Unconventional $^{17}$O and $^{63}$Cu NMR shift components in cuprate superconductors

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Nuclear magnetic resonance (NMR) is a fundamental bulk probe that provides key information about the electronic properties of materials. Very recently, the analysis of all available planar copper shift as well as relaxation data proved that while the shifts cannot be understood in terms of a single temperature dependent spin component, relaxation can be explained with one dominating Fermi liquid-like component, without enhanced electronic spin fluctuations. For the shifts, a doping dependent isotropic term, as well as doping independent anisotropic term became obvious. Here we focus on planar $^{17}$O NMR shifts and quadrupole splittings. Surprisingly, we find that they demand, independently, a similar two-component scenario and confirm most of the previous conclusions concerning the properties of the spin components, in particular that a negative spin polarization survives in the superconducting state. This should have consequences for the pairing scenario.

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1. Introduction

Soon after the discovery of cuprate superconductivity [1] nuclear magnetic resonance (NMR), which was the first probe to prove BCS theory [2, 3], uncovered essential nuclear shift and relaxation data that theory tried to turn into a physical picture of these materials (for reviews of cuprate NMR see [4, 5]).

Among the important early NMR findings was spin singlet pairing that was deduced from the vanishing of some low-temperature shifts and relaxation. A so-called spin gap was discovered, as well, since for the underdoped systems the shifts were temperature dependent already far above the superconducting transition temperature $T_c$, different from what one expected from the uniform response ($\chi_0$) of a Fermi liquid (Pauli susceptibility). It was also concluded that NMR favors a single-fluid description [8, 10], as shifts measured at planar Cu (for one orientation) and O seemed to follow the overall temperature dependence of the uniform magnetic susceptibility. This fluid appeared to violate the Korringa ratio between nuclear relaxation and shift, a hallmark of Fermi liquids, which was explained with enhanced electronic spin fluctuations that increase nuclear relaxation of planar Cu compared to what one would expect from its spin shift [11, 12].

Unfortunately, most of the conclusions had to be drawn from a small number of materials, and the YBa$_2$Cu$_{4+y}$O$_{6+y}$ family was rather instrumental. The reason for this is not only that it can have a high transition temperature, but also that other cuprates have excessive NMR linewidths that make measurements tedious and question the quality of the crystals.

A particular early conundrum was a missing, negative spin shift for Cu NMR from an expected spin in the partially filled $3d(x^2-y^2)$ orbital when the external field is parallel to the crystal $c$-axis ($c \parallel B_0$), i.e. for $K_{||}$. In fact, for this orientation it was concluded that there is no spin shift at all. And since $K_{\perp}$ did show a temperature dependence, cf. Fig. 1, it was assumed that there is an accidental cancellation from two hyperfine coefficients for the Cu shifts,

$$K_{||,\perp}(T) = (A_{||,\perp} + 4B') \cdot \chi_0(T),$$

i.e., $A_{||} + 4B' \approx 0$, for spin from the onsite atom ($A_{||,\perp}$) and the four neighboring Cu atoms ($B'$) in a single band scenario, cf. Fig. 2 (A). One should note that there were

\[\text{Figure 1. Typical planar } ^{63}\text{Cu shift data in the curates for 5 different samples [6–8] and two directions of the external field, parallel (c } \parallel \text{B}_0\text{) and perpendicular (c } \perp \text{B}_0\text{) to the crystal c-axis, } K_{||,\perp} \text{ (total shifts are shown). Left panel: Optimaly (OP) or overdoped (OV) systems have a rather temperature independent } K_{||} \text{ that rapidly decreases below } T_c \text{ to reach some similar low temperature values. As the doping level is lowered the shifts begin to decrease already at increasingly higher temperatures above } T_c. \text{ Right panel: } K_{\perp} \text{ for the same materials; note that for the YBa}_2\text{Cu}_3\text{O}_y \text{ family of materials this shift was considered largely temperature independent after a diamagnetic correction [9] (dashed line) and represent the orbital shift value for c } \parallel \text{B}_0 \text{ (for YBa}_2\text{Cu}_4\text{O}_y \text{ it is temperature independent without the correction [10]); some materials show rather large temperature dependent } K_{||} \text{, pointing to rather different hyperfine coefficients in the old scenario.}\]
APH [17] that the spin shifts must be suppressed for most from those of a Fermi liquid. Rather, it was argued by cial electronic spin fluctuations that are very different becomes apparent that there is no reason to invoke spe-

sible as a function of doping, which says that a large amount of $K_{\parallel}(T \rightarrow 0)$ duet to the size of the diamagnetic correction considered [9], cf. Fig. 1. With the appearance of Cu shift data that showed a significant temperature dependence for $c \parallel B_0$, cf. Fig. 1, the old hyperfine scenario was not revisited. Over the last decade, with a number of special experiments these assumptions were questioned, and a two-component scenario was proposed [6, 13–15]. In such a scenario, two different spin components couple to each nucleus with two different hyperfine coefficients and have different temperature dependences, cf. Fig. 2(B). In general, a coupling between the two spin components is to be expected and this leads to another coupling term, cf. Fig. 2(C).

Finally, by just reviewing the literature body of Cu shifts (these are most reliable even in the mixed state since they are large), a rather different Cu shift phe-
nomenology appears from simple plots [16], and the failure of a single spin component description becomes obvious.

For example, an isotropic Cu shift term becomes visible as a function of doping, which says that a large amount of $K_{\parallel}$ should be spin shift, as well, and not orbital shift. One also notices that $K_{\parallel}$ is always greater than $K_{\perp}$, so that one is lead to assume a negative spin component that, together with the very anisotropic hyperfine constant from the $3d(x^2−y^2)$ orbital ($|A_{\perp}| \ll |A_{\parallel}|$ and $A_{\parallel} < 0$) produces an additional positive shift only for $K_{\parallel}$. The particular temperature dependent shift variations are more complicated, but seem to obey simple rules, as well [16].

Another very recent discovery concerns the Cu nuclear relaxation. By inspecting all literature data [17, 18] it becomes apparent that there is no reason to invoke special electronic spin fluctuations that are very different from those of a Fermi liquid. Rather, it was argued by APH [17] that the spin shifts must be suppressed for most cuprates (and not the relaxation enhanced), causing the Korringa relation to fail. This can be understood with the two spin susceptibilities, as well, cf. Fig. 2.

$$K_{\perp}(T) = A_{\perp} \cdot \chi_1(T) + B \cdot \chi_2(T),$$

we prefer to use $B = 4B'$ compared to the old picture. Then, the two susceptibilities lead to two spin polarizations in a magnetic field: $(a + c) \equiv \chi_1$ and $(b + c) \equiv \chi_2$, where $c$ represents a coupling term that can always be present [13]. One then has,

$$K_{\perp}(T) = A_{\perp} \cdot (a + c) + B \cdot (b + c),$$

and a negative $c$ may cause an antiferromagnetic alignment of two uncoupled spins $a$ and $b$, and lead to a re-
duced spin response. This is illustrated in Fig. 2(C).

Here we would like to focus on $^{17}$O NMR data. While sparse due to the necessary isotope exchange, we find with the new understanding of the charge distribution in the CuO$_2$ plane that the rather unusual $^{17}$O NMR shifts and lineshapes that were discussed, but not understood, nearly 20 years ago, are in direct support of a the basic model proposed by APH [17], and in particular a doping dependent isotropic Cu shift that relates to the charge. That is, a proper understanding of shift and splitting demands a two-component spin response, even a negative $^{17}$O shift that is a direct consequence of the negative spin component proposed by APH is found.

### 2. NMR shift contributions

Before we discuss the shifts in more detail, we need to point to the various NMR shift terms. For a particular direction ($\alpha$) of the magnetic field with respect to the crystal axes we can simply write,

$$\tilde{K}_\alpha = K_{\text{core}} + K_{L,\alpha} + K_{\alpha}(T) + K_{\text{dia,}\alpha}(T).$$

The first two terms are orbital shifts, from the core electrons ($K_{\text{core}}$) and from bonding orbitals ($K_{L,\alpha}$, also called van Vleck term). The third term is the spin shift ($K_{\alpha}$), due to a rather isotropic electronic spin, which ac-
quires its orientational dependence from hyperfine coeffi-
cients. A partial diamagnetic response from the super-
fluid in the mixed state is described by ($K_{\text{dia,}\alpha}$). While we do not know $K_{\text{dia,}\alpha}$ precisely, it can safely be ne-
glected for the large Cu NMR and even the planar O in typical magnetic fields of several Tesla where the penetration depth is large compared to the distance between fluxoids. Experimentally, we know this from the much smaller NMR shifts and broadenings of Y, Hg, or api-
cal O that must experience very similar $K_{\text{dia,}\alpha}$, i.e., their shifts and broadenings represent an upper limit for the effect.
Then, if one chooses a suitable reference compound with small $K_{\alpha\alpha}$ and $K_\alpha$, the measured total shift (relative to the reference) is basically given by,

$$K_\alpha(T) = K_{L\alpha} + K_\alpha(T),$$

i.e. an orbital and a spin shift component (for related problems with definitions in the literature cf. [16]).

In addition to the shifts there is the electric quadrupole interaction that splits the $^{63,65}$Cu and $^{17}$O NMR resonances ($I = 3/2; I = 5/2$) into $2I + 1$ lines. However, this splitting can be measured so that the quadrupole effects can be largely removed from the shifts (see below). In fact, the quadrupole splittings in the cuprates are determined quantitatively by the planar Cu and O hole densities [19].

As mentioned in the introduction, for YBa$_2$Cu$_{3-y}$O$_{6+y}$ one finds for Cu that $^{63}K_\perp$ is nearly temperature independent while $^{63}K_\parallel$ is not. So it was concluded, early on,

$$^{63}K_\parallel = ^{63}K_{L\parallel},$$

$$^{63}K_\perp(T) = ^{63}K_{L\perp} + ^{63}K_\perp(T).$$

However, it was pointed out early on [20] that the thus defined orbital shift anisotropy of $^{63}K_{L\parallel}/^{63}K_{L\perp} \sim 4$ fits a single Cu ion value, but should be far too large for a hybridization with planar O (a value of 2.3 is perhaps more appropriate [21]).

With a rather isotropic uniform spin response and single spin component $K_\alpha = H_\alpha\chi_0$ it was assumed,

$$H_\parallel = A_\parallel + 4B' \approx 0$$

$$H_\perp = A_\perp + 4B' > 0,$$

where $A_\parallel, A_\perp$ are the core polarization hyperfine coefficients for a spin in the 3d($x^2-y^2$) orbital, which have the very reliable property [20],

$$A_\parallel = -|A_\parallel| \text{ and } |A_\parallel| \gtrsim 6A_\perp.$$

When cuprates with a substantial temperature dependent shift for $c \parallel B_0$ appeared, i.e., $^{63}K_\parallel(T) = ^{63}K_{L\parallel} + ^{63}K_\parallel(T)$, the accidental cancellation did not hold. And, if one plots their total shifts $^{63}K_\perp$ vs. $^{63}K_\parallel$ (without any assumptions about the orbital shifts) one sees that $^{63}K_\perp(T)$ is not a linear function of $^{63}K_\parallel(T)$ [6]. This is shown for the HgBa$_2$CuO$_{4+y}$ family of materials in Fig. 3 [6]. Note that a high-temperature offset between parallel lines is found (except for the lowest doping), but the offset disappears at low temperatures. In a single component view this cannot be understood since a single temperature dependent spin component must lead to proportional shift changes, i.e.,

$$\Delta K_\parallel/\Delta K_\perp = H_\parallel/H_\perp = \text{const.}$$

which is clearly not the case.

![Figure 3](image-url)

**Figure 3.** Typical element of a $K_\perp$ vs. $K_\parallel$ plot with temperature as an implicit parameter, here for the HgBa$_2$CuO$_{4+y}$ family of materials (adopted from [6]). All shift points are located below a nearly isotropic shift line (dashed line with slope $\sim 1$). For higher doping the temperature independent high-temperatures shifts are all located on the isotropic shift line, cf. also Fig. 1, but depart from it at a temperature (NMR pseudogap temperature) that can be larger than $T_c$ (indicated by the arrows). Some underdoped systems may not reach up to the isotropic shift line (limited data).

### 3. Unconventional planar Cu spin shift

By plotting all available literature Cu shifts similar to what is shown for HgBa$_2$CuO$_{4+y}$ in Fig. 3, various observations were made, which become obvious in their figure 7 [16]; a sketch in Fig. 4 helps summarizing them. Proportional shift changes (straight lines in Fig. 4) as required by a single component view (10) are restricted to small intervals of doping or temperature so that a two-component picture has to be adopted. Obviously, all experimental points as function of doping or temperature can be found below isotropic shift lines [16], i.e., in the lower right triangle of the $^{63}K_\perp$ vs. $^{63}K_\parallel$ plot, cf. Fig. 4. This line with slope close to 1 is formed by the high-temperature, doping dependent shifts for both orientations of the field, i.e.,

$$^{63}K_\perp(x_2) - ^{63}K_\perp(x_1) \approx 1,$$

where $x_i$ refers to particular doping levels. While unlikely on general grounds, even if one tries to explain this finding with an orbital shift variation, the slope of 1 cannot be understood. Firstly, a factor of $\sim 4$ follows for an isolated Cu$^{2+}$ ion [20], and a value of 2.4 is more realistic for a hybridization with oxygen [21]). Secondly, $^{63}K_\parallel(T \rightarrow 0)$ is rather doping and family independent, pointing to a largely doping and family independent $^{63}K_{L\perp}$, while $^{63}K_{L\parallel}$ differs significantly between different materials (arrows in Fig. 4).
Figure 4. Schematic representation of total planar $^{63}K_{||}$ Cu shifts, plotted against each other as function of temperature that is an implicit parameter, as well as doping. Main observations are: (a) All shifts are found in the shaded lower right triangle. (b) The presence of isotropic shift lines, i.e. isotropic change of both shifts with respect to doping at high temperatures. (c) The presence of various $\Delta x^{63}K_{\perp}/\Delta x^{63}K_{||}$ slopes; for example the steep slope, as seen for YBa$_2$Cu$_3$O$_{6+y}$, a slope of 2.5 for HgBa$_2$CuO$_{4+\delta}$, and a slope 1 at low T for highly overdoped TI-based systems. (d) All low temperature ($T \to 0$) $^{63}K_{\perp}$ reach a similar value of $^{63}K_{||} \approx 0.35\%$, the perpendicular orbital shift value (arrow to the left). However, $^{63}K_{\parallel}(T \to 0)$ shows a larger distribution (indicated by arrows on the abscissa). The intersection of an isotropic shift line with $^{63}K_{\parallel}(T \to 0)$ could define $^{63}K_{||}$ not far from the predicted orbital shift anisotropy of 2.4 [21].

On the other hand, we do expect an isotropic hyperfine coefficient $B$ to be present on general grounds, and it would even demand the observed dependence. This means that $^{63}K_{||}$ is partly spin shift, not orbital shift, which is an important conclusion. APH [17] showed that these findings can be understood in a two-component scenario (3), by suitable variations of $a$, $b$, and $c$, and that a negative spin component $a+c$ is present (inverted with respect to the external field, e.g., from the coupling with a dominating positive spin component $b$, cf. Fig. 2(C)). This leads to the suppression of the spin shift compared to what one would expect from a Fermi liquid-like relaxation (note that the relaxation was found to be rather ubiquitous for all cuprates, except La$_{2-x}$Sr$_x$CuO$_4$ that has an additional relaxation mechanism [17, 18]). Therefore, it is desirable to have independent evidence for the new scenario.

4. Planar charge distribution and $^{63}$Cu and $^{17}$O quadrupole splittings

Today we know that the macroscopic chemical doping $x$ can be calculated from the average local hole densities of the Cu 3$d$(${}^2S - {}^2P$) and the oxygen 2$p_x$ bonding orbitals, $n_d$ and $n_p$, respectively, which are measured with NMR [19, 22]. As expected,

$$x = \langle n_d \rangle + 2\langle n_p \rangle - 1. \quad (12)$$

In parent materials $x = 0$, but $n_p$ and $n_d$ differ between families. Upon doping, holes ($x > 0$) or electrons ($x < 0$) enter the CuO$_2$ plane in a family specific way [22], and the sum of the doped hole content $x = \Delta \langle n_d \rangle + 2\Delta \langle n_p \rangle$ leads to the well-known dome-like dependence of $T_c$ on $x$ with the maximum occurring near $x \approx 15\%$, i.e. also if measured with NMR, and this value is independent on family [22]. However, the maxima of the domes for different cuprate families are proportional to the corresponding parent’s $\langle n_p \rangle$ and thus $(1 - n_d)$, i.e. the relocation of charge from planar O to Cu raises the maximum achievable $T_c$ [22, 23]. In fact, a number of cuprate properties appear to be determined by $n_p$ or $n_d$, rather than $x$ [18]. This casts doubt on the efforts to discuss the cuprate properties in the old $T_c(x)$ phase diagram only [23].

The hole contents $n_d$ and $n_p$ follow from the NMR quadrupole splittings [19, 22].

$$^{63}\nu^{Q,C} \approx 94.3\text{ MHz} \cdot n_d - 5.7\text{ MHz} \cdot (8 - 4n_p) \quad (13)$$
$$^{17}\nu^{Q,C} \approx 1.27\text{ MHz} \cdot n_p + 0.2\text{ MHz} \quad (14)$$

Note that spatial variations of hole contents lead to quadrupolar linewidths, which for planar O depend only on $n_p$ [24]. Typical $^{63}$Cu satellite linewidths are 10% for La$_{2-x}$Sr$_x$CuO$_4$, 1% for YBa$_2$Cu$_3$O$_{6+y}$, and 12% for HgBa$_2$CuO$_{4+\delta}$ [25], however, since the linewidths seem to vary with crystal preparation, crystal quality was often associated with it. Interstitial or mixed valence doping are likely to cause inhomogeneities for local probes, and indeed, the stoichiometric compounds YBa$_2$Cu$_3$O$_8$ and YBa$_2$Cu$_3$O$_{7}$ show the smallest linewidths. Furthermore, co-doping other ions increases the linewidths as well. For electron doped systems, the linewidths can even exceed the small average splitting [26]. In view of (13) it is clear that even small variations of $n_d$ lead to large Cu linewidths (a 2.8% hole variation on Cu corresponds to 3 MHz of linewidths observed for HgBa$_2$CuO$_{4+\delta}$).

Typical $^{17}$O quadrupole satellite linewidths range from about 1% to 3% [18]. Interestingly, the materials with the smallest Cu linewidths, YBa$_2$Cu$_3$O$_8$ and YBa$_2$Cu$_3$O$_{7}$, show split oxygen satellites. Only very recently it was proven experimentally [27] that the $^{17}$O NMR double peak pattern in YBa$_2$Cu$_3$O$_{6+y}$ is not due to the orthorhombicity, as widely assumed, but indeed the result of an intra unit cell charge density variation of planar oxygen charge that was proposed already 2003 [28]. It can also be responsible for the linewidths of the planar Cu through (13). This charge density variation is about ±1% of the total oxygen charge, and can be larger in some systems, and there is good reason to believe that this kind of intra-cell charge variation is ubiquitous to the cuprates [18].
In order to be able to discuss the local charges and their variation and not confuse it with the average doping $x$, we introduce a new variable, 
\[ \zeta = n_d + 2n_p - 1, \] (15)
that is the local hole content for a particular CuO$_2$ unit of the material. Then,
\[ x = \langle \zeta \rangle = \langle n_d \rangle + 2\langle n_p \rangle - 1. \] (16)
Note that the intra-cell charge variation is not captured by $\zeta$.

5. Unconventional spin shifts and planar charges

Adopting the notation introduced above, an isotropic shift line demands,
\[
\frac{63 \hat{K}_\perp \langle \langle \zeta_2 \rangle \rangle - 63 \hat{K}_\parallel \langle \langle \zeta_1 \rangle \rangle}{63 \hat{K}_\parallel \langle \langle \zeta_2 \rangle \rangle - 63 \hat{K}_\perp \langle \langle \zeta_1 \rangle \rangle} = \frac{\Delta \zeta}{\Delta \zeta} \approx 1. \] (17)

We can always assume that this is true for $\zeta$ as an average over some local scale (see below), and the isotropic shift line is dominated by the isotropic shift component,
\[ \Delta \zeta = B \cdot \Delta \zeta \chi_2. \] (18)
Clearly, if it is the spin shift $\chi_2$ that changes with $\zeta$, a similar equation must hold for planar oxygen, as well,
\[ \Delta \zeta = B \cdot \Delta \zeta \chi_2. \] (19)
We define $E_\alpha$ and $F_\alpha$ as the two hyperfine coefficients that relate the two spin components to the spin shift,
\[ 17K_\alpha = E_\alpha \cdot \chi_1 + F_\alpha \cdot \chi_2. \] (20)
Note that the orbital shift can be neglected for O [29].

Early $^{17}$O NMR experiments focussed on the question whether the planar O and Cu temperature dependent shifts track each other. For YBa$_2$Cu$_3$O$_{6+y}$ [7] and YBa$_2$Cu$_3$O$_6$ [10] this was found to be the case for all planar O shifts but only $^{63,65}K_\parallel(T)$ since the temperature independent $K_\perp$ for YBa$_2$Cu$_3$O$_{6+y}$ was assumed to be orbital shift.

More elaborate research into the doping dependence of the shifts appeared almost 20 years ago, by Haase et al. [30–32], but a deeper understanding could not be reached. In these publications an unexpected, direct relationship between the planar O magnetic shift and quadrupole splitting was reported. If one remembers that the planar O shifts in typical magnetic fields of ~8 Tesla, have a similar size as the doping related changes of the quadrupole splitting, a correlation between both can lead to the reported peculiar effects that we review now.

The first effect concerns the average shift [32] (it was noticed after the asymmetric lineshapes [30] that we discuss as the second effect further below).

The $2I+1 = 5$ transitions of planar O ($I = 5/2$, in leading order in the Zeeman interaction, can be written in frequency units (which are more useful for this purpose since the quadrupole splitting does not depend on field) in this simple form,
\[ 17f_\parallel,m = 17f_\parallel + m \cdot 17\nu_{Q,c}, \] (21)
where $17f_\parallel = 17K_\parallel B_0$ represents the total shift in frequency units, $B_0$ is the external field; $\nu_{Q,c}$ is the quadrupole splitting from (14), and $m = 0, \pm 1, \pm 2$ denotes the particular transition ($m = 0$ is the central transition). Since only spectra for $c \parallel B_0$ were recorded, we do not consider $17f_\perp$.

It is important to note that the magnetic shift is the same for all transitions while the quadrupole splitting changes sign since it is proportional to $m$, as well, cf. Fig. 5(A).

It was observed, first for La$_{2-x}$Sr$_x$CuO$_4$ [32], that if one plots the total high-temperature spectra for different doping levels $x$ (at least form $x = 0.10$ to $x = 0.20$) on top of each other, the $m = -1$ satellite does not change its position. This is a very striking experimental result, and it says,
\[ 17f_\parallel,-1(x) = 17f_\parallel(x) - 17\nu_{Q,c}(x) = \text{const.} \] (22)
With other words, over a large range of doping the only change of shift at high-temperature is the same as the change in quadrupole frequency.

Lowering the temperature changes the constant in (22), so it is independent of \( \langle \zeta \rangle \), but not of temperature, which is shown in Fig. 5(C).

Available spectra for \( \text{YBa}_2\text{Cu}_3\text{O}_{6+y} \) show the same behavior, cf. Fig. 5(B), for more evidence see further below.

Today, we know with (12) how \( x \) is related to \( n_p \), i.e., it is the charge at planar O that changes linearly with \( x = \langle \zeta \rangle \), which in turn leads to a proportional change of the splitting,

\[
\Delta \nu_{Q,\zeta} = R \Delta \langle \zeta \rangle
\]

(23)

according to (14), with

\[
R = \frac{d^1\nu_{Q,\parallel}}{d\zeta} = 1.27 \text{ MHz} \frac{d n_p}{d \zeta},
\]

and we can estimate \( d n_p/d \zeta \) from \( d n_p/\partial \zeta = 1/2 \) and the slopes of \( \Delta n_p/(2\Delta n_p) \) in figure 5 of [22] (for \( \text{La}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_8 \) we obtain \( d n_p/d \zeta = 1/2.4 \)).

This proves that at high temperatures the planar oxygen shift \( ^{17}K \) is a linear function of \( \langle \zeta \rangle \), as well. From the Cu NMR isotropic shift lines we know that it is \( \chi_2(\zeta) \) that causes this behavior, which leads us to the conclusion,

\[
\Delta \zeta \nu_{Q,\parallel} = F \Delta \zeta \chi_2 = M \cdot \Delta \langle \zeta \rangle,
\]

(24)

where \( M \) is just the proportionality constant (see below).

With other words, we have the relation,

\[
^{17}f_{\parallel,-1} = f_0 - n_0 + (M - R)(\zeta) = \text{const.}
\]

(25)

with \( R = M \), and \( f_0 \) and \( n_0 \) being the magnetic shift and quadrupole splitting, respectively, at the lowest doping level where (25) holds. Before we continue the discussion, we point to the 2nd observation [30].

This second peculiar effect concerns the \( ^{17}\text{O} \) NMR line-shapes that are quite asymmetric, cf. Figs. 5 and 6. It was observed, but not discussed already in the first publications on \( \text{YBa}_2\text{Cu}_3\text{O}_{6+y} \) (Takigawa et al. [35] in their figure 1 the satellite resonances appear to have similar heights, but their amplification factors given underneath the spectra reveal that the \( m = -1 \) satellite is much larger). For \( \text{Tl}_2\text{Ba}_2\text{CuO}_y \), Kambe et al. [34] show similarly distorted spectra, cf. Fig. 6. For \( \text{La}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_8 \) the asymmetry was discovered and discussed in greater detail by Haase et al. [30]. It was shown that this asymmetry can be understood by assuming a linear expansion of shift and splitting in some local parameter \( h \) that is distributed across the \( \text{CuO}_2 \) plane, in their notation [30],

\[
^{17}f_{\parallel}(h) = f_0 + M \cdot h
\]

(26)

\[
^{17}\nu_{Q,\parallel}(h) = \nu_0 + R \cdot h
\]

(27)

where

\[
M = d^1f_{\parallel}/dh, \quad R = d^1\nu_{Q,\parallel}/dh,
\]

(28)

which for \( h = \langle \zeta \rangle \) gives (23) and (24).

In the original paper it was also shown that one can use the distribution function of \( h \) as obtained from the central transition lineshape (which is entirely magnetic), and predict the whole spectrum for optimally doped \( \text{La}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_8 \) and \( \text{YBa}_2\text{Cu}_3\text{O}_{6+y} \) with the ratio \( R/M \approx 2 \), not \( R/M \approx 1 \). If one sets \( h = \zeta \), one has to note that a spatial variation of \( \zeta \) modulates the planar O hole content \( n_p \) that, in turn, changes the quadrupole splitting. While the latter is a very local property, this is not likely to be the case for the spin shift so that \( R/M \) may depend on the wavelength of spatial oscillation of the charge, and \( R/M \) is expected to be larger at the shortest wavelengths. We believe that the discrepancy between the linewidths and average splittings and shifts are to be expected.

We note that while there have been only a few studies with respect to the overall independence of the \( m = -1 \) satellite, the effects behind (25), (26) and (27) describe the same phenomenon and thus support each other.

Another important early finding [30] revealed that the magnetic linewidth associated with \( M \) has a very different temperature dependence compared to that of the mean spin shift. In fact, we see in Fig. 6 that the lines become symmetric only near entering the superconducting state (below \( T_c \) significant magnetic linewidth remains that is still in excess of what one expects from the fluxoid lattice [31]). Similar observations were made for \( \text{HgBa}_2\text{CuO}_{4+\delta} \) [36], i.e., the magnetic linewidth associated with the charge variation does not follow the temperature dependence of the shift, but can decrease below \( T_c \).

We can return to relative shift units and just write,

\[
^{17}K_{\parallel} = f_0 + M' \langle \zeta \rangle,
\]

(29)
For example, we know that isotropic coupling coefficient ($K_{\alpha}$) explains this finding, rather, an electronic spin with an orbital shift variations with doping cannot be explained. Therefore, the isotropic shift line was summarized in the first part of the manuscript. A new, overall phenomenology [16] cemented the failure of the traditional view of the cuprates from NMR, which sets the oxygen quadrupole splitting, cf. (14).

Since the planar Cu NMR shifts are very reliable and the new, overall phenomenology [16] summarized recent progress in the understanding of the charge distribution in the CuO$_2$ plane. For example, we know that $x = n_d + 2n_p$ is the local charge per planar unit cell, and that $n_p$, only, sets the oxygen quadrupole splitting, cf. (14).

Finally, we investigated the validity of such a two-component approach by exploring the $^{17}$O NMR shifts and quadrupole splittings. Here, we find that the peculiar, yet ubiquitous behavior of planar $^{17}$O NMR, which was reported some time ago [30, 32], but not understood, actually demands a two-component scenario much of the kind suggested by APH [17].

In those studies [30, 32], it was observed that the quadrupole splitting and high temperature shifts are intimately linked for planar O, documented by a doping-independent $m = -1$ satellite and special asymmetric total lineshapes. Both are a manifestation of a correlation of $n_p$ with $\chi_2(\zeta)$, cf. Figs. 5 and 6.

Thus, just based on planar O data we concluded on a doping dependent susceptibility $\chi_2(\zeta)$ that increases linearly with $\zeta$ and that is temperature independent at higher temperatures, very similar to what we concluded from the Cu data [17]. However, the temperature dependence of $\chi_2(\zeta)$ is not well known. The more elaborate data set for the HgBa$_2$CuO$_{4+y}$ family clearly showed this component [6], but we believe that the low temperature value is not entirely of orbital origin, which changes some conclusions made earlier (the possibility was indeed considered [6]). It is also not clear whether this could be caused by a loss in correlation with planar charge that changes the shifts and widths through $\chi_2$ since significant broadening remains below $T_c$. Extensive experiments for YBa$_2$Cu$_3$O$_{6+y}$ showed that the planar O NMR shift anisotropy is rather temperature independent even below $T_c$ [37], but does not track the isotropic shift, in support of our findings.

From the temperature dependences of the shifts alone it is difficult to determine more details, except that the planar $^{17}$O NMR shift becomes negative for various systems [7, 8, 38], as predicted for a negative $\chi_1$ by APH [17], it leads for planar Cu to a positive shift for $c \parallel B_0$ due to the large anisotropy of $\Delta_p$. However, the measurements of the shifts below $T_c$ are very sparse, in particular down towards the lowest temperatures.

The asymmetric planar O spectra are due to the same phenomenon. Here a spatial variation of $n_p$, and with it that of $\chi_2(\zeta)$ leads to the special asymmetric lineshapes. This also explains the quite general observation that magnetic and quadrupolar linewidths appear together in cuprate NMR. A spatial variation of $n_p$ affects the planar Cu NMR linewidth, cf. (13), but the same equation shows that a variation of $n_p$ is more effective.

The materials with the most narrow NMR lines are the stoichiometric systems, but these exhibit split oxygen satellite resonances that have been proven to be caused by intra unit cell charge density variations [27]. The difference in quadrupole splittings point to a total O hole variation of $\sim 1\%$. The difference in the magnetic shifts between these two oxygen sites within the unit cell is less than what one expects from the mere difference in charge [39], which is to be expected due to the small length scale.

$\left( M^{\prime} = M/B_0 \right)$, and if we take the difference between the central transition shift for two doping levels, we have,

$^{17}K_{\|}(\langle \zeta_2 \rangle) - ^{17}K_{\|}(\langle \zeta_1 \rangle) = M^{\prime}(\langle \zeta_2 \rangle - \langle \zeta_1 \rangle)$,

which is independent of $f_0$. Indeed, for the available data we find that the difference does not change significantly above $T_c$. This also proves the different temperature dependences of both components.

We are finally able to conclude with $f_0 = E_\| \chi_1$ and $M^{\prime} \zeta = F_\| \chi_2$,

$^{17}K_\alpha(\zeta) = E_\alpha \cdot \chi_1 + F_\alpha \cdot \chi_2,$ (30)

the same two-component description as proposed for the planar Cu data by APH [17].

6. Discussion

Since the planar Cu NMR shifts are very reliable and they have been investigated for many different cuprates, the new, overall phenomenology [16] cemented the failure of the traditional view of the cuprates from NMR, which was summarized in the first part of the manuscript. A main feature in this new phenomenology is the appearance of an isotropic shift line at high enough temperatures, i.e. both Cu shifts change at the same rate as a function of doping, $\Delta_x^{\delta_1}K_{\perp} / \Delta_x^{63}K_{\|} \approx 1$. It was shown that orbital shift variations with doping cannot explain this finding, rather, an electronic spin with an isotropic coupling coefficient ($B$) is a suitable candidate, in particular since it is expected to be present. However, such an explanation is in striking disagreement in particular with the old assumption for YBa$_2$Cu$_3$O$_{6+y}$, that is $^{63}K_{\|} = K_{\perp}$, which was the basis of the traditional NMR scenario.

Since the doping plays a special role in the description of the data, we summarized recent progress in the understanding of the charge distribution in the CuO$_2$ plane. For example, we know that $x = \zeta$, where $\zeta = n_d + 2n_p$ is the local charge per planar unit cell, and that $n_p$, only, sets the oxygen quadrupole splitting, cf. (14).
It appears that this intra unit cell charge variation is the source for the instability towards charge modulations in the CuO$_2$ plane [40]. A possible sketch of the charge and spin density variation is depicted in Fig. 7.

Again, NMR of planar Cu and O demands a doping dependent shift term that is quite unusual. In addition, the second term that remains there even below $T_c$ is very unusual, as well, and it points to a magnetic ground state that involves Cu 3$d(x^2−y^2)$ spin. Since the nuclear relaxation freezes out universally in the cuprates [17, 18], APH argued that relaxation originates from exchange coupling. Clearly, one has to such a scenario a change in $b$ for a doping independent universal Cu relaxation. In APH introduced the main concepts and had the main leadership; all authors were involved in data analysis and discussion equally, as well as in preparing the manuscript.

Finally, we see no reason to challenge the explanation of NMR in terms of two spin components, given the fact that components with $a + c$ being independent on doping. However, we believe it is also possible that doping changes predominantly $b$ at higher temperature, and that $a$ is responsible for a doping independent universal Cu relaxation. In such a scenario a change in $b$ would explain the observed change in the relaxation anisotropy. Clearly, one has to demand that the fluctuations $(a(t)a(t+\tau))$ need to freeze out below $T_c$, together with those of $(b(t)b(t+\tau))$. The exchange coupling $c$ turn on the pseudogap effect and is perhaps involved the paring, as well.

The planar $^{17}$O NMR shifts and quadrupole splittings discussed here demand a two spin component scenario, i.e. an electronic spin susceptibility $\chi = \chi_1 + \chi_2$. One component is a linear function of local doping, $\Delta \chi_2(\zeta) \propto \Delta T$, and thus of the planar oxygen hole content $\eta_p$. It is temperature independent at higher temperatures, different from the component $\chi_1$, which is rather independent of doping, but causes high temperature shift changes. $\chi_1$ appears to be determined by the parent system and favors spin alignment opposite to the external field since there is negative shift at the lowest temperatures.

While similar two-component models have been suggested earlier [6, 13–15], the findings here are in particular agreement with those proposed by APH, very recently [17]. APH found that $\chi_2$ couples isotropically to the Cu nucleus (isotropic hyperfine coupling constant $B$), while the spin from $\chi_1$ couples through the anisotropic hyperfine constant $A_{||,\perp}$ and is sizeable even below $T_c$, but negative, which would lead to a negative planar O shift.

We showed that a spatial variation of the local charge and thus of the oxygen hole content $\eta_p$, together with the doping dependent $\chi_2(\zeta)$, lead to correlated magnetic and quadrupolar linewidths, common in the cuprates. This spatial variation of $\eta_p$ can be affected by crystal chemistry, but it cannot be reduced below the intrinsic, intra unit cell planar O charge variation [27, 28].

The unconventional shift of planar Cu and O have the same origin and must be relevant to the understanding of the cuprates above and below $T_c$.

7. Conclusions

The planar $^{17}$O NMR shifts and quadrupole splittings discussed here demand a two spin component scenario, i.e. an electronic spin susceptibility $\chi = \chi_1 + \chi_2$. One component is a linear function of local doping, $\Delta \chi_2(\zeta) \propto \Delta T$, and thus of the planar oxygen hole content $\eta_p$. It is temperature independent at higher temperatures, different from the component $\chi_1$, which is rather independent of doping, but causes high temperature shift changes. $\chi_1$ appears to be determined by the parent system and favors spin alignment opposite to the external field since there is negative shift at the lowest temperatures.

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We showed that a spatial variation of the local charge

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Author contributions

J.H. introduced the main concepts and had the main leadership; all authors were involved in data analysis and discussion equally, as well as in preparing the manuscript.

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