Anomalous temperature dependence of magnetic interactions in the $p$-orbital spin-1/2 antiferromagnet CsO$_2$

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Using $^{133}$Cs nuclear magnetic resonance, we follow the magnetic response of CsO$_2$, coming from the $p$-orbital $S = 1/2$ spins of magnetic O$_2^-$ anions, across the structural phase transition occurring at $T_{	ext{a1}} = 61$ K on cooling. Above $T_{	ext{a1}}$, where spins form a square magnetic lattice, we extract and model an anomalous temperature dependence of the exchange coupling $J(T)$ originating from thermal librations of O$_2^-$ dumbbells. Below $T_{	ext{a1}}$, we detect a clear sign of the spin Tomonaga-Luttinger liquid demonstrating the formation of magnetic spin chains as a result of the static tilt of O$_2^-$ dumbbells and accompanying orbital ordering. The extracted $J(T)$ allows us to conclude that orbital overlaps in the orbitally-ordered state are maximized, thereby providing an important clue about the microscopic origin of orbital ordering.

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The appeal of magnetic insulators as model systems for studying the collective phenomena comes from their simple Hamiltonians completely defined by a set of short-range magnetic exchange interactions. The exchange coupling $J$, determined by the overlap of the involved atomic orbitals, is affected by pressure-induced lattice contraction [1, 2], but the effect of thermal lattice expansion is usually negligible. Exceptions are materials with a large coefficient of thermal expansion, where $J$ significantly decreases with temperature $T$ [3–5]. Only in a few cases, an anomalous, i.e., increasing $J(T)$ was observed, which was suggested to originate from the modulation of orbital overlaps by lattice phonons [6, 7]. The temperature dependence of $J$ arising from both effects together was theoretically treated in Ref. [8], but it was later shown that the contribution of lattice phonons in this treatment is negligible [9]. A clear demonstration of the phononic modulation of $J$ is thus still missing.

In addition to the continuous temperature dependence, orbital overlaps responsible for $J$ can also undergo an instantaneous change as a result of orbital ordering arising from the cooperative Jahn-Teller effect [9]. The prototypical examples are LaMnO$_3$ [10, 11] and KCuF$_3$ [12] where the degeneracy of atomic orbitals hosting the magnetic spin is lifted along with the structural phase transition occurring at $\sim 750$ K and $\sim 800$ K on cooling, respectively. The effect is particularly spectacular in KCuF$_3$ where orbital ordering switches the magnetic lattice dimensionality from three-dimensional (3D) to 1D [13, 14]. Even in these two simplest cases, the origin of orbital ordering is still debated [15, 16].

As both phenomena, the phononic modulation of $J$ and orbital ordering, combine lattice and orbital physics, they are closely related: the first phenomenon scans over available lattice-orbital configurations and could, when measurable, provide an insight into the particular configuration realized in the orbitally-ordered state. Indeed, we demonstrate this relation in the study of orbital ordering occurring below $\sim 70$ K in CsO$_2$, whose magnetism comes from the $p$-orbital $S = 1/2$ spins of O$_2^-$ anions [17]. First, we observe an anomalous $J(T)$ between neighboring spins in the high-$T$, paramagnetic phase of CsO$_2$, with a total variation of as much as 50%, and explain it with a model based on thermal librations of O$_2^-$ "dumbbells". This represents the first clear example of the phononic modulation of $J$. Second, the observed $J(T)$ allows us to conclude that orbital overlaps in the low-$T$, orbitally-ordered phase are maximized, thereby providing a microscopic explanation for the orbital ordering. And third, we conclusively demonstrate the formation of spin chains in the orbitally-ordered phase of CsO$_2$ by observing the characteristic 1D spin dynamics described in terms of the Tomonaga-Luttinger liquid (TLL) [18].

The materials containing magnetic O$_2^-$ anions, i.e., alkali superoxides, AO$_2$ ($A =$ Na, K, Rb, Cs) [19, 20], and alkali sesquioxides, $A_2$O$_6$ ($A =$ Rb, Cs) [21–24], exhibit two key features that make them appealing for investigation of the coupling between lattice, orbital and spin physics [21, 25] as an alternative to the more established $d$-orbital materials, such as LaMnO$_3$ and KCuF$_3$ [10–12, 13, 16–18]. First, the O$_2^-$ dumbbells can easily reorient down to the low temperatures, thereby modulating the overlaps of $p$ orbitals and, consequently, $J$ between the neighboring $S = 1/2$ spins [20]. And second, as the $S = 1/2$ spin is localized in a pair of $p$-derived, degenerate $\pi^*$ orbitals, a mechanism similar to the Jahn-Teller effect...
leads to orbital ordering accompanied by the structural phase transition, which involves the cooperative tilting of \( \text{O}_2^- \) dumbbells. This was demonstrated in \( \text{CsO}_2 \) \[17\] where orbital ordering was suggested to switch the magnetic lattice dimensionality from 2D to 1D, with the formation of antiferromagnetic spin chains [Fig. 1(a)]. As the spin dynamics in the orbitally-ordered phase of \( \text{CsO}_2 \) remained unexplored, we set out to study it.

The \( \text{CsO}_2 \) powder, prepared by oxidation of the freshly distilled \( \text{Cs} \) metal with dried molecular \( \text{O}_2 \) gas, was sealed in a glass tube for nuclear magnetic resonance (NMR) and magnetization measurements. The sample was \(~50\%\) enriched by \(^{17}\text{O}\) isotope for \(^{17}\text{O}\) NMR experiments. As these turned out to be difficult because of a very fast \(^{17}\text{O}\) spin-spin relaxation, we resorted to \(^{133}\text{Cs}\) NMR experiments. Fig. 1(a) shows a schematic crystal structure of \( \text{CsO}_2 \) combining structural and orbital details of the low-\( T \) and high-\( T \) phases as suggested in Ref. \[17\]. The structural transition between the two phases is of first order, which we clearly demonstrate in Fig. 1(b) by the temperature evolution of the \(^{133}\text{Cs}\) NMR spectrum in a magnetic field of \( B = 9.4 \text{ T} \) with the Larmor frequency 52.461 MHz. The transition occurs at \( T_{s1} = 61 \text{ K} \) on cooling and at \( T_{s2} = 75 \text{ K} \) on warming, with hysteresis spanning the range of \(~15 \text{ K} \). The shift and width of the spectrum are related to the magnetic response of \( \text{O}_2^- \) anions through the hyperfine coupling tensor \( \mathbf{A} \). The shift is given by the isotropic part of \( \mathbf{A} \), while the width, being typically \(~20\)-times smaller than the shift, is given by the correspondingly smaller anisotropic part of \( \mathbf{A} \). The perfect linear dependence of the shift with \( T \) follows static susceptibility \( \chi(T) \) (red line) down to 40 K where 1D magnetic correlations start to develop (blue background). Both data are taken on warming. Dotted vertical line indicates an anomaly at \( T_{s2} \) signalling the structural phase transition. Upper inset shows a linear dependence of the relative \(^{133}\text{Cs}\) shift on \( T \) above 40 K where the slope yields a hyperfine coupling constant \( A = 1.16 \text{ T} \). Lower inset shows the field dependence of the \( \text{O}_2^- \) magnetic moment \( \mu(B) \) as calculated from the measured magnetization. Red line is a linear fit with \( \partial \mu / \partial B = 0.0142 \mu_B / \text{T} \).

**FIG. 1:** (color online) Structural and magnetic properties of \( \text{CsO}_2 \). (a) Schematic crystal structure with representative \( \text{O}_2^- \) \( \pi_{x,y} \) orbitals (yellow) and \( \text{Cs}^+ \) \( p_z \) orbitals (green). Above \( T_{s2} \), the average direction of \( \text{O}_2^- \) dumbbells is along the \( c \) axis (top \( ab \) layer) resulting in degenerate \( \pi_{x,y} \) orbitals and frustrated-square magnetic lattice with exchange couplings \( J = J' \) between nearest (next nearest) neighboring spins (top). Below \( T_{s1} \), the tilt of \( \text{O}_2^- \) dumbbells is staggered along the \( b \) axis (bottom \( ab \) layer) resulting in \( \pi_{x,y} \) orbital ordering and formation of magnetic chains with exchange coupling \( J \) along \( b \) (bottom) \[18\]. (b) Hysteretic evolution of \(^{133}\text{Cs}\) NMR spectrum across the structural phase transition taken on warming (solid lines, \( T_{s2} = 75 \text{ K} \)) and cooling (dashed lines, \( T_{s1} = 61 \text{ K} \)). The presence of high-\( T \) (low-\( T \)) phase is indicated by red (blue) spectra. (c) \(^{133}\text{Cs}\) shift as a function of temperature \( T \) shows static susceptibility \( \chi(T) \) (red line) down to 40 K where 1D magnetic correlations start to develop (blue background). Both data are taken on warming. Dotted vertical line indicates an anomaly at \( T_{s2} \) signalling the structural phase transition. Upper inset shows a linear dependence of the relative \(^{133}\text{Cs}\) shift on \( T \) above 40 K where the slope yields a hyperfine coupling constant \( A = 1.16 \text{ T} \). Lower inset shows the field dependence of the \( \text{O}_2^- \) magnetic moment \( \mu(B) \) as calculated from the measured magnetization. Red line is a linear fit with \( \partial \mu / \partial B = 0.0142 \mu_B / \text{T} \).
FIG. 2: (color online) Spin dynamics in CsO2. \( T_1^{-1} \) as a function of temperature \( T \) taken on warming in three different magnetic fields \( B \). Solid red, blue and green lines are power-law fits characteristic of the TLL behavior (blue background) valid in the range from 15 K up to \( T_{\text{TLL}} \) (indicated by dashed line). Solid gray lines are the joint fit to the high-\( T \) paramagnetic behavior (red background) for three magnetic field values. Arrows indicate the divergence in \( T_1^{-1}(T) \) at \( T_N \) signalling the transition into the ordered Néel state. Dotted vertical line indicates the jump in \( T_1^{-1}(T) \) at \( T_{\text{s2}} \) = 75 K signalling the structural phase transition. Inset outlines the low-\( T \) phase diagram obtained from data in the plot.

\( \mu \) to saturate to the value \( g\mu_BS = 1.05\mu_B \) (\( \mu_B \) is Bohr magneton) at \( B_s \approx 2J_{1D}/(g\mu_B) \) = 56 T.

A conclusive test for the presence of spin chains in the low-\( T \) phase is the nature of spin dynamics for \( T \lesssim J_{1D}/k_B \) where 1D spin correlations emerge. Spin dynamics can be directly accessed by the NMR spin-lattice relaxation rate \( T_1^{-1} \), which probes the low-energy limit of the local spin-spin correlation function \( \langle S_i \cdot S_j \rangle \). As shown in Fig. 2 \( T_1^{-1}(T) \) datasets measured in three different magnetic fields exhibit a clear power-law behavior up to the field-dependent temperature \( T_{\text{TLL}} \), slightly lower than \( J/k_B \). This behavior is outweighed by \( \sim 15\) K by the growth of 3D critical fluctuations preceding the 3D antiferromagnetic ordering \( \mathbf{17, 19} \). The transition occurs at the field-dependent Néel temperature \( T_N \), which is clearly marked by the characteristic peak in \( T_1^{-1}(T) \). The observed power-law behavior of \( T_1^{-1}(T) \) is a hallmark of the TLL state, a universal low-energy description of interacting physics in 1D \( \mathbf{18} \). In this state, transverse (i.e., perpendicular to the field) and longitudinal (i.e., parallel to the field) gapless spin fluctuations are possible \( \mathbf{37} \). In CsO2, the longitudinal fluctuations couple to \( ^{133}\)Cs through the small anisotropic part of \( A \), so that their contribution to \( T_1^{-1} \) is negligible with respect to the contribution of the transverse fluctuations coupled through the isotropic part \( A \). In this case, the power-law dependence adopts the form \( T_1^{-1} \propto (T/T_{\text{TLL}})^{1/(2K)-1}/u^{1/(2K)} \), where \( K \) is the interaction exponent and \( u \) is the velocity of spin excitations \( \mathbf{38-40} \). The corresponding fits of the \( T_1^{-1}(T) \) datasets in Fig. 2 allow us to extract the values of the TLL parameters \( K \) and \( u \) as a function of \( B \) \( \mathbf{11} \). We find \( K \) to converge to \( K_{\text{min}} = 1/4 \) for \( B = 0 \) (Fig. 3[a]), in contrast to the value 1/2 expected for the Heisenberg antiferromagnetic spin-1/2 chain \( \mathbf{18} \). The lowest possible value \( K_{\text{min}} \) is realized only in the presence of Ising-like exchange-coupling anisotropy \( \mathbf{18, 37} \). It is reached when the field is decreased to the critical field \( B_c \), below which the chain dynamics becomes gapped. As the measured \( \mu(B) \) in CsO2 is linear down to \( B \approx 0 \) [lower inset of Fig. 3(c)], \( B_c \) should be very close to 0, and the eventual exchange-coupling anisotropy should be small.

While the observed power-law behavior of \( T_1^{-1}(T) \) provides a qualitative indication of the TLL behavior, the ultimate quantitative test is a validity of the relation between the ratio \( u/K \) derived from spin dynamics and the zero-\( T \) susceptibility \( \partial\mu/\partial B \) as a static observable \( \mathbf{18} \):

\[
\frac{u}{K} = \frac{(g\mu_B)^2}{k_B} \frac{1}{\pi \left( \frac{\mu_B}{\mu_B} \right)^2}.
\]

(1)

Fig. 3(b) shows a comparison between \( u/K \) determined above from the \( T_1^{-1}(T) \) datasets and the prediction of Eq. (1) using the field-independent value \( \partial\mu/\partial B = 0.0142\) T/\( \mu_B \) extracted from the measured \( \mu(B) \) [lower inset of Fig. 3(c)]. As the TLL description is expected to fail when approaching the critical field \( \mathbf{39} \), \( B_c \approx 0 \) in this case, the agreement in Fig. 3(b) can be considered as excellent. Furthermore, plotting the field dependence of \( T_{\text{TLL}} \) and \( T_N \) [inset of Fig. 2] reveals a standard phase diagram of the spin TLL systems \( \mathbf{42} \). A clear realization of the TLL state conclusively demonstrates the formation of spin chains in the orbitally-ordered phase of CsO2.

A clue about the origin of orbital ordering in the low-\( T \) phase unexpectedly comes from the high-\( T \) data. In the paramagnetic phase above \( T_{s2} \), \( T_1^{-1}(T) \) exhibits an unusual, nonmonotonic and strongly field-dependent behavior (Fig. 2). This is in marked contrast to the standard convergence to a \( T \)-independent value at high temperatures \( \mathbf{35} \). The field dependence can be understood by realizing that the magnetic fields used in our experiments reach the energy scale comparable to the exchange coupling \( J \approx J_{1D}/4 \) in the high-\( T \) phase [given that the electron density is now split between a pair of \( p \) orbitals, see Fig. 1(a)]. In this case, the field-dependent Zeeman term for electron spins cannot be neglected as in Ref. \( \mathbf{35} \). Adding it to the exchange term, we extend the high-\( T \) derivation for \( T_1^{-1} \) and obtain \( \mathbf{41} \):

\[
T_1^{-1} = \frac{\sqrt{\pi}}{2} \gamma^2 a^2 \frac{1}{\sqrt{2}J + (g\mu_B B)^2},
\]

(2)
press it as a function of $T$ thus postulate the temperature-dependent $J$ nonmonotonic behavior of $T$ neighboring O decrease of spin, to be of the same magnitude the linear exchange path. For simplicity, we assume both plannings along the diagonals are likely ferromagnetic due to couplings along the sides of the square magnetic lattice ratio and $\hbar$ data in Fig. 2 using Eq. (2). The best collapse of the three $J$ dependence of the exchange coupling $\mu$ $K$ exponent $K$ $T$ line is fit with the function $J$ $B$ $\vartheta$ (shaded yellow) is obtained for $J$ where

$$\vartheta = 5^\circ \text{ K, } B = 19 \text{ K and } J_1/K_B = -28 \text{ K.}$$

Inset shows a schematic dependence of the overlap between $O_2^-$ $\pi_{\varphi,\psi}$ orbitals (yellow) and Cs $p_z$ orbitals (green) on the tilt $\vartheta$ of the $O_2^-$ dumbbell from the $c$ axis. An optimal overlap (shaded yellow) is obtained for $\vartheta_{\text{max}} = 5.2^\circ$ reached at 225 K where $J(T)$ exhibits a maximum.

where $z$ is a number of neighboring $O_2^-$ spins to each $O_2^-$ spin, $\gamma/(2\pi) = 5.585 \text{ MHz/T}$ is nuclear gyromagnetic ratio and $\hbar$ is reduced Planck constant. The exchange couplings along the sides of the square magnetic lattice in Fig. II(a) are antiferromagnetic [17], whereas the couplings along the diagonals are likely ferromagnetic due to the linear exchange path. For simplicity, we assume both to be of the same magnitude $J$ and so $z = 8$. We also assume, as before, that $^{133}\text{Cs}$ is coupled equally to six neighboring $O_2^-$ spins and add a factor of 6 to the right side of Eq. (2). While Eq. (2) can explain the observed decrease of $T_1^{-1}$ with increasing $B$, it cannot explain the nonmonotonic behavior of $T_1^{-1}(T)$ if $J$ is a constant. We thus postulate the temperature-dependent $J(T)$ and express it as a function of $T_1^{-1}$ and $B$ from Eq. (3). If this postulate is correct, the three $J(T)$ datasets calculated from the $T_1^{-1}(T)$ datasets in Fig. 4 should collapse on the same curve. Indeed, we achieve this in the high-$T$ range above 150 K [Fig. 4(c)] by setting $A = 0.82 \text{ T}$, a value close to the one extracted in Fig. (c). The obtained $J(T)/k_B$ exhibits an unusual dependence with a maximum of $\sim 9.3 \text{ K,}$ nicely matching the above estimated value $J_{1D}/(4k_B) = 9.9 \text{ K.}$

Finally, we show that the obtained temperature dependence $J(T)$ comes from the modulation of the involved orbital overlaps by fast librations of $O_2^-$ dumbbells. The exchange frequency $\omega_e = 2J/\hbar = 2.6 \cdot 10^{12} \text{ s}^{-1}$ for a typical value $J/k_B = 10 \text{ K}$ is an order of magnitude smaller than the frequency of $O_2^-$ librations, $\omega_l = 3.9 \cdot 10^{13} \text{ s}^{-1}$ [13]. The exchange coupling $J$ thus only depends on the average orbital overlap and, in turn, on the quadratic mean $\sqrt{\langle \vartheta^2 \rangle}$ of the $O_2^-$ dumbbell tilt $\vartheta$ from the $c$ axis. We can estimate it by treating the $O_2^-$ dumbbell as a harmonic oscillator with the moment of inertia $I = 2.3 \cdot 10^{-46} \text{ kgm}^2$, whose kinetic energy $\frac{1}{2}I\omega_l^2\langle \vartheta^2 \rangle$ is calculated as the thermal average over the oscillator states, $\hbar\omega_l/[e^{\hbar\omega_l/(k_BT)}-1]$. This leads to

$$\sqrt{\langle \vartheta^2 \rangle} = \frac{\vartheta_0}{\sqrt{e^{\hbar\omega_l/k_BT}}-1}.$$  

(3)

where $\vartheta_0 = \sqrt{2\hbar/(I\omega_l)} = 8.7^\circ$ and $T_0 = \hbar\omega_l/k_B = 303 \text{ K.}$ Eq. 3 allows us to translate the $J(T)$ dependence into the $J(\vartheta)$ dependence (Fig. 3 using the upper horizontal scale) in the picture of frozen, tilted $O_2^-$ dumbbells (i.e., replacing $\sqrt{\langle \vartheta^2 \rangle}$ by $\vartheta$). This clearly reveals the origin of the maximum in $J(T)$: it simply reflects the maximum in $J(\vartheta)$ reached at the tilt $\vartheta_{\text{max}}$, for which the orbital overlap in the exchange path scenario over the Cs $p_z$ orbital [17] is maximized [inset of Fig. 3(c)]. The obtained value $\vartheta_{\text{max}} = 5.2^\circ$ [Fig. 3(c)] is model-independent, relying only on $O_2^-$ dumbbell being treated as a harmonic oscillator. As only small tilts $\vartheta$ are involved, we can expand $J(\vartheta) = J_0 + J_2(\vartheta/\vartheta_0)^2 + J_4(\vartheta/\vartheta_0)^4$, where the odd terms are zero for symmetry reasons and we neglect higher-order terms. This $J(\vartheta)$ produces an excellent fit of the collapsed $J(\vartheta)$ datasets in Fig. 3(c). Fig. 2 shows the corresponding joint fit of the three $T_1^{-1} \text{ datasets using Eqs. } (2) \text{ and } (3).$ The crucial point here is that the obtained $\vartheta_{\text{max}}$ value coincides perfectly with the static tilt of $O_2^-$ dumbbells in the low-$T$ phase as inferred from the Raman-spectroscopy data [17]. It thus appears that the low-$T$, orbitally-ordered phase maximizes the orbital overlaps and hence the exchange energy. This suggests an exchange-driven origin of orbital ordering, simply followed with the structural instability as a secondary effect.

In summary, we conclusively demonstrated the formation of spin chains in the orbitally-ordered phase of CsO$_2$ by a clear observation of the TLL state reflecting the 1D spin dynamics. This adds CsO$_2$ with its O$_2^-$-based $p$-orbital magnetism to the short list of Cu- and Co-based...
orbital overlaps in the high-\textit{T} phase of CsO$_2$ are maximized for a certain lattice-orbital configuration, precisely the one that is realized in the low-\textit{T}, \textit{orbitally-ordered} state. This suggests an exchange-driven origin of orbital ordering, a mechanism involved in the Kugel-Khomskii picture [3]. Important lessons learnt here should be used to elucidate the details of orbital ordering also in other similar materials. We acknowledge the financial support by the European Union FP7-NMP-2011-EU-Japan project LEMSU-PER under Contract No. 283214. We thank W. Schnelle and R. Koban for performing SQUID magnetization measurements.

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41. See Supplemental Material for the extraction of the TLL parameters from the $T_1^{-1}(T, B)$ in the paramagnetic state in high magnetic fields.
SUPPLEMENTAL MATERIAL

Analysis of the NMR spin-lattice relaxation in the Tomonaga-Luttinger-liquid state

To analyze the dynamics of the spin Tomonaga-Luttinger-liquid (TLL) state in CsO$_2$, we use an analytical expression for the TLL spin-lattice relaxation rate $T_1^{-1}$ derived for the case of dominant transverse spin fluctuations in the antiferromagnetic spin-1/2 chain [39]:

$$T_1^{-1} = \frac{\hbar^2 A^2 A_x}{k_B u} \cos\left(\frac{\pi}{4K}\right) B \left(1 + \frac{1}{2K}\right)^2 \frac{2\pi T}{u},$$

where the (unitless) interaction exponent $K$ and the velocity of spin excitations $u$ (in kelvin units) are TLL parameters, $A_x$ is the amplitude of the transverse correlation function $A_y/(2\pi)$ is nuclear gyromagnetic ratio (5.585 MHz/T for $^{133}$Cs), $A$ is a relevant element of the hyperfine coupling tensor, $k_B$ is Boltzmann constant, $\hbar$ is reduced Planck constant and $B(x, y) = \Gamma(x) \Gamma(y)/\Gamma(x + y)$ where $\Gamma$ is the gamma function. In case of the CsO$_2$ powder, we use an isotropic part of the hyperfine coupling tensor $A = 1.16$ T [extracted from the scaling of the NMR shift with magnetic susceptibility in Fig. 1(c)]. We need to add an extra factor of 4 = 2·2 to the right side of Eq. 4: the first factor of 2 because each $^{133}$Cs is coupled to two neighboring $O^-$ spins along the $c$ axis [Fig. 1(a)] (while the total coupling to four neighboring $O^-$ spins in the $ab$ plane is zero due to antiferromagnetic nature of spin fluctuations in the chains), and the second factor of 2 because two correlation functions (in two directions perpendicular to the chain) describe the transverse spin fluctuations. For $A_x$ we take 0.12, which holds for $\mu < 0.15\mu_B$ [39], the condition fulfilled in our magnetic field range [lower inset of Fig. 1(c)]. Fitting the $T_1^{-1}(T)$ datasets in Fig. 2 with Eq. 4 then yields the values of the TLL parameters $u$ and $K$ as a function of $B$.

NMR spin-lattice relaxation in the paramagnetic state in high magnetic fields

The calculation of the NMR spin-lattice relaxation rate $T_1^{-1}$ for the Heisenberg antiferromagnet in the paramagnetic state was carried out by Moriya in Ref. 52. In this calculation, the fluctuations of the electron spins responsible for the NMR relaxation are derived for the field-independent exchange term only. We extend Moriya’s calculation by including also the field-dependent Zeeman term for electron spins, which becomes relevant when the energy scales of the magnetic field $B$ and of the exchange coupling $J$ are comparable. This is the case in CsO$_2$ where $J/k_B$ is of the order of 10 K and the magnetic fields used in the experiment are of the order of $B = 10$ T, which translates to the value $\mu_B B/k_B = 14.1$ K ($\mu_B$ is Bohr magneton and $q = 2.1$, an isotropic part of the measured gyromagnetic ratio $g$)-tensor [19]) comparable to $J/k_B$. In a lot of materials studied so far, the exchange couplings are of the order of 100 K or even 1000 K, and in these cases the original Moriya’s calculation has been applicable. In addition, we are interested in the high-temperature limit, i.e., $k_BT >> J$. This limit is realized typically for $k_BT > 10$ J, i.e., for $T > 100$ K in CsO$_2$.

In case of an isotropic hyperfine coupling $A$ between the nuclear spin and the electron spin residing at site $l$, the NMR spin-lattice relaxation rate can be written [36]

$$T_1^{-1} = \frac{1}{2} \gamma^2 \int_{-\infty}^{\infty} dt e^{i\omega_{\text{NMR}} t} \cdot \left\{ A^2 \langle S_l^x(t) S_l^x \rangle + A^2 \langle S_l^y(t) S_l^y \rangle \right\},$$

where $S_l^x$ and $S_l^y$ are spin operators, $t$ is time and $\omega_{\text{NMR}} = \gamma B$ is the NMR frequency. We start by calculating the thermal spin correlation function $\langle S_l^x(t) S_l^x \rangle$. The time evolution of the spin operator is $S_l^x(t) = e^{iHt/\hbar} S_l^x e^{-iHt/\hbar}$ where

$$H = \sum_j J_{jl} S_j^x S_l^x - g\mu_B BS_l^z$$

is a part of the Hamiltonian relevant for the spin at site $l$, now containing both the Heisenberg and the Zeeman term. The sum runs over all neighboring spins. Following Moriya, each exponential factor is developed in a Taylor series over $t$ leading to

$$\langle S_l^x(t) S_l^x \rangle = \langle S_l^x S_l^x \rangle + \frac{t^2}{\hbar} \langle [H, S_l^x] S_l^x \rangle + \frac{1}{2} \left( \frac{t^2}{\hbar} \right)^2 \langle [H, S_l^x] [S_l^x, H] \rangle + \cdots$$

The thermal average for an arbitrary operator $P$ is calculated as $\langle P \rangle = \text{tr}\{ e^{-\beta H} P \}$ where $\beta = 1/(k_B T)$ and $T$ is temperature. In the high-temperature limit, we can approximate $e^{-\beta H}$ to 1, so that $\langle P \rangle = \text{tr}\{ P \}$. For the $S = 1/2$ spin, the first term on the right side of Eq. 7 then evaluates to 1/4, the second term evaluates to zero, while in the third term $\text{tr}\{ [H, S_l^x] [S_l^x, H] \} = \frac{1}{2} (g\mu_B B)^2 + \frac{1}{2} \sum_j J_j^2$. When the exchange couplings to all of the $z$ neighboring electron spins are the same in magnitude, and this magnitude amounts to $J$, we can
set \( \sum_j J_j^2 = zJ^2 \). Finally, the correlation function can be written as

\[
\langle S^x_l(t)S^x_l \rangle = 1 - \frac{1}{4} \left( \frac{t^2}{\hbar^2} \left( zJ^2 + 2(g\mu_B B)^2 \right) \right)
\]

\[
\approx \frac{1}{4} e^{-\frac{1}{4} \frac{t^2}{\hbar^2} (zJ^2 + 2(g\mu_B B)^2)},
\]

where the first line has been recognized as the beginning of the Taylor expansion of the exponential function and the corresponding replacement has been made. This is the Gaussian approximation \([35]\). The result for the correlation function \( \langle S^y_l(t)S^y_l \rangle \) is identical.

Capturing the result from Eq. (8) into a standard Gaussian form \( \frac{1}{4} e^{-\omega_e^2 t^2 / 2} \), we introduce the exchange frequency

\[
\omega_e = \frac{1}{\hbar} \sqrt{\frac{1}{2} zJ^2 + (g\mu_B B)^2}.
\]

(9)

This is a characteristic frequency of the spin fluctuations. For \( J/k_B \sim 10 \text{ K} \) and \( B \sim 10 \text{ T} \), \( \omega_e \) is of the order of THz, much higher than \( \omega_{NMR} \) in the MHz range, meaning that we can set \( \omega_{NMR} = 0 \) in Eq. (5). Plugging the result from Eq. (8) into Eq. (5) and evaluating the integral, we obtain the final result

\[
T_1^{-1} = \frac{\sqrt{\pi}}{2} \frac{\gamma^2 \hbar A^2}{\gamma B} \frac{1}{\sqrt{zJ^2 + (g\mu_B B)^2}}.
\]

(10)

Setting \( B = 0 \), this result recovers the well known and widely used Moriya’s expression in the high-temperature approximation \([35]\).

We note that \( T_1^{-1} \) in Eq. (10) exhibits a strong field dependence when the energy scales of \( B \) and \( J \) are comparable. The reason for this is not a modified \( \omega_{NMR} = \gamma B \), it is rather the change of spin dynamics. Namely, in presence of the sizeable magnetic field, the spin system becomes stiffer, the characteristic frequency \( \omega_e \) of its fluctuations increases, meaning that the zero-frequency spectral density picked by \( T_1^{-1} \) decreases. This is the physical meaning of Eq. (10).