Divergence of the orbital nuclear magnetic relaxation rate in metals

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We analyze the nuclear magnetic relaxation rate $(1/T_1)_{orb}$ due to the coupling of nuclear spin to the orbital moment of itinerant electrons in metals. In the clean noninteracting case, contributions from large-distance current fluctuations add up to cause a divergence of $(1/T_1)_{orb}$. When impurity scattering is present, the elastic mean free time τ cuts off the divergence, and the magnitude of the effect at low temperatures is controlled by the parameter $\ln(\mu\tau)$, where μ is the chemical potential. The spin-dipole hyperfine coupling, while having the same spatial variation $1/r^3$ as the orbital hyperfine coupling, does not produce a divergence in the nuclear magnetic relaxation rate.

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I. INTRODUCTION

The nuclear magnetic resonance (NMR) provides a powerful experimental tool in materials science. One prominent example in the condensed matter is that measurements and analysis of the Knight shift and nuclear magnetic relaxation rate (also called nuclear spin-lattice relaxation rate) proved to be a decisive test[1] of the validity of the BCS theory of superconductivity. In general, the NMR signal carries information on the interactions which couple the nuclear magnetic moments to their environment. In such a situation, the theoretical understanding of various possible contributions to the total measured quantity is very important.

For metals, the most important hyperfine coupling is the one with the itinerant electrons.[2,3] The magnetic hyperfine interaction of each nucleus with the electrons may be written as $\mathcal{H}_{hf}=-\gamma_n \mathbf{I}\cdot\mathbf{h}$, where γ_n is the nuclear gyromagnetic ratio and $\mathbf{I}$ is the spin of the nucleus located at the position $\mathbf{R}$. The units $\hbar=k_B=1$ are used throughout except in Sec. VI. The effective hyperfine magnetic field $\mathbf{h}$ has three contributions:

$$\mathbf{h}(\mathbf{R}) = \gamma_e \int d^3r \left[-\frac{8\pi}{3}\mathbf{s}\delta(\boldsymbol{\rho}) + \frac{\mathbf{s}-3\hat{\boldsymbol{\rho}}(\mathbf{s}\cdot\hat{\boldsymbol{\rho}})}{\rho^3} - \frac{\mathbf{l}}{\rho^3}\right], \quad (1)$$

where $\mathbf{s}$ and $\mathbf{l}$ are the spin and the orbital moment of the conduction electron located at $\mathbf{r}$, and we use the notations $\boldsymbol{\rho}=\mathbf{r}-\mathbf{R}$, $\rho=|\boldsymbol{\rho}|$, and $\hat{\boldsymbol{\rho}}=\boldsymbol{\rho}/\rho$. In Eq. (1), the integration is over the sample volume V and $\gamma_e=e/(mc)$ is the electron gyromagnetic ratio, c is the speed of light, $-e$ is the electron charge (with $e>0$), and m is the free-electron mass. The first term in Eq. (1) originates from the Fermi-contact hyperfine interaction, the second term is due to the spin-dipole hyperfine interaction, and the third term is due to the orbital hyperfine interaction.

In this paper, we would like to draw attention to an interesting property of the nuclear magnetic relaxation rate $(1/T_1)_{orb}$ arising as a result of orbital hyperfine interaction: For a perfectly clean metallic system of infinite spatial dimensions, and in the absence of an external magnetic field, $(1/T_1)_{orb}$ is infinitely large. This fact has already been reported by Lee and Nagaosa.[4] Here, we provide a thorough discussion of the situation using the Green's-function method. The nature of the effect is related to the properties of long-range static fluctuations of orbital fields and currents. Mathematically, the divergence of $(1/T_1)_{orb}$ appears upon integrating the relevant electronic two-particle correlation function over the momentum transfer $\mathbf{q}$: the integral diverges at $\mathbf{q}=0$. The divergence is thus related to the behavior of the electrons that are far away from the nucleus. In this paper, the influence of the finite sample size is included via a cutoff of the wave-vector integrals, and possible surface effects are not considered explicitly.

The divergence of $(1/T_1)_{orb}$ means that, in principle, in a sufficiently clean sample, the orbital mechanism for the nuclear magnetization relaxation is very efficient and the total T_1 can be very small. In real material, some impurities are always present. We show that electron scattering off impurities removes the divergence. The magnitude of $(1/T_1)_{orb}$ at low temperatures is controlled by the parameter $\ln(\mu\tau)$, where μ is the chemical potential and τ is the mean free time for itinerant electrons. This means a logarithmic dependence on the impurity concentration. Our numerical estimates for Li and Sr_2RuO_4 show that even for values of τ characteristic of the cleanest samples, the long-range part of $(1/T_1)_{orb}$ is not dominant, but it can be big enough, we believe, to be experimentally determined.

The rest of the paper is organized as follows. In Sec. II, we present the formula for the relaxation rate which is used for the calculation. In Sec. III, we evaluate $(1/T_1)_{orb}$ in a simple model in which the normal metal is described by the free-electron gas. We study both clean and impure cases, with the details regarding the vertex corrections relegated to the Appendix. In Sec. IV, we show that, unlike the orbital hyperfine interaction, the long-range contribution to $1/T_1$ due to the spin-dipole hyperfine interaction is finite. In Sec. V, we demonstrate that the singularity of $(1/T_1)_{orb}$ in a clean metal is, in fact, quite general. First, we show that placing the free-electron gas into a periodic potential (the simplest model for a crystalline solid) does not remove the singularity. Next, following the idea of Ref. 4, we show how metallic systems with an arbitrary electronic dispersion can be analyzed using the connection between $(1/T_1)_{orb}$ and the nonuniform static electric conductivity $\sigma_{\alpha\beta}(\mathbf{q})$. Recognizing the fact that the static electric conductivity of the perfectly clean electronic system is infinite perhaps makes the divergence of $(1/T_1)_{orb}$ in such a system less surprising and puzzling. Section VI contains a discussion, where, in particular, we esti-

mate the magnitude of the effect, and the concluding remarks.

II. THE RELAXATION RATE FORMULA

The expression for the nuclear magnetic relaxation rate that is most suitable for our purposes has the following form:[5–7]

$$\frac{1}{T_1} = -\frac{\gamma_n^2}{2}\coth\left(\frac{\omega_0}{2T}\right)\mathrm{Im}\, K_{+-}^R(\omega_0,\mathbf{R}), \tag{2}$$

where $\omega_0=\gamma_n H$, with H being the external magnetic field oriented along the z axis. In the derivation of Eq. (2), the hyperfine interaction is treated as a perturbation for the electronic Hamiltonian, which can be quite general. The main object in Eq. (2) is the Fourier transform of the retarded correlator of the effective magnetic fields $\mathbf{h}(\mathbf{R})$:

$$K_{+-}^R(t,\mathbf{R}) = -i\theta(t)\langle[h_+(t,\mathbf{R}),h_-(0,\mathbf{R})]\rangle, \tag{3}$$

where $h_\pm \equiv h_x \pm i h_y$. We take the origin of the coordinate system at the location of the nucleus (i.e., $\mathbf{R}=0$).

The correlator $K_{+-}^R(\omega)$ can be computed starting from the explicit expression for the orbital hyperfine fields in the formalism of the second quantization. We follow the standard procedure and find at first the corresponding Matsubara correlator $K_{+-}^M(i\nu_n)$ and then apply the analytical continuation from the imaginary axis to just above the real axis: $K_{+-}^R(\omega) = K_{+-}^M(i\nu_n \to \omega + i0^+)$. Alternatively, using Maxwell's equations, one can express the real frequency correlator $K_{+-}^R(\omega)$ through the current-current correlator and thus through the electrical conductivity, for which there exist well developed methods of calculation including the kinetic equation approach and the linear-response theory.

Based on the magnitude of the nuclear magneton, the approximation relevant to experiments in typical laboratory magnetic fields and not too low temperatures is $\omega_0 \to 0$. Then, Eq. (2) gives

$$\frac{1}{T_1 T} = -\gamma_n^2 \lim_{\omega_0\to 0}\frac{1}{\omega_0}\,\mathrm{Im}\, K_{+-}^R(\omega_0,\mathbf{R}=0). \tag{4}$$

The approximation $\omega_0 \to 0$ also implies that statistical averages have to be calculated for the system in zero external magnetic field H.

The magnetic field to be inserted in Eq. (4) is the effective magnetic field given by Eq. (1). We would like to comment that there is one approximation which is implicit in presenting the fluctuating magnetic field at nucleus in this form. It consists in neglecting the influence of the magnetic field on the electrons themselves. This feedback effect may be phenomenologically accounted for by replacing $\mathbf{h}$ on the left-hand side of Eq. (5) with $(1+4\pi\chi)\mathbf{h}$, where χ is the magnetic susceptibility of the material. For ordinary metals $|\chi| \sim 10^{-5}$, and we will not include this contribution in what follows. The complete treatment of the feedback effect, which would be necessary when $|\chi|$ is large, in particular, in superconductors, requires taking into consideration dynamical fluctuations of the vector potential $\mathbf{A}$ of the electromagnetic field. This is beyond the scope of the present paper.

III. CALCULATION OF $(1/T_1)_{orb}$ FOR A SIMPLE MODEL OF NORMAL METAL

In this section, we consider in detail the nuclear magnetic relaxation rate due to orbital hyperfine interaction $(1/T_1)_{orb}$ in the situation where electronic system is modeled by the three-dimensional electron gas (moving in the positively charged uniform background). The electrons do not interact between themselves but could elastically scatter off randomly distributed nonmagnetic impurities.

This model is sufficient to demonstrate that for the relaxation of nuclear magnetization in the absence of an external magnetic field, $(1/T_1)_{orb}$ diverges in the clean case. This divergence is cut off when impurities are present. An extension of the argument to more general situations is presented in Sec. V.

In the second-quantization representation, the operator of the orbital magnetic field at the origin $\mathbf{R}=0$ has the form

$$\hat{\mathbf{h}} = -\gamma_e \int d^3r \sum_\sigma \hat{\psi}_\sigma^\dagger(\mathbf{r})\frac{\mathbf{r}\times(-i\nabla)}{r^3}\hat{\psi}_\sigma(\mathbf{r}), \tag{5}$$

which can be obtained from the third term in Eq. (1) by combining the second-quantized representation of the momentum operator $\hat{\mathbf{p}}$ with the definition of the angular momentum. The hats denoting the operators will be omitted below in order to simplify notation. Note that expression for the magnetic field is consistent with the Biot-Savart law. Indeed, Eq. (5) can be obtained if in the expression for the magnetic field[8] at $\mathbf{R}=0$, given by the integral $\mathbf{h} = -(1/c)\int d^3r[\mathbf{j}(\mathbf{r})\times\mathbf{r}]/r^3$, the standard second-quantized representation for the orbital electric current is inserted and the integration by parts is performed while neglecting the surface term.

A. Free-electron gas in the plane-wave basis

The ψ operators can be expanded in the basis of plane waves, which are solutions of the Schrödinger equation in empty space:

$$\psi_\sigma(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} c_{\mathbf{k}\sigma}, \tag{6}$$

where V is the volume of the system. When this expansion is inserted in the definition of $\mathbf{h}$ in Eq. (5), a straightforward $\mathbf{r}$ integration leads to the following expression for the effective magnetic field due to the electron orbital motion:

$$\mathbf{h} = \gamma_e \frac{4\pi i}{V}\sum_{\mathbf{k},\mathbf{k}'}\frac{\mathbf{k}\times\mathbf{k}'}{(\mathbf{k}-\mathbf{k}')^2}\sum_\sigma c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}'\sigma}. \tag{7}$$

The corresponding Matsubara correlator $K_{+-}^M(i\nu_n) = -\int_0^\beta d\tau e^{i\tau\nu_n}\langle T_\tau h_+(\tau)h_-(0)\rangle$ has the form

$$K_{+-}^M(i\nu_n) = 2\frac{(4\pi\gamma_e)^2}{V^2}\sum_{\mathbf{k}_1,\mathbf{k}_2}\frac{(\mathbf{k}_1\times\mathbf{k}_2)_x^2 + (\mathbf{k}_1\times\mathbf{k}_2)_y^2}{|\mathbf{k}_1-\mathbf{k}_2|^4} \times S(i\nu_n,\mathbf{k}_1,\mathbf{k}_2). \tag{8}$$

The quantity S is related to the electron bubble:

$$\mathcal{B}(i\nu_n,\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2') \equiv \int_0^\beta d\tau e^{i\tau\nu_n} \sum_{\sigma_1\sigma_2} \langle T_\tau c^\dagger_{\mathbf{k}_1\sigma_1}(\tau) c_{\mathbf{k}_1'\sigma_1}(\tau) c^\dagger_{\mathbf{k}_2\sigma_2}(0) c_{\mathbf{k}_2'\sigma_2}(0)\rangle, \tag{9}$$

where $\beta=1/T$, with T being the temperature. The angular brackets denote the thermodynamic average with the given electronic Hamiltonian, and T_τ is the imaginary time ordering operator. For the free-electron gas, we have

$$\mathcal{B}(i\nu_n,\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2') = -2\delta_{\mathbf{k}_1,\mathbf{k}_2'}\delta_{\mathbf{k}_2,\mathbf{k}_1'} S(i\nu_n,\mathbf{k}_1,\mathbf{k}_2), \tag{10}$$

and the quantity S has the following form:

$$S(i\nu_n,\mathbf{k}_1,\mathbf{k}_2) = T\sum_m G_0(\mathbf{k}_1,i\omega_m+i\nu_n)G_0(\mathbf{k}_2,i\omega_m) = \frac{f(\xi_{\mathbf{k}_1})-f(\xi_{\mathbf{k}_2})}{\xi_{\mathbf{k}_1}-\xi_{\mathbf{k}_2}-i\nu_n}, \tag{11}$$

where $\omega_m=2\pi T(m+1/2)$ and $\nu_m=2\pi Tm$, $m=0,\pm1,\ldots$, are the fermionic and bosonic Matsubara frequencies, respectively. Also, in Eq. (11), $G_0(\mathbf{k},i\omega_m)=1/(i\omega_m-\xi_{\mathbf{k}})$ is the free-electron Green's function, with $\xi_{\mathbf{k}}=\varepsilon_{\mathbf{k}}-\mu$, and $f(x)=1/[\exp(x/T)+1]$ is the Fermi distribution function. Note that S depends on the momenta $\mathbf{k}$ only through the energies $\varepsilon_{\mathbf{k}}=\mathbf{k}^2/(2m)$.

To arrive at Eq. (8), the factors with the vector products of four $\mathbf{k}$ vectors in the integrand of the expression for the correlator K^M_{+-} were simplified using the delta functions of Eq. (10):

$$\frac{(\mathbf{k}_1\times\mathbf{k}_1')_+}{(\mathbf{k}_1-\mathbf{k}_1')^2}\frac{(\mathbf{k}_2\times\mathbf{k}_2')_-}{(\mathbf{k}_2-\mathbf{k}_2')^2} \to -\frac{(\mathbf{k}_1\times\mathbf{k}_2)_x^2+(\mathbf{k}_1\times\mathbf{k}_2)_y^2}{|\mathbf{k}_1-\mathbf{k}_2|^4}. \tag{12}$$

For the quadratic dispersion of the free electrons, the density of electronic states per one spin projection $N(\varepsilon)=m\sqrt{2m\varepsilon}/(2\pi^2)$ does not depend on angular variables. Converting the $\mathbf{k}$ summations into integrations and separating the angular variables, we can write

$$K^M_{+-}(i\nu_n) = 2(4\pi\gamma_e)^2\int_0^{+\infty} d\varepsilon_1 d\varepsilon_2 N(\varepsilon_1) \times N(\varepsilon_2) K_\Omega(\varepsilon_1,\varepsilon_2) S(i\nu_n,\varepsilon_1,\varepsilon_2), \tag{13}$$

where we have introduced the quantity K_Ω defined as an angular integral, which, in the present case, contains just one nontrivial integration over the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$ that can be performed exactly:

$$K_\Omega(\varepsilon_1,\varepsilon_2) \equiv \frac{2}{3}\oint \frac{d\Omega_{\mathbf{k}_1}}{4\pi}\frac{d\Omega_{\mathbf{k}_2}}{4\pi}\frac{(\mathbf{k}_1\times\mathbf{k}_2)^2}{|\mathbf{k}_1-\mathbf{k}_2|^4} = \frac{1}{6}\left[a\ln\frac{a+1}{a-1}-2\right]. \tag{14, 15}$$

Here, $k_{1,2}=|\mathbf{k}_{1,2}|$ and $a\equiv(k_1^2+k_2^2)/(2k_1k_2)=(\varepsilon_1+\varepsilon_2)/(2\sqrt{\varepsilon_1\varepsilon_2})$, which, in turn, implies that $a\pm1=(k_1\pm k_2)^2/(2k_1k_2)=(\sqrt{\varepsilon_1}\pm\sqrt{\varepsilon_2})^2/(2\sqrt{\varepsilon_1\varepsilon_2})$.

Now, we perform the analytic continuation of $S(i\nu_n)$ given by Eq. (11) on the imaginary axis to the frequencies just above the real axis and expand in $\omega\ll\mu$, keeping in mind that we actually need only the imaginary part for small ω. Introducing the notation $S(\omega)\equiv S(i\nu_n\to\omega+i0^+)$, we write

$$\mathrm{Im}\, S(\omega) \approx \pi\delta(\xi_1-\xi_2-\omega)[\omega f'(\xi_2)+\mathcal{O}(\omega^2)], \tag{16}$$

where $f'(\xi)\equiv\partial f(\xi)/\partial\xi$. The delta function in Eq. (16) allows us to eliminate one energy integral in Eq. (13), while the derivative of the Fermi distribution places the energy close to the Fermi surface. This allows us to use, for the degenerate electron gas, the standard approximation of the constant DOS at the Fermi level and switch in Eq. (13) from the ε integrations to the ξ integrations from $-\infty$ to $+\infty$. Additionally, the angular factor K_Ω reduces to

$$K_\Omega(\xi_1,\xi_2) = \frac{1}{3}\ln\frac{\bar\mu}{|\xi_1-\xi_2|}, \tag{17}$$

where $\bar\mu\equiv(4/e)\mu\approx1.47\mu$. It is worth emphasizing that the angular integral K_Ω brings in a nonanalytic energy dependence. Thus, at small ω, we arrive at the following integral:

$$\lim_{\omega\to0}\frac{\mathrm{Im}\, K^R_{+-}(\omega)}{\omega} = \frac{2\pi}{3}[4\pi\gamma_e N(\mu)]^2\int_{-\infty}^{+\infty} d\xi_1 d\xi_2 f'(\xi_2)\delta(\xi_1-\xi_2-\omega)\ln\frac{\bar\mu}{|\xi_1-\xi_2|}. \tag{18}$$

The final expression for the relaxation time has the form:

$$\frac{1}{T_1T} = \frac{2\pi}{3}[4\pi\gamma_n\gamma_e N(\mu)]^2\ln\left(\frac{\bar\mu}{\omega}\right), \tag{19}$$

where the right-hand side does not depend on temperature. Note that this expression diverges logarithmically at $\omega\to0$, which can be traced back to the logarithmic behavior of the angular integral K_Ω in Eqs. (14) and (15) at $\varepsilon_1\to\varepsilon_2$ or $\mathbf{k}_1\to\mathbf{k}_2$.

B. Free-electron gas in the spherical harmonics expansion

It is instructive to trace the origin of the divergence using the basis of spherical harmonics around $\mathbf{R}=0$, where nuclear spin is located. For this purpose, we substitute in Eq. (6) the following expansion of the plane waves:

$$\exp(i\mathbf{k}\cdot\mathbf{r}) = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l} i^l j_l(kr) Y^*_{lm}(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}}), \tag{20}$$

in terms of the spherical harmonics Y_{lm} and the spherical Bessel functions $j_l(kr)$.[9] An advantage of this approach is that we can use in Eq. (5) the well-known matrix elements of the angular momentum operator $\mathbf{l}$. The radial part can be integrated to give

$$h_{\pm} = -\gamma_e \frac{(4\pi)^2}{V} \sum_{\mathbf{k}_1\mathbf{k}_2\sigma} c^{\dagger}_{\mathbf{k}_1\sigma} c_{\mathbf{k}_2\sigma} \sum_{l=1}^{\infty} Z_l \left[\frac{4k_1k_2}{(k_1+k_2)^2} \right] \times \sum_{m=-l}^{+l} \sqrt{(l\pm m)(l\mp m+1)}\, Y^*_{l,m\pm1}(\hat{\mathbf{k}}_1) Y_{l,m}(\hat{\mathbf{k}}_2),$$

$$Z_l(z) = \frac{\sqrt{\pi}}{4} \frac{\Gamma(l)}{\Gamma(l+3/2)} \left(\frac{z}{4}\right)^l F[l, l+1; 2(l+1); z],$$

where $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$ and $F[a,b;c;z]$ is the hypergeometric function.[9] Calculation of the Matsubara correlator proceeds as in the previous section and produces $S(i\nu_n)$ of Eq. (11) and $S(\omega)$ of Eq. (16) after the analytic continuation, leading to $\delta(\varepsilon_{\mathbf{k}_1} - \varepsilon_{\mathbf{k}_2})$ and $k_1 = k_2$ at $\omega = 0$. At this stage, the angular parts of $\mathbf{k}$ integrations are performed and then all the summations except one can be evaluated. The final result reads

$$\frac{1}{T_1 T} = \frac{2\pi}{3} [4\pi\gamma_n\gamma_e N(\mu)]^2 \sum_{l=1}^{\infty} \frac{16/\pi}{l}, \tag{21}$$

where finite terms have been omitted. Since we have set up explicitly $\omega = 0$, this expression is divergent. In accordance with what has been found previously in Eq. (19), the divergence is logarithmic and, in this case, occurs in the sum over orbital quantum number as $l \to \infty$.

C. The impurity dependence of $(1/T_1)_{orb}$

In this section, we consider the electron gas interacting with pointlike elastic scatterers. The disorder is treated perturbatively using the standard impurity averaging technique.[10] In the Appendix, we show that in the isotropic situation considered here, the vertex corrections to the impurity averaged electronic bubble, given by Eq. (9), vanish exactly. Therefore, the impurity averaged correlator of the orbital magnetic fields $K^M_{+-}(i\nu_n)$ is given by the same expression as in the clean case, Eq. (8), with unchanged angular part K_Ω, Eq. (15), but with

$$S(i\nu_n, \mathbf{k}_1, \mathbf{k}_2) = T \sum_m G(\mathbf{k}_1, i\omega_m + i\nu_n) G(\mathbf{k}_2, i\omega_m), \tag{22}$$

expressed through the impurity averaged Green's functions:

$$G(\mathbf{k}, i\omega_m) = [i\omega_m - \xi_{\mathbf{k}} + i\,\mathrm{sgn}(\omega_m)/(2\tau)]^{-1}. \tag{23}$$

Here, $1/(2\tau) = \pi N(\mu) n_{imp} V^2_{imp}$ is the elastic scattering time, where n_{imp} is the impurity density and V_{imp} is the Fourier transform of the impurity potential. The Matsubara summation in Eq. (22) can be conveniently performed using the spectral representation for the Green's functions. The result is

$$\lim_{\omega' \to 0} \frac{\mathrm{Im}\, S(\omega', \xi_1, \xi_2)}{\omega'} = \pi \int_{-\infty}^{+\infty} d\omega f'(\omega) A(\xi_1, \omega) A(\xi_2, \omega), \tag{24}$$

where $A(\xi, \omega) \equiv A(\xi_{\mathbf{k}}, \omega) = -\mathrm{Im}\, G(\mathbf{k}, i\omega_m \to \omega + i0^+)/\pi$ is the electronic spectral function in the dirty normal metal, which is sharply peaked around $\xi = \omega$. The presence of $f'(\omega)$ in Eq. (24) then allows us to switch to the ξ integration with the infinite limits in the expression for the correlator $K^R_{+-}(\omega)$ as in the clean case [see Eqs. (13) and (18)]. Now, these ξ integrations give $\int_{-\infty}^{+\infty} d\xi_1 d\xi_2 A(\omega, \xi_1) A(\omega, \xi_2) K_\Omega(\xi_1, \xi_2) = \frac{1}{3} \ln(\tau\bar{\mu})$, which leads to the following final result:

$$\frac{1}{T_1 T} = \frac{2\pi}{3} [4\pi\gamma_n\gamma_e N(\mu)]^2 \ln(\tau\bar{\mu}). \tag{25}$$

We see that $1/\tau$ replaces the frequency ω, which was present in the expression for the relaxation rate for the clean case [see Eq. (19)], and thus removes the divergence at $\omega \to 0$.

IV. COMPARISON OF THE ORBITAL CONTRIBUTION TO $1/T_1$ WITH OTHER CONTRIBUTIONS

We extend our analysis to include all the hyperfine magnetic fields of Eq. (1), using the same model for electrons as in the previous section. In the plane-wave basis [see Eq. (6)], one has the following for three-dimensional system:

$$\mathbf{h}_{F\text{-}c} = -\frac{4\pi}{3} \frac{\gamma_e}{V} \sum_{\mathbf{k},\mathbf{q}} \boldsymbol{\sigma}_{\alpha\beta} c^{\dagger}_{\mathbf{k}\alpha} c_{\mathbf{k}-\mathbf{q},\beta}, \tag{26}$$

$$\mathbf{h}_{s\text{-}d} = 2\pi \frac{\gamma_e}{V} \sum_{\mathbf{k},\mathbf{q}} \left[\frac{\mathbf{q}(\mathbf{q}\cdot\boldsymbol{\sigma}_{\alpha\beta})}{q^2} - \frac{\boldsymbol{\sigma}_{\alpha\beta}}{3} \right] c^{\dagger}_{\mathbf{k}\alpha} c_{\mathbf{k}-\mathbf{q},\beta}, \tag{27}$$

$$\mathbf{h}_{orb} = 4\pi \mathrm{i} \frac{\gamma_e}{V} \sum_{\mathbf{k},\mathbf{q}} \frac{\mathbf{q}\times\mathbf{k}}{q^2} c^{\dagger}_{\mathbf{k}\alpha} c_{\mathbf{k}-\mathbf{q},\alpha}. \tag{28}$$

In these equations, the summations over all repeated spin component indices are assumed. We observe that the operator of the Fermi-contact effective magnetic field, $\mathbf{h}_{F\text{-}c}$, and the operator of the spin-dipole effective magnetic field, $\mathbf{h}_{s\text{-}d}$, can be combined into a single object, for which the $\mathbf{q}$ dependence inside the sums appears only through the transverse projector $\delta_{ij} - q_i q_j/q^2$. This simplifies the next step of the relaxation rate calculation, which is to evaluate the Matsubara correlator K^M_{+-}. We obtain

$$K^M_{+-}(i\nu_n) = 2\frac{(2\pi\gamma_e)^2}{V^2} \sum_{\mathbf{k},\mathbf{q}} \left[2 - \frac{q_+ q_-}{q^2} + 4\frac{(\mathbf{q}\times\mathbf{k})_+ (\mathbf{q}\times\mathbf{k})_-}{q^4} \right] S(i\nu_n, \mathbf{k}, \mathbf{k}-\mathbf{q}). \tag{29}$$

In the clean case, the quantity S is given by Eq. (11). In Eq. (29), the first two terms in the square brackets represent the combined contribution of the Fermi-contact and the spin-dipole hyperfine interactions. The third term is the contribution due to the orbital hyperfine interaction, which was considered before. It is the same as in Eq. (8) but written with the change of the summation variables $(\mathbf{k}_1, \mathbf{k}_2) \to (\mathbf{k}, \mathbf{q})$, where $\mathbf{k} = (\mathbf{k}_1 + \mathbf{k}_2)/2$ and $\mathbf{q} = \mathbf{k}_1 - \mathbf{k}_2$. In this form, the behavior of different contributions as functions of $q = |\mathbf{q}|$ is clearly displayed. In fact, both Fermi-contact and spin-dipole contributions depend on q through S function only, while the orbital contribution contains the additional factor $1/q^2$.

The divergence in $(1/T_1)_{orb}$ in the clean system appears now as the divergence of the $\mathbf{q}$ sum as $q\to 0$. On the other hand, the spin-dipole hyperfine interaction produces a finite relaxation rate. This result contradicts expectations[4] that spin-dipole and orbital hyperfine interactions should bring about similar contributions to $1/T_1$, because in the real space, they both vary with the distance from the nucleus as $1/r^3$ [see Eq. (1)].

V. GENERAL CHARACTER OF THE DIVERGENCE OF $(1/T_1)_{orb}$ IN CLEAN METALS

In this section, we demonstrate that the divergence of $1/T_1$ in a clean metal is quite general and is not an artifact of the free-electron model we used in previous sections. We now concentrate on the orbital hyperfine interaction that is responsible for the effect. First, we consider the electron gas in an arbitrary periodic potential and show that the divergence does not disappear. Then, we relate the correlator of orbital magnetic fields to the current-current correlator and therefore to the electrical conductivity. This formulation allows one to treat an arbitrary electronic dispersion quite generally. The divergence is shown to be a consequence of the behavior of the static nonuniform conductivity in the long-wavelength limit.

A. The electron gas in a periodic potential

Now, add to the Hamiltonian of the clean Fermi gas a periodic potential, and consider the effect it has on the correlator of orbital magnetic fields in the definition of $1/T_1$ in Eq. (2). The solutions to the corresponding Schrödinger equation are the Bloch functions, which can be used as the basis for the second-quantized description:

$$\psi_\sigma(\mathbf{r}) = \frac{1}{\sqrt{V}}\sum_n \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) c_{n\mathbf{k}\sigma}, \tag{30}$$

where n enumerates the electron bands and the wave vector $\mathbf{k}$ is now limited to the first Brillouin zone. Functions $u_{n\mathbf{k}}(\mathbf{r})$ are periodic in $\mathbf{r}$ and can be expanded in the Fourier series:

$$u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} U_{n\mathbf{G}}(\mathbf{k}) e^{i\mathbf{G}\cdot\mathbf{r}}, \tag{31}$$

where $\mathbf{G}$ is a reciprocal-lattice vector. The operator of the effective magnetic field at the origin, $\mathbf{R}=0$, due to the electron orbital motion has the form

$$\mathbf{h} = \gamma_e \frac{4\pi i}{V}\sum_{\mathbf{k}\mathbf{k}'}\sum_{\mathbf{G}\mathbf{G}'} \frac{(\mathbf{k}+\mathbf{G})\times(\mathbf{k}'+\mathbf{G}')}{(\mathbf{k}+\mathbf{G}-\mathbf{k}'-\mathbf{G}')^2} \sum_{nn'} U_{n\mathbf{G}}(\mathbf{k})^* U_{n'\mathbf{G}'}(\mathbf{k}') \times \sum_\sigma c^\dagger_{n\mathbf{k}\sigma} c_{n'\mathbf{k}'\sigma}. \tag{32}$$

This expression is to be compared with Eq. (7). The Green's functions of the electrons in a periodic potential are diagonal in $\mathbf{k}$, as well as in the spin and band indices. Using these properties, we calculate the correlator of the orbital magnetic fields at the location of the nucleus. The expression for the relaxation time in the limit $\omega\to 0$ can be written as follows:

$$\frac{1}{T_1 T} = 2\pi \frac{(4\pi\gamma_n\gamma_e)^2}{V^2} \sum_{\mathbf{k}_1\mathbf{k}_2}\sum_{n_1 n_2} \delta(\varepsilon_{n_1,\mathbf{k}_1} - \varepsilon_{n_2,\mathbf{k}_2}) f'(\varepsilon_{n_2,\mathbf{k}_2}) \sum_{\{\mathbf{G}\}} \mathcal{U}^4 \mathbf{K}_{1+}\mathbf{K}_{2-}, \tag{33}$$

where $\{\mathbf{G}\}=\{\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3,\mathbf{G}_4\}$ and

$$\mathcal{U}^4 = U^*_{n1,\mathbf{G}_1+\mathbf{G}_2}(\mathbf{k}_1) U_{n1,\mathbf{G}_4}(\mathbf{k}_1) U^*_{n2,\mathbf{G}_3+\mathbf{G}_4}(\mathbf{k}_2) U_{n2,\mathbf{G}_2}(\mathbf{k}_2), \tag{34}$$

$$\mathbf{K}_1 = \frac{(\mathbf{k}_1-\mathbf{k}_2+\mathbf{G}_1)\times(\mathbf{k}_2+\mathbf{G}_2)}{(\mathbf{k}_1-\mathbf{k}_2+\mathbf{G}_1)^2}, \tag{35}$$

$$\mathbf{K}_2 = -\frac{(\mathbf{k}_2-\mathbf{k}_1+\mathbf{G}_3)\times(\mathbf{k}_1+\mathbf{G}_4)}{(\mathbf{k}_2-\mathbf{k}_1+\mathbf{G}_3)^2}. \tag{36}$$

Equation (33) is an exact expression. We show that it contains an infinite term. To separate the divergent contribution, we restrict the sums in Eq. (33) by the conditions $\mathbf{G}_1=\mathbf{G}_3=0$ and $n_1=n_2$ and change the summation variables $\mathbf{k}_1=\mathbf{k}+\mathbf{q}/2$ and $\mathbf{k}_2=\mathbf{k}-\mathbf{q}/2$. Then, we perform the small-$\mathbf{q}$ expansion of the arguments of the delta function and f' in Eq. (33), as well as of the $\mathcal{U}^4$ of Eq. (34). Accounting only for the leading term in these expansions, Eq. (33) is reduced to

$$\frac{1}{T_1 T} = 2\pi \frac{(4\pi\gamma_n\gamma_e)^2}{V^2} \sum_{\mathbf{k},\mathbf{q}}\sum_n \delta(\mathbf{q}\cdot\mathbf{v}_n(\mathbf{k})) f'(\varepsilon_n(\mathbf{k})) \frac{m^2}{q^4} [\mathbf{q}\times\mathbf{v}_n(\mathbf{k})]_+ [-\mathbf{q}\times\mathbf{v}_n(\mathbf{k})]_-, \tag{37}$$

where we have used the following expression[11] for velocity of the band electrons:

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{m}\sum_{\mathbf{G}} (\mathbf{k}+\mathbf{G}) |U_{n\mathbf{G}}(\mathbf{k})|^2 = \frac{\partial\varepsilon_n(\mathbf{k})}{\partial\mathbf{k}}. \tag{38}$$

To estimate the $\mathbf{q}$ sum in Eq. (37), we change it, for each band n, to the integral over the sphere of an appropriate volume. The integration over $q=|\mathbf{q}|$ extends from $q_{min}=0$ to $q_{max}\simeq 2q_{F,n}$, where $q_{F,n}$ is of the order of the average separation between two points on the Fermi surface in the n band. The final result has the form

$$\frac{1}{T_1 T} = \left(\frac{e\gamma_n}{c}\right)^2 \frac{4\pi}{V}\sum_{\mathbf{k},n} D_n f'(\varepsilon_n(\mathbf{k})) \frac{[\mathbf{v}_n(\mathbf{k})]^2 + [\hat{z}\cdot\mathbf{v}_n(\mathbf{k})]^2}{|\mathbf{v}_n(\mathbf{k})|}, \tag{39}$$

where $D_n=\ln(2q_{F,n}/q_{min})$ is the divergent factor. As long as the electrons do not interact with each other, $q_{min}=0$ at any temperature. The reason is that the delta function, which appears in Eqs. (33) and (37) and ultimately brings in the divergence is, in fact, the electronic spectral function of the noninteracting system. Thus, the same logarithmic divergence as found in Sec. III for free electrons appears here. For finite samples of the linear size L, we have $q_{min}=1/L$. When impurities are present, from the result of Sec. III C, it is expected that $q_{min}\simeq 1/(v_F\tau)$ which is, in general, different for different bands. In the next section, we confirm this form of q_{min} for one band with an arbitrary electronic dispersion.

To conclude this section, we note that for band electrons we found the logarithmically divergent contribution to $(1/T_1)_{orb}$ and the factor in front of it [see Eq. (39)], which depends only on the averages of the Fermi velocities and does not involve the position of the nuclear spin in the unit cell.

B. Expressing $K^R_{+-}(\omega,\mathbf{q})$ in terms of the current-current correlator

We now use another method to demonstrate the singular behavior of the nuclear magnetic relaxation rate due to orbital hyperfine interaction. It also allows us to obtain a useful expression for $(1/T_1)_{orb}$ for an anisotropic metal. The idea, first used by Lee and Nagaosa,[4] is to express the correlator of effective orbital magnetic fields $K^R_{+-}(\omega,\mathbf{R}=0)=\Sigma_{\mathbf{q}}K^R_{+-}(\omega,\mathbf{q})$, which appears in Eq. (4), through the current-current correlator and, consequently, through the nonuniform electrical dc conductivity.

The fluctuating magnetic fields are calculated using Maxwell's equation, assuming that the electric currents are given: $\nabla\times\mathbf{h}(\omega,\mathbf{r})=[4\pi\mathbf{j}(\omega,\mathbf{r})-i\omega\mathbf{E}(\omega,\mathbf{r})]/c$. In metals, it is a good approximation to neglect the second term containing the electric field $\mathbf{E}$. Then, applying the Fourier transform to find the magnetic field, we get $\mathbf{h}(\omega,\mathbf{q})=(4\pi i/c)[\mathbf{q}\times\mathbf{j}(\omega,\mathbf{q})]/q^2$, and the required retarded correlator of the orbital magnetic fields is given by the following expression:

$$K^R_{+-}(\omega,\mathbf{q})=\left(\frac{4\pi}{c}\right)^2\frac{q_m q_k}{q^4}[\epsilon_{xmi}\epsilon_{xkj}+\epsilon_{ymi}\epsilon_{ykj}-i\epsilon_{zlp}\epsilon_{lmi}\epsilon_{pkj}]\Pi_{ij}(\omega,\mathbf{q}), \tag{40}$$

where $\Pi_{ij}(\omega,\mathbf{q})$ is the retarded current-current correlator, ϵ_{ijk} is the totally antisymmetric tensor, and summation over the repeated indices, which run through x, y, and z, is assumed. In the end, we are interested in the situation when the constant external magnetic field is absent. Therefore, we take the Π_{ij} tensor to be symmetric, namely, $\Pi_{ij}=\Pi_{ji}$. In this case, the third term in the square brackets in Eq. (40) vanishes.

In general, Π_{ij} contains both paramagnetic and diamagnetic terms. However, for the calculation of $1/T_1$, we need only $\mathrm{Im}\,\Pi_{ij}$ [see Eq. (2)], and the diamagnetic part, which is real, drops out. The retarded current-current correlator can be related to the electrical conductivity tensor.[10] Using $\mathrm{Im}\,\Pi_{ij}(\omega,\mathbf{q})=-\mathrm{Re}[\omega\sigma_{ij}(\omega,\mathbf{q})]$, we obtain from Eq. (40) the following expression:

$$\lim_{\omega\to 0}\frac{\mathrm{Im}\,K^R_{+-}(\omega,\mathbf{q})}{\omega}=-\left(\frac{4\pi}{c}\right)^2\frac{1}{q^4}\mathrm{Re}[(q_x^2+q_y^2)\sigma_{zz}+q_z^2(\sigma_{xx}+\sigma_{yy})-2q_xq_z\sigma_{xz}-2q_yq_z\sigma_{yz}], \tag{41}$$

where arguments of the conductivity tensor $\sigma_{ij}(\omega=0,\mathbf{q})$ are not shown explicitly. The expression (41) has to be inserted in Eq. (4).

In the simple case of an isotropic system, the conductivity tensor is diagonal in the coordinate frame with the z axis parallel to $\mathbf{q}=(q,\theta,\phi)$, namely, $\mathrm{Re}\,\sigma_{ij}(q)=\mathrm{diag}[\sigma_\perp(q),\sigma_\perp(q),\sigma_\parallel(q)]$. This tensor should be transformed to the coordinate frame defined by the initial orientation of the nuclear magnetic moment (i.e., $\hat{z}\|\mathbf{H}$) using an appropriate rotation of coordinate frame and then inserted into Eqs. (4) and (41). The final expression for nuclear magnetic relaxation rate contains only the perpendicular conductivity $\sigma_\perp(q)$:

$$\frac{1}{T_1T}=\frac{8}{3}\left(\frac{\gamma_n}{c}\right)^2\int_0^\infty dq\sigma_\perp(q). \tag{42}$$

It is known from the theory of the anomalous skin effect[11] that in a clean metal, the nonuniform conductivity $\sigma_\perp(q)$ behaves as $1/q$ at small wave vectors q. This leads to the logarithmic divergence for the nuclear magnetic relaxation rate $(1/T_1)_{orb}$.

In order to clarify this statement and obtain a useful formula for $(1/T_1)_{orb}$ for electrons with an arbitrary dispersion in the presence of impurities, the q-dependent electric conductivity tensor is now evaluated using the kinetic equation approach. The electric current is given by

$$\mathbf{j}(\omega,\mathbf{q})=2e\sum_{\mathbf{k}}\mathbf{v}_k n(\omega,\mathbf{k},q), \tag{43}$$

where $\mathbf{v}\equiv\mathbf{v}_\mathbf{k}=\partial\xi_\mathbf{k}/\partial\mathbf{k}$ is the electron group velocity, and the factor of 2 is due to the spin. The distribution function $n(\omega,\mathbf{k},\mathbf{q})=f(\xi_\mathbf{k})+\delta n(\omega,\mathbf{k},\mathbf{q})$ is a sum of the equilibrium Fermi distribution f and a correction δn proportional to the small perturbing electric field $\mathbf{E}(\mathbf{q})=\mathbf{E}$. Within the relaxation time approximation for the impurity collision integral, we have

$$[1/\tau-i(\omega-\mathbf{q}\cdot\mathbf{v})]\delta n=-e(\partial f/\partial\xi)\mathbf{v}\cdot\mathbf{E}, \tag{44}$$

leading to

$$\delta n(\omega,\mathbf{k},q)=-\frac{e\tau(\partial f/\partial\xi)\mathbf{v}\cdot\mathbf{E}}{1-i\tau(\omega-\mathbf{q}\cdot\mathbf{v})}. \tag{45}$$

The final result for the conductivity reads

$$\sigma_{ij}(\omega,\mathbf{q})=2e^2\int_{-\mu}^\infty d\xi\left(-\frac{\partial f}{\partial\xi}\right)\oint\frac{d\Omega_\mathbf{k}}{4\pi}N(\xi,\Omega_\mathbf{k})\times\frac{\tau(1+i\tau\omega)v^iv^j}{1+\tau^2(\omega-\mathbf{q}\cdot\mathbf{v})^2}. \tag{46}$$

This form of $\sigma_{ij}(\omega,\mathbf{q})$ is valid for an arbitrary electronic band $\xi_\mathbf{k}$, which enters through the angle dependent density of electronic states $N(\xi,\Omega_\mathbf{k})$. Using the form of the conductivity tensor form Eq. (46) in Eq. (41), we arrive at the following expression for $1/T_1$ due to the orbital hyperfine interaction:

$$\frac{1}{T_1T}=\frac{8}{\tau}\left(\frac{e\gamma_n}{c}\right)^2\int_0^\infty\frac{dq}{2\pi^2}\int_{-\mu}^\infty d\xi\left(-\frac{\partial f}{\partial\xi}\right)\times\left\langle N(\xi,\Omega_\mathbf{k})\frac{v_z^2+v^2\hat{q}_z^2-2(\hat{q}_zv_z)(\hat{\mathbf{q}}\cdot\mathbf{v})}{1/\tau^2+q^2(\hat{\mathbf{q}}\cdot\mathbf{v})^2}\right\rangle_{\Omega_\mathbf{k},\Omega_\mathbf{q}}, \tag{47}$$

where the z direction is set by the initial orientation of the

TABLE I. Numerical values of various contribution to $1/(T_1T)$ [in the units $(\mathrm{K\,s})^{-1}$] for some metals obtained as described in the text. For Sr_2RuO_4, the data are related to ^{17}O in the position O2, which is out of the conducting basal plane.

Material	$\left.\frac{1}{T_1T}\right\|_{F\text{-}c}$	$\left.\frac{1}{T_1T}\right\|_{orb}^{l\text{-}r}$	$\left.\frac{1}{T_1T}\right\|_{orb}^{loc}$	$\frac{(1/T_1)_{orb}^{l\text{-}r}}{(1/T_1)_{F\text{-}c}}$	$\frac{(1/T_1)_{orb}^{l\text{-}r}}{(1/T_1)_{\mathrm{orb}}^{loc}}$
Li	0.019	4.05×10^{-4}	1.14×10^{-3}	2.2×10^{-2}	0.37
Na	0.213	1.20×10^{-4}	0	5.6×10^{-4}	
Sr_2RuO_4	1.1×10^{-4}	1.3×10^{-5}	8.5×10^{-4}	0.12	0.015

nuclear polarization. The angular brackets denote averaging over both **k**- and **q**-angular variables. The magnitude of the group velocity $\mathbf{v}\equiv\mathbf{v}_{\mathbf{k}}$ is fixed at the Fermi velocity by the derivative of the Fermi distribution. For an anisotropic system, the Fermi velocity is angle dependent. For electrons with quadratic dispersion, the calculation of $1/T_1$ based on Eq. (47) gives the result identical to that given by Eq. (42).

The q integral should be cut off by $2q_F$ at the upper limit, which is necessary in the present approach due to the fact that the kinetic equation does not capture the large-q behavior of the nonuniform conductivity correctly. On the other hand, the q integral is convergent at the lower limit. The clean limit corresponds to $1/\tau\to0$. In this case, the right-hand side of Eq. (47) contains the following δ function:

$$\frac{1/\tau}{1/\tau^2+(\mathbf{q}\cdot\mathbf{v})^2}\to\pi\delta[q(\hat{\mathbf{q}}\cdot\mathbf{v})]=\frac{\pi}{q}\delta[\hat{\mathbf{q}}\cdot\mathbf{v}]. \tag{48}$$

After the integration over $\Omega_{\mathbf{q}}$ is performed, we can see explicitly that the remaining q integral diverges as $1/q$ at the lower limit.

VI. DISCUSSION

It was found experimentally[12] that the nuclear magnetic relaxation in many metals is dominated by the Fermi-contact hyperfine interaction, for which $(1/T_1T)_{F\text{-}c}=(4\pi k_B/9)\times[4\pi\gamma_n\gamma_e\hbar^2N(\mu)]^2\langle|u_{\mathbf{k}}(\mathbf{0})|^2\rangle_{FS}^2$ (in this section, we restore k_B and $\hbar$). The situations where this is not so and the contributions of hyperfine orbital and/or spin-dipole interactions are significant are worthy of detailed analysis. Loosely speaking, the physical reason for the large magnitude of the Fermi-contact interaction is that the conduction band usually contains a large portion of the atomic s orbitals which give a large contribution to the electronic spin density at the nuclear site, specified by the overlap factor $\langle|u_{\mathbf{k}}(\mathbf{0})|^2\rangle_{FS}^2$. The relative importance of the other hyperfine interactions increases when the density of states at the Fermi level is dominated by the d and f bands as in transition metals and their compounds,[13–16] or when the conduction band happens to be almost free of s orbitals.[17–19]

We would like to emphasize that both orbital and spin-dipole hyperfine contributions to $1/T_1$ commonly discussed in the literature are, in fact, the "local" contributions which we did not touch upon in this paper. It is usually argued that since the orbital and spin-dipole hyperfine interactions decay fast enough with distance [they both vary as $1/r^3$, see Eq. (1)], the nuclear spin of a given atom is only affected by the magnetic fields generated by the electron orbitals centered at this very atom. In contrast, the contribution we analyzed in the previous sections comes from large distances. It has to be added to the local orbital contribution.

Below, we attempt to estimate the magnitude of the relaxation rate due to the long-range part of the orbital hyperfine interaction [denoted as $(1/T_1)_{orb}^{l\text{-}r}$] in some metals, and compare it with the contributions due to local part of the orbital hyperfine interaction [denoted as $(1/T_1)_{orb}^{loc}$] and Fermi-contact interaction. We first consider alkaline metals. In this case, the estimates based on the quadratic dispersion produce the correct order of magnitude for $(1/T_1)_{F\text{-}c}$, as compared to experimental values. This makes our further estimates of $(1/T_1)_{orb}^{l\text{-}r}$ trustworthy. Next, we discuss Sr_2RuO_4, the compound which is likely to be suitable for studing the orbital nuclear magnetic relaxation due to the peculiarities of its electronic structure. Additionally, in this case, very clean samples with a long mean free path are available. The results of our estimates are summarized in Table I.

A. Alkaline metals

We consider Na and Li metals. For both of them, the Fermi surface lies within the first Brillouin zone and the electronic dispersion can be taken as $\varepsilon(\mathbf{k})=\hbar^2\mathbf{k}^2/(2m^*)$ for all energies up to the Fermi level.[20] This means that the results of Sec. III C are directly applicable. Numerical values are $m^*/m=1.45$, $q_F=1.3\times10^8$ cm^{-1} for Li and $m^*/m=0.98$, $q_F=9.2\times10^7$ cm^{-1} for Na, as quoted in Ref. 21. The nuclear magnetic moments are $3.26\mu_N$ for ^{7}Li and $2.22\mu_N$ for ^{23}Na, where μ_N is the nuclear magneton.

In the case of the Fermi-contact interaction, the necessary overlap factors were obtained using the results of the first-principles calculations of Kohn[22] and Kjeldaas and Konh:[23] 16^2 for Li and 144^2 for Na. Thus, our theoretical estimate for Li is $(1/T_1T)_{F\text{-}c}\approx0.019$ $(\mathrm{K\,s})^{-1}$, which is to be compared to the experimental values 0.023 $(\mathrm{K\,s})^{-1}$ of Ref. 24 or 0.06 $(\mathrm{K\,s})^{-1}$ of more recent work in Ref. 25. In the case of Na, our theoretical estimate is $(1/T_1T)_{F\text{-}c}\approx0.213$ $(\mathrm{K\,s})^{-1}$, while the experimental value from Ref. 24 is 0.196 $(\mathrm{K\,s})^{-1}$.

The expression for the nuclear magnetic relaxation due to the long-range part of orbital hyperfine interaction for quadratic dispersion can be obtained from Eqs. (25) and (39) as follows: $(1/T_1T)_{orb}^{l\text{-}r}=(2\pi/3)[4\pi\gamma_n\gamma_e\hbar^2N(\mu)]^2(m/m^*)^2$

$\ln(2q_F l)$. For our estimates, we use $l=10^{-5}$ cm and obtain that $(1/T_1T)^{l\text{-}r}_{orb}=4.05\times10^{-4}$ (K s)$^{-1}$ in Li and 1.20×10^{-4} (K s)$^{-1}$ in Na. We present here a useful formula that defines the ratio of the two discussed relaxation rates:

$$\frac{(1/T_1)^{l\text{-}r}_{orb}}{(1/T_1)_{F\text{-}c}}=\frac{3}{2}\left(\frac{m}{m^*}\right)^2\frac{\ln(2q_F l)}{\langle|u_{\mathbf{k}}(\mathbf{0})|^2\rangle^2_{FS}}. \tag{49}$$

For Li this ratio is 2.2%, while for Na it is 0.056%. Such large difference is explained by the fact[22] that the wave function of Li at the Fermi level contains about 73% of the $l=1$ spherical harmonic and only 20% of the spherically symmetric $l=0$ harmonic.

The magnitude of the local part of the orbital magnetic nuclear relaxation in both metals was obtained experimentally by Hecht and Redfield[26] from the measurements of the Overhauser effect. They found that $[(1/T_1)^{loc}_{orb}]/[(1/T_1)_{F\text{-}c}]\approx0.06\pm0.03$ in Li, while there is no local contribution in Na. Thus, the local and long-range contributions to $1/(T_1)_{orb}$ appear comparable in Li, and both are quite noticeable.

It appears that metallic Li could be the system of choice to look for the long-range orbital contribution to the nuclear magnetic relaxation. One can use the characteristic logarithmic dependence of $(1/T_1T)^{l\text{-}r}_{orb}$ on the impurity concentration.

It is worth noting that the NMR experiments are often done with collections of relatively small metallic particles.[24] This is dictated by the experimental requirement that a large volume of the sample should be subjected to a radio-frequency magnetic field which only penetrates within the skin depth. Such experimental setup would limit the magnitude of the long-range orbital effect even for the very clean metals.

B. Sr_2RuO_4

The electronic properties of this material are well studied,[27] both theoretically and experimentally, in connection with unconventional superconductivity, which appears at temperature of about 1 K. For the purpose of a rough estimate for the long-range orbital magnetic relaxation rate, we use the model of three two-dimensional bands, with cylindrical Fermi surfaces and $q_{F,1}=3.04\times10^7$ cm^{-1}, $q_{F,2}=6.22\times10^7$ cm^{-1}, and $q_{F,3}=7.53\times10^7$ cm^{-1}, as quoted in Ref. 27. The lattice parameter along the tetragonal symmetry axis is $a_3=1.27\times10^{-7}$ cm. To obtain a convenient formula from Eq. (39), we assume that $v_z^2/(v_x^2+v_y^2)\ll1$ and the cutoff wave vector q_{min} is the same for all bands. Using the density of the electronic states for each band in the form $N_{2D}(\mu)=m^*/(2\pi\hbar^2a_3)$ and taking $\hat{z}$ along the tetragonal symmetry axis, we obtain

$$\left.\frac{1}{T_1T}\right|^{r\text{-}l}_{orb}=\frac{2k_B}{\hbar}\left(\frac{e\gamma_n}{c}\right)^2\sum_{n=1}^{3}\frac{q_{F,n}}{a_3}\ln(2q_{F,n}l). \tag{50}$$

The best samples of Sr_2RuO_4 used in the de Haas–van Alphen experiments[27] are very clean, with the elastic mean free path reaching 3×10^{-5} cm. For the relaxation of the magnetic moment of ^{17}O nucleus, with $\gamma_n=-3.63\times10^3$ (s G)$^{-1}$, we obtain $(1/T_1T)^{r\text{-}l}_{orb}=1.3\times10^{-5}$ (K s)$^{-1}$. This value can be compared with the local part of the orbital nuclear relaxation rate. For example, from the band-structure calculations, Pavarini and Mazin[19] found that $(1/T_1T)^{loc}_{orb}=8.5\times10^{-4}$ (K s)$^{-1}$ for the so-called O2 oxygen, located out of the basal conducting planes. The ratio is $[(1/T_1)^{l\text{-}r}_{orb}]/[(1/T_1)^{loc}_{orb}]=0.015$.

The O2 position of the oxygen is very favorable for studies of the long-range orbital mechanism of the nuclear magnetic relaxation, because the local orbital contribution is much smaller than for the other oxygen site, O1. The Fermi-contact contribution is also numerically quite small for the O2 position, $(1/T_1T)_{F\text{-}c}=1.1\times10^{-4}$ (K s)$^{-1}$ as calculated in Ref. 19. It is still larger than the long-range orbital contribution, but not substantially: $[(1/T_1)^{l\text{-}r}_{orb}]/[(1/T_1)_{F\text{-}c}]=0.12$.

Comparison of our predictions with experiments is complicated by the fact that the experimental values of $1/T_1T$ for O2 oxygen[28] are 2 orders of magnitude greater than values given by the band-structure calculations. The experimental results necessarily include the effect of electronic correlations, which are strong in Sr_2RuO_4. Such effects were completely ignored in our discussion of $(1/T_1)^{r\text{-}l}_{orb}$ in this paper.

C. Concluding remarks

We would like to point out that besides the elastic impurity scattering, other scattering mechanisms for electrons should also affect to $(1/T_1)_{orb}$. One expects that inelastic scattering, for example, by phonons, should lead to $1/(T_1T)\sim\ln T$, because of the temperature dependence of the inelastic-scattering rate.

The NMR relaxation mechanism through the orbital hyperfine interaction that we have discussed in this paper is quite general. It is not limited to metals and should exist in any system with mobile charge carriers. On the basis of Eq. (49), one expects that a small effective mass of the charge carriers should significantly enhance the effect. Small masses are typically found in semiconductors.[29] In such systems, the NMR techniques have also been very successful, though the analysis should be modified compared to the case of metals.[30]

Finally, we would like to comment on calculations of $(1/T_1)_{orb}$ from the first principles using band-structure methods. These calculations typically use the expansions in a set of basis functions that involve the spherical harmonics centered at the nuclear site, and an appropriate radial part obtained from the solution of the Schrödinger equation inside the Wigner-Seitz sphere or the muffin-tin sphere.[15,16,18] The series in the orbital quantum number l is truncated at some stage of the computation based on an empirical estimate of convergence. However, we have demonstrated in this paper, that this expansion is expected to diverge as $\ln l$, which is usually difficult to capture numerically. The presence of this divergence calls for a careful examination of the conditions used to justify the truncation of the l expansion.

In conclusion, in this paper, we have discussed the nuclear magnetization relaxation rate due to the orbital hyperfine interaction of nuclear spins with itinerant electrons. For an infinite clean metal, $(1/T_1)_{orb}$ would become divergent at zero temperature. The reason for the divergence is that the

total fluctuating magnetic field created by all the electrons at the site of a given nucleus contains a contribution from distant electrons. The divergence is removed when there are scattering mechanisms in the system. At low temperatures, the scattering is predominantly elastic. In this case, $(1/T_1)_{orb}$ depends logarithmically on impurity concentration. Based on our estimates, it seems to be feasible to observe this effect, e.g., in metallic Li.

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APPENDIX: IMPURITY AVERAGED CORRELATOR OF ORBITAL MAGNETICFIELDS

The operator of the magnetic field created by the orbital motion of the electrons at $\mathbf{R}=0$ is given in Eq. (7). Here, we want to compute the impurity averaged correlator of such orbital magnetic fields at a given Matsubara frequency $i\nu_n$. This quantity can be written as follows:

$$\langle K^M_{+-}(i\nu_n)\rangle_{imp} = \frac{(4\pi\gamma_e)^2}{V^2}\sum_{\{\mathbf{k}\}}\frac{(\mathbf{k}_1\times\mathbf{k}_1')_+}{(\mathbf{k}_1-\mathbf{k}_1')^2}\frac{(\mathbf{k}_2\times\mathbf{k}_2')_-}{(\mathbf{k}_2-\mathbf{k}_2')^2} \times\langle\mathcal{B}(i\nu_n,\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2')\rangle_{imp}, \tag{A1}$$

where $\{\mathbf{k}\}\equiv\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2'$ and $\langle\cdots\rangle_{imp}$ means the average over impurity configurations. The electronic bubble $\mathcal{B}(i\nu_n,\mathbf{k}_1,\mathbf{k}_1',\mathbf{k}_2,\mathbf{k}_2')$ is defined in Eq. (9). For the following discussion, it is more convenient to use a different set of wave-vector variables, namely, $\mathbf{Q}_a=(\mathbf{k}_a+\mathbf{k}_a')/2$ and $\mathbf{q}_a=\mathbf{k}_a-\mathbf{k}_a'$ with $a=1,2$.

The impurity averaging restores the translational invariance of the system, and the result for the electronic bubble, after the spin summation is performed, can be written as

$$\langle\mathcal{B}(i\nu_n,\mathbf{Q}_1,\mathbf{q}_1,\mathbf{Q}_2,\mathbf{q}_2)\rangle_{imp} = -2\delta_{\mathbf{q}_1,-\mathbf{q}_2}\mathcal{S}_{\mathbf{Q}_1,\mathbf{Q}_2}(i\nu_n,\mathbf{q}_1).$$

The function $\mathcal{S}$ has the following general structure:[31]

$$\mathcal{S}_{\mathbf{Q}_1,\mathbf{Q}_2}(i\nu_n,\mathbf{q}) = T\sum_m G(\mathbf{Q}_{1+},i\omega_{m+})G(\mathbf{Q}_{1-},i\omega_m)\Big[\delta_{\mathbf{Q}_1,\mathbf{Q}_2} + \frac{1}{V}\Gamma_{\mathbf{Q}_1,\mathbf{Q}_2}(\mathbf{q},i\omega_m,i\nu_n)G(\mathbf{Q}_{2+},i\omega_{m+})G(\mathbf{Q}_{2-},i\omega_m)\Big], \tag{A2}$$

where $\mathbf{Q}_{a\pm}\equiv\mathbf{Q}_a\pm\mathbf{q}/2$ for $a=1,2$, $\omega_{m+}\equiv\omega_m+\nu_n$, and $G(\mathbf{k},i\omega_m)$ is the impurity averaged Green's function defined in Eq. (23). The first term in the square brackets in Eq. (A2) corresponds to the bare bubble contribution to $\mathcal{S}$. Here, the interaction with impurities is included through the electronic Green's functions only. The second term in the square brackets in Eq. (A2) represents the vertex corrections, which are defined in terms of the four-point vertex function $\Gamma_{\mathbf{Q}_1,\mathbf{Q}_2}(\mathbf{q},i\omega_m,i\nu_n)$. This function satisfies the following integral equation:[31]

$$\Gamma_{\mathbf{Q}_1,\mathbf{Q}_2} = U_{\mathbf{Q}_1,\mathbf{Q}_2} + \frac{1}{V}\sum_{\mathbf{Q}} U_{\mathbf{Q}_1,\mathbf{Q}}G(\mathbf{Q}_+,i\omega_{m+})G(\mathbf{Q}_-,i\omega_m)\Gamma_{\mathbf{Q},\mathbf{Q}_2}, \tag{A3}$$

where the dependence of Γ and U on $\mathbf{q},i\omega_m$ and $i\nu_n$ is not shown explicitly.

The function $U_{\mathbf{Q}_1,\mathbf{Q}_2}(\mathbf{q},i\omega_m,i\nu_n)$, which appears in Eq. (A3), contains all the information about the effective interaction between electrons arising due to impurity scattering and can be very complicated in general. For good metals, it is usually a good approximation to consider impurities as pointlike scatterers and take them into account in the Born approximation. In this case, the function $U_{\mathbf{Q}_1,\mathbf{Q}_2}(\mathbf{q},i\omega_m,i\nu_n)$ is essentially a constant, equal to $u=n_{imp}V_{imp}^2$. Then, Eq. (A3) has the following simple solution:

$$\Gamma^{-1}(q,i\omega_m,i\nu_n) = \frac{1}{u} - \frac{1}{V}\sum_{\mathbf{Q}} G(\mathbf{Q}_+,i\omega_{m+})G(\mathbf{Q}_-,i\omega_m).$$

This result contains the sum of the ladder diagrams and correctly reproduces the diffusive dynamics of the electrons at low wave vectors and frequencies.

We now return to the correlator of the orbital magnetic fields $K^M_{+-}(i\nu_n)$ in Eq. (A1), and split it into the two pieces, $K^M_{+-}(i\nu_n)=K_{bare}(i\nu_n)+K_{vert}(i\nu_n)$, corresponding to the two terms in the square brackets of Eq. (A2). The bare bubble contribution has the form

$$K_{bare}(i\nu_n) = 2\frac{(4\pi\gamma_e)^2}{V^2}\sum_{\mathbf{q},\mathbf{Q}}(\mathbf{q}\times\mathbf{Q})_+(\mathbf{q}\times\mathbf{Q})_-\frac{1}{q^4}S(\mathbf{Q},\mathbf{q},i\nu_n),$$

where the function S was defined in the main text in Eq. (22), but using the variables $\mathbf{k}_1=\mathbf{Q}+\mathbf{q}/2$ and $\mathbf{k}_2=\mathbf{Q}-\mathbf{q}/2$. This bare bubble contribution has been analyzed in Sec. III C. The vertex correction part can be written as

$$K_{vert}(i\nu_n) = 2\frac{(4\pi\gamma_e)^2}{V}T\sum_{\mathbf{q},m}(\mathbf{q}\times\mathbf{L}(\mathbf{q}))_+(\mathbf{q}\times\mathbf{L}(\mathbf{q}))_-\frac{1}{q^4}\Gamma(q,i\omega_m,i\nu_n),$$

$$\mathbf{L}(\mathbf{q})\equiv\mathbf{L}(\mathbf{q},i\omega_m,i\nu_n) = \frac{1}{V}\sum_{\mathbf{Q}}\mathbf{Q}G(\mathbf{Q}_+,i\omega_{m+})G(\mathbf{Q}_-,i\omega_m).$$

We see that for an isotropic system, $\mathbf{L}(\mathbf{q})\|\mathbf{q}$ and the vertex corrections to the correlator of the orbital magnetic fields vanish exactly due to its particular vector structure.

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