagnetic shieldings. In view of the calculated diamagnetic shieldings for Cu in various ions and molecules as discussed in Sec. III A, this condition is certainly fulfilled for copper and, ignoring small deviations in the order of 20 ppm, we can therefore write

$$63K_{L}^{ii}(t-r) = 63\sigma_{p}^{ii}(r) - 63\sigma_{p}^{ii}(t).$$  

For oxygen, however, the diamagnetic parts in the target substance and in the reference substance (H$_2$O) differ too much and therefore Eq. (9) should be considered.

The quantities of interest in Eq. (10) are, of course, not the chemical shifts $63K_{L}^{ii}(t-r)$ but rather the contributions of the target, i.e., $-63\sigma_{p}^{ii}(t)$. We denote them by

$$63K_{L}^{ii}(t) = 63K_{L}^{ii}(t-r) - 63\sigma_{p}^{ii}(r)$$

and call them the paramagnetic (field) modifications at the copper nucleus in the target substance. It is important to note that $63K_{L}^{ii}(t)$ is independent of the reference substance.

### C. Chemical shieldings in CuCl

Since most published values for the copper shifts seem to be relative to the reference substance CuCl we calculated the chemical shieldings for the cluster (CuCl)$_{3}^{-}$ described in Sec. II (see also inset of Fig. 2) surrounded by 83 pseudopotentials. The isotropic part$^{17}$ is shown in Fig. 2 as a function of the basis set size. It is seen that with increasing size of the basis set, the values converge to $63\sigma^{iso}$ (CuCl) = $(700 \pm 200)$ ppm which, with $63\sigma_{p}^{iso}$ (CuCl) = 2400 ppm, implies $63\sigma_{p}^{iso}$ (CuCl) = $-(1700 \pm 200)$ ppm with a negligible anisotropy.

At first we were surprised to get such a substantial paramagnetic contribution but then we discovered that the value obtained agrees well with the precise result of $63\sigma_{p}^{iso}$ (CuCl) = $-1500$ ppm (with an error of about 10 ppm) which was deduced from experiments in a detailed analysis by Lutz et al.$^{28,29}$
Thus, if $^{63}K_{L}^{ii}(t-CuCl)$ denotes the chemical shift with respect to CuCl, we then get for the paramagnetic field modification at $^{63}$Cu in the target material

$$^{63}R_{L}^{ii}(t) = ^{63}K_{L}^{ii}(t-CuCl) + 0.150\%,$$

(12)

using $^{63}\sigma_{p}^{iso}(CuCl) = -1500$ ppm.

This change of reference is of course irrelevant for the presentation of data. Whenever one wants to compare experimental copper shifts with theoretical models, however, it is absolutely necessary to reduce the data to the paramagnetic field modification in the target material. It is evident that Eq. (2) refers to $^{63}K_{L}^{ii}(t)$ and must not be applied to shifts $^{63}K_{L}^{ii}(t-r)$. We will discuss some consequences of Eq. (12) for the interpretation of NMR data in cuprates in Sec. IV.

To illustrate that a correct reference point can be crucial for theoretical interpretations we mention that the Knight shift in metallic copper is 0.232% when referenced to CuCl but 0.382% when compared to a pure diamagnetic sample (see Ref. 28 and Fig. 1 in Ref. 29). It is this latter value which ought to be used in the Korringa relation for the calculation of the spin-lattice relaxation time $T_1$. For a free electron gas $^{63}K(t-r)$ leads to a value of $T_1 = 2.3$ ms at room temperature which is shorter than the experimental one ($T_1 \approx 3$ ms) and thus contrary to the expectation. This difference has been explained as being due to many-body effects with a corrected value of 4 ms. Using $^{63}K(t) = 0.382\%$ leads to a Korringa relaxation time of $T_1 = 0.85$ ms which, using the same correction, is still shorter than the observed time of 3 ms.

D. Paramagnetic field modifications in La$_2$CuO$_4$

We summarize the results of all calculations performed for the chemical shieldings for Cu in La$_2$CuO$_4$ in Fig. 3. According to the discussion in the previous subsections, the shieldings $^{63}\sigma^{ii}$ have been converted into paramagnetic field modifications as follows:

$$^{63}R_{L}^{ii} = -^{63}\sigma_{p}^{ii} = -^{63}\sigma^{ii} + 2400\;\text{ppm}.$$  

(13)

In Fig. 3 the three different cluster sizes are denoted by $N=1$, 2, and 5, respectively, indicating the number of copper atoms. For $N=5$ only the results for the central copper nucleus are given but we note that the deviations at the other copper sites are small. The different methods for the calculations of the shieldings distinguished by circles (SGO) and squares (CSGT and IGAIM) yield values that are somewhat different for the smallest basis size $A$. With increasing basis set size, however, the calculated shielding constants become independent of the particular method. This behavior is completely in agreement with the experience in NMR shielding calculations for molecules.

For the cluster with $N=2$, both possible spin configurations were calculated. The open symbols denote the results for the singlet ($M = 1$) and the filled symbols those for the triplet ($M = 3$). It is seen that the values for $^{63}R_{L}^{ii}$ do not depend appreciably on the spin configuration. For $N=5$, the multiplicities $M = 4$ and $M = 6$ give somewhat different results for the smallest basis set $A$ but again these small differences are further reduced with increasing basis set size.

Assessing the results depicted in Fig. 3 from the viewpoint of quantum chemical shielding calculations, it may be concluded that the results are nearly converged with respect to cluster size and basis set quality.

We thus conclude that $^{63}R_{L}^{zz} = (0.72 \pm 0.03)\%$ and $^{63}R_{L}^{xx} = (0.30 \pm 0.03)\%$, where the error bars account for the dependence on cluster size, spin multiplicity, method, and basis set size.

IV. DISCUSSION OF RESULTS

It is evident that a comparison of any theoretical result for the paramagnetic field modification, $^{63}K_{L}^{ii}(t)$, with the results deduced from experiments for the chemical shifts, $^{63}K_{L}^{ii}(t-r)$, is meaningless. We therefore have collected in Table II some originally published shifts for $^{63}K_{L}^{ii}(t-r)$ with respect to CuCl for various cuprates together with the correspondingly corrected values $^{63}R_{L}^{ii}(t)$ and the ratios $^{63}R_{L}^{xx}$ and $^{63}R_{L}^{zz}$. The first three lines refer to the materials mentioned in the introductory section.

We note that the present values are smaller than those derived from experiments. Before we discuss these differences it is instructive to compare the previous theoretical understanding that relies on the perturbation theoretical approach of Eq. (2) with the present rigorous quantum chemical results. We recall that Eq. (2) originally was erroneously used to explain the shift values $^{63}K_{L}^{ii}(t-r)$, whereas by definition it gives an estimate of the paramagnetic field modifications $^{63}R_{L}^{ii}(t)$ of the target substance. Furthermore,


TABLE II. A compilation of copper chemical shifts measured with respect to CuCl (nonoverlined quantities) and the paramagnetic field modifications at the copper nucleus for some selected cuprates (overlined quantities) in %. The anisotropy ratios are defined by \( \bar{6}^{3}R_{L}^{(\ast)} = \bar{6}^{3}K_{L}^{(\ast)} \bar{6}^{3}K_{L} \) and \( \bar{6}^{3}R_{L}^{(\ast)} = \bar{6}^{3}K_{L}^{(\ast)} \bar{6}^{3}R_{L} \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \bar{6}^{3}K_{L} )</th>
<th>( \bar{6}^{3}K_{L}^{(\ast)} )</th>
<th>( \bar{6}^{3}R_{L} )</th>
<th>( \bar{6}^{3}R_{L}^{(\ast)} )</th>
<th>( \bar{6}^{3}K_{L}^{(\ast)} )</th>
<th>( \bar{6}^{3}R_{L}^{(\ast)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBa_{2}Cu_{3}O_{7}</td>
<td>0.82</td>
<td>0.98</td>
<td>5.47</td>
<td>6.24</td>
<td>3.33</td>
<td>3.50</td>
</tr>
<tr>
<td>YBa_{2}Cu_{3}O_{6.63}</td>
<td>0.83</td>
<td>0.99</td>
<td>5.44</td>
<td>6.01</td>
<td>3.37</td>
<td>3.53</td>
</tr>
<tr>
<td>La_{2}−Sr_{2}Cu_{4}O_{8}</td>
<td>0.72</td>
<td>0.89</td>
<td>4.92</td>
<td>5.49</td>
<td>3.29</td>
<td>3.46</td>
</tr>
<tr>
<td>YBa_{2}Cu_{4}O_{8}</td>
<td>0.91</td>
<td>1.05</td>
<td>5.81</td>
<td>6.66</td>
<td>3.76</td>
<td>3.94</td>
</tr>
<tr>
<td>TI_{2}Ba_{2}Cu_{3}O_{7}</td>
<td>0.72</td>
<td>0.92</td>
<td>4.91</td>
<td>5.61</td>
<td>3.29</td>
<td>3.46</td>
</tr>
<tr>
<td>TI_{5}Sr_{2}Ca_{4}Cu_{2}O_{8} &amp; 0.72 &amp; 0.92</td>
<td>4.91</td>
<td>5.61</td>
<td>3.29</td>
<td>3.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgBa_{2}Cu_{4}O_{8+δ}</td>
<td>1.27</td>
<td>1.45</td>
<td>5.90</td>
<td>6.59</td>
<td>3.77</td>
<td>3.94</td>
</tr>
<tr>
<td>HgBa_{2}Ca_{2}Cu_{3}O_{6+δ}</td>
<td>1.10</td>
<td>1.28</td>
<td>4.92</td>
<td>5.73</td>
<td>3.29</td>
<td>3.46</td>
</tr>
</tbody>
</table>

This work: 0.72 ± 0.24%

\( a \)Ref. 3.
\( b \)Ref. 5.
\( c \)Ref. 6.
\( d \)Ref. 31.
\( e \)Ref. 32.
\( f \)Ref. 33.
\( g \)Ref. 34.
\( h \)Ref. 35.

The previous theoretical estimates of the chemical shifts were based on a simplistic model of an isolated Cu^{2+} ion. In the following, we argue that a correct interpretation of Eq. (2) together with a more sophisticated picture of the electronic structure in the CuO_{2} planes actually leads to values for \( \bar{6}^{3}K_{L}^{(t)} \) which, in accordance with the present quantum chemical results, are also appreciably smaller than the data.

The essential point is that it is not appropriate to model the copper ions in the CuO_{2} planes as isolated. This was already recognized in Ref. 3, where it was mentioned that if the \( d \) hole extends onto neighboring atoms the results should be modified. We can do this as follows. If the copper is embedded in a cluster, the ground state \( |0\rangle \) is a molecular orbital (MO) which is an antibonding linear combination of AO’s,

\[
|0\rangle = c|3d_{x^2−y^2}\rangle − s|2p_x\rangle, \tag{14}
\]

where here and below, \( c \) and \( s \) are the positive values of the corresponding MO coefficient. The angular momentum operators \( L^2 \) and \( L^z \) centered at the Cu nucleus connect this state to the AO’s \( 3d_{xy} \) and \( 3d_{yz} \), respectively. The \( 3d_{xy} \) occurs in two MO’s: in the antibonding (−) and in the bonding (+) combinations,

\[
|\varphi_\pm\rangle = c_\pm|3d_{xy}\rangle ± s_\pm|2p_x\rangle, \tag{15}
\]

with energy differences \( \Delta_{xy} \) with respect to the ground state. The modified expression then reads

\[
\bar{6}^{3}K_{L}^{(t)} = 4\mu_{B}^2\rho(r) \rho(−r)3\Delta_{xy}c^2(x^2|\Delta_{xy} + c^2|\Delta_{xy}^\perp). \tag{16}
\]

Although \( c^2 + c^2 \) almost equals unity, the second term contributes much less than the first term since \( \Delta_{xy} \) is much larger than \( \Delta_{xy}^\perp \). Compared to the pure ionic result we thus get a reduction by a factor of \( c^2 \times c^2 = 0.7 \times 0.7 = 0.5 \). Analogously, we obtain

\[
\bar{6}^{3}K_{L}^{(t)} = 4\mu_{B}^2\rho(r) \rho(−r)3\Delta_{xy}c^2(d^2|\Delta_{xy} + d^2|\Delta_{xy}^\perp). \tag{17}
\]

To leading order, the ratio

\[
\bar{6}^{3}K_{L}^{(t)} = \bar{6}^{3}K_{L}^{(t)} / \bar{6}^{3}K_{L}^{(t)} = 4\bar{6}^{3}K_{L}^{(t)} \Delta_{xy} / (d^2 \Delta_{xy}^\perp) \tag{18}
\]

depends not only on \( \Delta_{xy} / \Delta_{xy}^\perp \) but also on \( d^2 / \Delta_{xy}^\perp \). It is obvious that \( d^2 > \Delta_{xy}^\perp \) since the distance from Cu to the apical oxygens is larger than that to the planar oxygens. In summary, the appropriately modified formula (2) leads to smaller values for both \( \bar{6}^{3}K_{L}^{(t)} \) and \( \bar{6}^{3}R_{L}^{(t)} \) than those that are obtained for an isolated Cu^{2+} ion.

We next compare the present quantum chemical results with the data. We note that our value for \( \bar{6}^{3}K_{L}^{(t)} = (0.30 ± 0.03) \% \) is smaller than the experimental values of about 0.43% measured at helium temperatures in the YBa_{2}Cu_{3}O_{6.63} and La_{2}−Sr_{2}Cu_{4}O_{8} systems. Data from other cuprates (some of which are included in Table II) give somewhat lower values, e.g., for the Hg compounds, which are in the range of 0.35%. Most astonishing, however, is the field dependence of the magnetic shifts that has been measured in the superconducting state. For example, Zheng et al. found that, at helium temperatures, \( \bar{6}^{3}K_{L}^{(t)} \) in YBa_{2}Cu_{4}O_{8} attains a value of 0.41% at high fields (23.2 T) but is reduced at lower fields and becomes 0.35% when extrapolated to zero field. The authors explain this field dependence by a field induced finite density of states at the Fermi level, which is interpreted as due to quasiparticles outside the vortex cores. Whatever the reason for a field dependence of \( \bar{6}^{3}K_{L}^{(t)} \), it is clear that the theoretical values refer to the limit where \( H \rightarrow 0 \). In view of all experimental results for \( \bar{6}^{3}K_{L}^{(t)} \) we conclude that the present theoretical value, (0.30 ± 0.03) %, is lower than the data but not excessively.

The situation for the components \( \bar{6}^{3}K_{L}^{(t)} \), however, is quite different since the theoretical predictions are far below the measurements and we have, at present, no explanation for this discrepancy. Again, in certain substances a strong dependence of \( \bar{6}^{3}K_{L}^{(t)} \) on the field is reported. Thus, for TlSr_{2}CaCu_{2}O_{8+δ} a reduction of the shift by as much as 0.4% occurs when going from high fields to zero field. Furthermore, there are cuprates where \( \bar{6}^{3}K_{L}^{(t)} \) depends appreciably on temperature as has been shown in Refs. 32, 33, 38, and 39. From room temperature to helium temperature the reduction of the value is in the range of 0.15% to 0.4%.

As concerns the chemical shifts at the planar oxygen, we note that only the cluster CuO_{11} is symmetric about the oxygen site. The absolute values of the shielding tensor are of the same order as those for the reference substance H_{2}O with \( 17^{a}_{\text{iso}}(\text{H}_{2}O) = 325 \) ppm. Relative to \( 17^{a}_{\text{O}} \) in water, the calculated chemical shifts are \( 17^{a}_{\text{K}_{L}^{(t)}}(−r) = −(0.004 \pm 0.005) \% \) for the direction along the bond, \( 17^{a}_{\text{K}_{L}^{(t)}} = −(0.011 \pm 0.010) \% \) perpendicular to the bond but in...
the plane, and $^{17}K_{L}^{zz} = -(0.034 \pm 0.020)\%$ perpendicular to the plane. These values are in agreement with those derived by Bankay et al.\textsuperscript{31} from extrapolations using the Korringa relation but disagree with shift data directly measured at lowest temperatures. The smallest “error bars” are obtained for $^{17}K_{z}^{xx}$ as expected, while the largest uncertainties are for the $z$ direction due to the small difference in the electron densities in the $\text{Cu}_2\text{O}_{11}$ cluster for the multiplicities $M = 1$ and $M = 3$.

V. SUMMARY AND CONCLUSIONS

We have calculated chemical shieldings for copper in CuCl which exhibit a substantial paramagnetic contribution. We argued therefore that NMR shift data for Cu in target solids which are measured relative to CuCl should be scaled appropriately to represent the paramagnetic field modifications $^{63}K_{L}^{xx}(t)$ of the target nucleus. The latter quantities should be compared with theoretical models.

The quantum chemical calculations of $^{63}K_{L}^{xx}$ for three different clusters that model La$_2$CuO$_4$ provide values for $^{63}K_{L}^{xx}$ that are somewhat smaller but still in reasonable agreement with the data. The theoretical values for $^{63}K_{L}^{xx}$, however, are substantially smaller than the values obtained from experiments at low temperatures and assuming that the spin susceptibility vanishes at $T = 0$. We do not understand this discrepancy. We also showed, however, that the hitherto given explanations of the chemical shifts in terms of Eq. (2) fail since covalency effects reduce the estimated values and the observed shifts are larger when referred to a diamagnetic environment.

Although our calculations are performed for undoped La$_2$CuO$_4$, we do not expect the chemical shifts to change substantially in the metallic state considering that the experimental magnetic shifts at low temperatures do not strongly depend on doping. In addition, it should be remarked that some magnetic shift experiments\textsuperscript{6} have been interpreted in terms of “residual shifts” that remain even at $T = 0$ due to a nonvanishing density of states. Furthermore, the shifts in the superconducting state sometimes depend appreciably on the strength of the applied field, i.e., they decrease when weakening the field, as, e.g., in $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{TlSr}_2\text{CaCu}_2\text{O}_{7-\delta}$ (Refs. 36 and 39). In this respect, one should note that theoretical shift values are in the limit of vanishing field strength and do not account for the complex impacts of strong applied fields on the field distribution in the vortex state of superconducting cuprates.

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4 The number 63 is used to mark the copper nucleus and not the particular isotope. Within the experimental resolution, both $^{63}$Cu and $^{65}$Cu exhibit the same shift.


8 In more recent experiments, however, somewhat different values for the copper chemical shifts were observed in other cuprate materials. This will be discussed in Sec. IV.


18 Note that the generalized version of Eq. (3), $\sigma(\mathbf{r}) = -\Delta H(\mathbf{r})/\mathbf{H}$, defines the shieldings at an arbitrary point in space and is not restricted to a nuclear site.

19 See the special issue number 11 of J. Comput. Chem. 20 (1999) for a survey on quantum chemical calculations of magnetic properties.


The anisotropy of the shielding components is negligibly small (<2 ppm).

