Berry-Phase Blockade in Single-Molecule Magnets

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We formulate the problem of electron transport through a single-molecule magnet (SMM) in the Coulomb blockade regime taking into account topological interference effects for the tunneling of the large spin of a SMM. The interference originates from spin Berry phases associated with different tunneling paths. We show that, in the case of incoherent spin states, it is essential to place the SMM between oppositely spin-polarized source and drain leads in order to detect the spin tunneling in the stationary current, which exhibits topological zeros as a function of the transverse magnetic field.

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Single-molecule magnets (SMMs), such as Mn_{12} [1,2] and Fe_8 [3,4], have become the focus of intense research since experiments on bulk samples demonstrated the quantum tunneling of a single magnetic moment on a macroscopic scale. These molecules are characterized by a large total spin, a large magnetic anisotropy barrier, and anisotropy terms which allow the spin to tunnel through the barrier. Transport through SMMs offers several unique features with a potentially large impact in applications for magnetic devices based on the SMM, such as high-density magnetic storage as well as quantum computing applications [5]. Recently, experiments have pointed out the importance of the interference between spin tunneling paths in molecules and its effects on electron transport scenarios involving SMMs. For instance, measurements of the magnetization in bulk Fe_8 have observed oscillations in the tunnel splitting $\Delta E_{s,-s}$ between states $S_z = s$ and $-s$ as a function of a transverse magnetic field at temperatures between 0.05 and 0.7 K [6]. This effect of macroscopic quantum tunneling (MQT) [7], where the initial and final spin states do not retain their coherence, can be explained by the interference between Berry phases acquired by spin tunneling paths of opposite windings using a coherent spin-state path integral approach [8,9], which accounts for the coherence of the virtual states over which the spin tunnels. To date, several experiments have shown the possibility to work with an individual SMM preserving the magnetic properties [10], thereby demonstrating the Coulomb blockade (CB) effect at a low temperature in a single SMM transistor geometry [10]. The theoretically predicted Kondo effect in SMMs [11,12] has not been observed yet. A theoretical description of the observed CB effect has recently been given by means of *coherent* initial and final spin states in Ref. [13], where macroscopic quantum coherence (MQC) [7] is assumed. In this Letter, we propose the Berry-phase blockade effect by coupling an individual SMM to spin-polarized leads. We analyze the transport properties of the system in the CB regime for the ground state of a SMM in the presence of a longitudinal and transverse magnetic field. Since the decoherence time between degenerate spin states can be as small as $T_2 = 10^{-9}$ s [14,15], we work with *incoherent* initial and final spin states in the MQT regime. We show that, in the case of *incoherent* spin tunneling, it is essential to use oppositely spin-polarized source and drain leads in order to be able to observe variations of the stationary current as a function of longitudinal or transverse magnetic field. In particular, the current can be suppressed due to the Berry-phase interference of the spin tunneling paths [16]. In the case of fully polarized leads, complete current suppression coincides precisely with the topological zeros of the spin tunneling. In the case of partially polarized leads, a partial Berry-phase blockade is visible. In the following, we present our calculations. We derive the (generalized) master equation for the low energy states at a temperature of 0.01 K and calculate the stationary current through the SMM for the cases of unpolarized, fully, and partially polarized leads. We apply our results to the newly synthesized SMM Ni_4, which has a spin of $s = 4$ and a ground state tunnel splitting of $\Delta E_{s,-s} \approx 0.01$ K at zero magnetic field [17]. Consider a SMM in the CB regime which is tunnel-coupled to two polarized leads at the chemical potentials μ_l, where $l = L, R$ denote the left and the right lead, respectively. The total Hamiltonian is given by

$$H = H_l + \mathcal{H}_s + H_m + \mathcal{H}_{\rm gate}, \tag{1}$$

where $H_l = \sum_{lk\sigma} \epsilon_{lk} c^\dagger_{lk\sigma} c_{lk\sigma}$ represents the energy of the leads. $c^\dagger_{lk\sigma}$ creates an electron in lead l with orbital state k, spin σ, and energy ϵ_{lk}. The coupling of the leads to the molecule is described by $H_m = \sum_{lpk\sigma} t^\sigma_{lp} c^\dagger_{lk\sigma} d_{p\sigma} + \text{H.c.}$, where t^σ_{lp} denotes the tunneling amplitude and $d^\dagger_{p\sigma}$ creates an electron on the molecule in orbital state p. The term $\mathcal{H}_s$ is the spin Hamiltonian of a SMM in an external transverse magnetic field $H_\perp = H_x + iH_y = |H_\perp| e^{i\varphi}$ and a longitudinal magnetic field H_z, i.e.,

$$\mathcal{H}_s = -A_N S^2_{N,z} + \frac{B_N}{2}(S^2_{N,+} + S^2_{N,-}) + \frac{B_{4,N}}{3}(S^4_{N,+} + S^4_{N,-}) + g\mu_B H_z S_{N,z} + \frac{1}{2}(h^*_\perp S_{N,+} + h_\perp S_{N,-}), \tag{2}$$

where the easy axis is taken along z, $S_{N,\pm} = S_{N,x} \pm iS_{N,y}$, and the integer index N denotes the charging state of the

SMM; e.g., $N = 0$ when the SMM is neutral and $N = 1$ adds one electron to the SMM. We define $h_\perp = g\mu_B H_\perp$. The total electrostatic energy is taken into account by $\mathcal{H}_{\text{gate}} = (Ne - Q_{\text{gate}})^2/2C_{\text{leads}} = E_c(N - Q_{\text{gate}}/e)^2$, where $E_c = e^2/2C_{\text{leads}}$ is the charging energy [18], $Q_{\text{gate}} = C_{\text{SMM}}V_{\text{gate}}$ is the charge induced by the gate voltage V_{gate}, C_{SMM} is the capacitance between the SMM and gate lead, and C_{leads} is the total capacitance between the SMM and all leads. We chose $Q_{\text{gate}} = e/2$ for our calculations since tunneling becomes favorable for this gate charge value. The gate voltage will allow us to be in or out of resonance with the SMM energy levels, and, as a result, the leading contribution to the current is due to sequential or cotunneling processes, respectively. In Eq. (2), the dominant longitudinal anisotropy term creates a ladder structure in the molecule spectrum where the eigenstates $|\pm m_N\rangle$ of S_z are degenerate. The weaker transverse anisotropy terms couple these states. The coupling parameters depend on the charging state of the molecule. For example, it is known that Mn_{12} changes its easy-axis anisotropy constant (and its total spin) from $A_{N=0} = 56\ \mu\text{eV}$ ($S_{N=0} = 10$) to $A_{N=1} = 43\ \mu\text{eV}$ ($S_{N=1} = 19/2$) and $A_{N=2} = 32\ \mu\text{eV}$ ($S_{N=2} = 10$) when singly and doubly charged, respectively [19]. Experiments with Ni_4 show that $B_{4,N=0} = -0.003\ \text{K} < 0$ [17]. In this case, in order to see the Berry-phase oscillation, $H_\perp$ must be applied in the xy plane [9] along specific angles $\varphi(B_N, B_{4,N})$. It is also possible to tune the tunnel splitting by means of H_z. For weak coupling between the leads and the SMM, we use the standard formalism suitable to describe a system (SMM) coupled to a reservoir (polarized leads) [20]. The master equation describing the electronic spin states of the SMM is given in the Born and Markov approximation by

$$\dot{\rho}_{m,n} = \frac{i}{\hbar}[\rho, H]_{m,n} + \delta_{m,n}\sum_{l\neq m}\rho_n W_{m,l} - \gamma_{m,n}\rho_{m,n}, \quad (3)$$

where $\gamma_{m,n} = \frac{1}{2}\sum_l(W_{l,n} + W_{l,m}) + 1/T_2$ is the total decoherence rate which contains the spin decoherence time T_2 due to, e.g., nuclear spins and the rates $W_{m,n}$ of transition between the states of the SMM. Figure 1 shows the SMM placed between unpolarized and polarized leads; we represent available electronic states of the molecule by discrete lines. $w^{(l)}_{\downarrow\uparrow}$ represent the spin-dependent transition rate from the $l = L, R$ lead to the SMM and are defined in Fermi's golden rule approximation by $w^{(l)}_\downarrow = 2\pi D\nu^{(l)}_\downarrow|t^{(l)}_\downarrow|^2/\hbar$ and $w^{(l)}_\uparrow = 2\pi D\nu^{(l)}_\uparrow|t^{(l)}_\uparrow|^2/\hbar$, respectively, where D is the density of states and $\nu^{(l)}_\uparrow$ and $\nu^{(l)}_\downarrow$ are fractions of the number of spins polarized up and down, respectively, of lead l such that $\nu^{(l)}_\downarrow + \nu^{(l)}_\uparrow = 1$. $t^{(l)}_\uparrow$ and $t^{(l)}_\downarrow$ are the tunneling amplitudes of lead l. Typical values for the tunneling rate of the electron range from around $w = 10^6$ to $w = 10^{10}\ \text{s}^{-1}$ (see Refs. [10,21]).

In order to see coherent spin tunneling (MQC), the decoherence time must be increased, for example, by deuteration [22] such that $1/T_2 \ll \Delta E_{s,-s}/\hbar$, and at the same time the contact to the leads must be so weak that $W_{m,n} \ll \Delta E_{s,-s}/\hbar$. Another possibility is to increase the transverse magnetic field $|H_\perp|$ beyond the Berry-phase oscillations. In this case, unpolarized leads can be used to measure the tunnel splitting between the coherent spin states $(|s'\rangle + |-s'\rangle)/\sqrt{2}$ and $(|s'\rangle - |-s'\rangle)/\sqrt{2}$ by varying the gate or bias voltage. However, only partially or fully polarized leads allow us to probe the incoherent tunneling rate (MQT) $\Gamma_{s,-s}$ between the ground states s and $-s$ for $N = 0$ and also between s' and $-s'$ for $N = 1$. As we prove below, both $\Gamma_{s,-s}$ and $\Gamma_{s',-s'}$ contribute to the total polarized current through the SMM. If an electron is absorbed (emitted) by the SMM, the total spin state changes from s (s') to s' (s), which differ by the charging energy E_c due to electron-electron interaction. The sequential tunneling rates for absorption of an electron in Eq. (3) for ground states with spin s and s' and energy differences $\Delta_{\pm s',\pm s} = E_c + g\mu_B H_z(\pm s' \mp s)$ in the case of low temperatures are given by

$$W_{s',s} = \sum_l W^{(l)}_{s',s}, \quad W^{(l)}_{s',s} = w^{(l)}_\downarrow f_l(\Delta_{s',s}),$$
$$W_{-s',-s} = \sum_l W^{(l)}_{-s',-s}, \quad W^{(l)}_{-s',-s} = w^{(l)}_\uparrow f_l(\Delta_{-s',-s}), \quad (4)$$

and the tunneling rates for the emission of an electron are given by

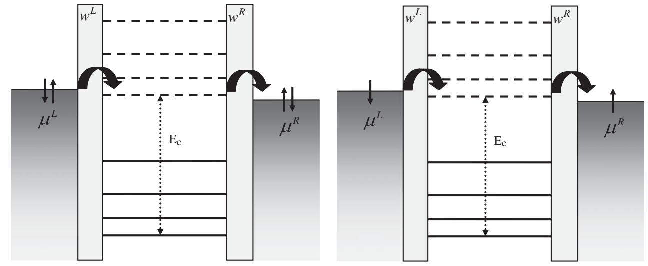
$$W_{s,s'} = \sum_l W^{(l)}_{s,s'}, \quad W^{(l)}_{s,s'} = w^{(l)}_\downarrow[1 - f_l(\Delta_{s,s'})],$$
$$W_{-s,-s'} = \sum_l W^{(l)}_{-s,-s'}, \quad W^{(l)}_{-s,-s'} = w^{(l)}_\uparrow[1 - f_l(\Delta_{-s,-s'})], \quad (5)$$

where $f_l(\Delta_{s',s}) = [1 + e^{(\Delta_{s',s} - \mu_l)/kT}]^{-1}$ is the Fermi function. The diagonal elements of (3) yield

$$\dot{\rho}_s = \frac{i}{\hbar}[\rho, H]_{s,s} + \sum_{n\neq s}\rho_n W_{s,n} - \rho_s\sum_{n\neq s}W_{n,s}, \quad (6)$$

and the off-diagonal elements of (3) yield

$$\dot{\rho}_{s,s'} = \frac{i}{\hbar}[\rho, H]_{s,s'} - \gamma_{s,s'}\rho_{s,s'}. \quad (7)$$



(a) (b)

FIG. 1. The diagrams show the SMM Ni_4 between (a) unpolarized leads and (b) fully oppositely polarized leads. The discrete lines represent available electronic states of the SMM, and E_c is the charging energy.

Since we are interested in the long time behavior $t \gg 1/\gamma_{m,n}$, we can set $\dot{\rho}_{s,s'} = 0$ in Eq. (7) to obtain

$$\dot{\rho}_s = \left(\frac{\Delta E_{s,-s}}{2\hbar}\right)^2 \frac{2\gamma_{s,-s}}{\{g\mu_B H_z[s-(-s)]\}^2/\hbar^2 + \gamma_{s,-s}^2} \times (\rho_{-s} - \rho_s) + W_{s,s'}\rho_{s'} - W_{s',s}\rho_s, \tag{8}$$

$$\dot{\rho}_{-s} = \left(\frac{\Delta E_{s,-s}}{2\hbar}\right)^2 \frac{2\gamma_{s,-s}}{\{g\mu_B H_z[s-(-s)]\}^2/\hbar^2 + \gamma_{s,-s}^2} \times (\rho_s - \rho_{-s}) + W_{-s,-s'}\rho_{-s'} - W_{-s',-s}\rho_{-s}. \tag{9}$$

The other two equations are obtained by replacing $s \leftrightarrow s'$. In the stationary case ($t \gg 1/W_{m,n}$), we obtain

$$\begin{aligned}\rho_s &= [W_{s,s'}(W_{-s',-s} + \Gamma_{s,-s})\Gamma_{s',-s'} \\ &\quad + W_{-s,-s'}(W_{s',s} + \Gamma_{s',-s'})\Gamma_{s,-s}]/\eta, \\ \rho_{-s} &= [W_{s,s'}(W_{-s,-s'} + \Gamma_{s',-s'})\Gamma_{s,-s} \\ &\quad + W_{-s,-s'}(W_{s',s} + \Gamma_{s,-s})\Gamma_{s',-s'}]/\eta,\end{aligned} \tag{10}$$

where η is a normalization factor such that $\sum_n \rho_n = 1$. The solutions for $\rho_{s'}$ and $\rho_{-s'}$ are obtained by replacing $s \leftrightarrow s'$. The incoherent tunneling rate is

$$\Gamma_{s,-s} = \left(\frac{\Delta E_{s,-s}}{2\hbar}\right)^2 \frac{2\gamma_{s,-s}}{\{g\mu_B H_z[s-(-s)]\}^2/\hbar^2 + \gamma_{s,-s}^2}. \tag{11}$$

We now proceed to define the current through the SMM in terms of the density matrix. In the case of Ni_4, we have $s = 4$ and $s' = 7/2$; therefore, the current reads

$$I = e(W_{4,7/2}\rho_{7/2} + W_{-4,-7/2}\rho_{-7/2}). \tag{12}$$

Taking into consideration the asymmetry of the leads, i.e., $w_{\downarrow\uparrow}^{(L)} \neq w_{\downarrow\uparrow}^{(R)}$, and restricting ourselves to the case of unpolarized leads, i.e., $\nu_\uparrow^{(L)} = \nu_\downarrow^{(L)} = \nu_\downarrow^{(R)} = \nu_\uparrow^{(R)} = 1/2$, we obtain the following conditions for the transition rates:

$$W_{7/2,4} = W_{-7/2,-4}, \qquad W_{4,7/2} = W_{-4,-7/2}. \tag{13}$$

Substituting the values of $\rho_{7/2}$ and $\rho_{-7/2}$ into Eq. (12) and using Eq. (13), we obtain

$$\frac{e}{I_{\text{unp}}} = \frac{1}{W_{7/2,4}} + \frac{1}{W_{-4,-7/2}}, \tag{14}$$

which does not depend on the tunnel splitting energy of the SMM. Thus, it is impossible to observe Berry-phase oscillations for the case of unpolarized leads and incoherent spin states. Equation (14) can be interpreted as two resistances in series [16] where the only transitions that contribute to the current through the SMM are $4 \leftrightarrow 7/2$ and $-4 \leftrightarrow -7/2$ [see Fig. 2(a)]. In the case of leads that are fully polarized in opposite directions, i.e., $\nu_\uparrow^{(L)} = \nu_\downarrow^{(R)} = 1$ or $\nu_\downarrow^{(L)} = \nu_\uparrow^{(R)} = 1$, we get one of the two following conditions for the transition rates, respectively:

$$W_{-4,-7/2} = W_{7/2,4} = 0 \quad \text{or} \quad W_{4,7/2} = W_{-7/2,-4} = 0. \tag{15}$$

Choosing the case $\nu_\uparrow^{(L)} = \nu_\downarrow^{(R)} = 1$ and using the condition $W_{-4,-7/2} = W_{7/2,4} = 0$, we have

$$\frac{e}{I_p} = \frac{2}{W_{-7/2,-4}} + \frac{1}{\Gamma_{4,-4}} + \frac{2}{W_{4,7/2}} + \frac{1}{\Gamma_{7/2,-7/2}}, \tag{16}$$

which reflects the fact that the current through the SMM depends on the tunnel splittings and can be interpreted as four resistances coupled in series in a loop [see Fig. 2(b)]. The transitions that contribute to the current through the SMM in the case of fully polarized leads $\nu_\uparrow^{(L)} = \nu_\downarrow^{(R)} = 1$ are $4 \to 7/2 \to -7/2 \to -4$.

Notice the clockwise direction of the transition rates between the different states s, s', $-s'$, and $-s$ of the SMM. If we chose to work with fully polarized leads of the form $\nu_\downarrow^{(L)} = \nu_\uparrow^{(R)} = 1$, then the direction of the transition rates between states would be the opposite, i.e., counterclockwise. Figure 3 shows the current as a function of $H_\perp$ for fully polarized leads. If the tunnel splitting $\Delta E_{4,-4}$ or $\Delta E_{7/2,-7/2}$ is topologically quenched [see Fig. 4], $\Gamma_{4,-4}$ or $\Gamma_{7/2,-7/2}$ vanishes [see Eq. (11)], which leads to complete current suppression according to Eq. (16). Since this current blockade is a consequence of the topologically quenched tunnel splitting, we call it *Berry-phase blockade*. Note that the current can also be suppressed by applying H_z, which follows immediately from Eqs. (11) and (16). If we consider partially polarized leads (i.e., $\nu_\uparrow^{(R)} > \nu_\downarrow^{(R)}$, $\nu_\downarrow^{(L)} > \nu_\uparrow^{(L)}$), the stationary current reads

$$\begin{aligned}I_{pp} = e[&\Gamma_{4,-4}W_{-4,-7/2}W_{4,7/2}(W_{-7/4,-4} + W_{7/2,4}) \\ &+ \Gamma_{4,-4}\Gamma_{7/2,-7/2}(W_{-4,-7/2} + W_{4,7/2}) \\ &\times (W_{-7/4,-4} + W_{7/2,4}) \\ &+ \Gamma_{7/2,-7/2}W_{-7/4,-4}W_{7/2,4}(W_{-4,-7/2} + W_{4,7/2})]/\eta.\end{aligned} \tag{17}$$

I_{pp} shows exactly the same qualitative features as I_p in Fig. 3 even at a spin polarization of 60%, where the

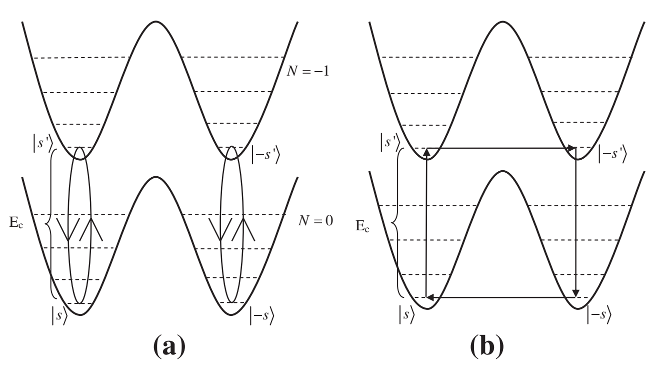


FIG. 2. (a) The transitions of the spin of the SMM in the case of unpolarized leads. The transitions arise from the sequential tunneling of unpolarized electrons in and out of the SMM. (b) The transitions in the case of fully polarized leads in opposite directions $\nu_\uparrow^{(L)} = \nu_\downarrow^{(R)} = 1$.

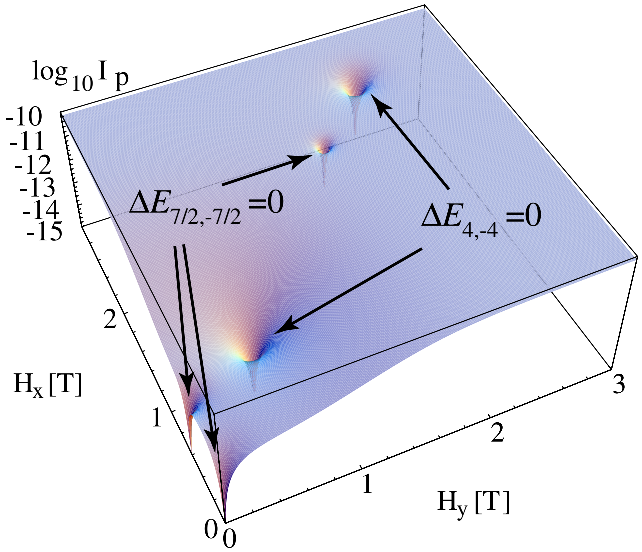


FIG. 3 (color online). The graph shows $\log_{10} I_p$ versus $H_\perp$ for $\nu_\uparrow^{(R)} = \nu_\downarrow^{(L)} = 1$, $\nu_\downarrow^{(R)} = \nu_\uparrow^{(L)} = 0$, $w_\downarrow^{(L)} = 1 \times 10^9\ \mathrm{s}^{-1}$, and $w_\downarrow^{(R)} = 10 w_\downarrow^{(L)}$. The polarizations of the left and right leads are given by $P^R = -P^L = \nu_\uparrow^R - \nu_\downarrow^R = 100\%$. At the zeros of the tunnel splitting $\Delta E_{s,-s}$ or $\Delta E_{s',-s'}$, the current is completely suppressed. The scale varies from $I_p = 0.1$ nA to 1 fA.

suppression of the stationary current due to the Berry phase is about a factor of 3. Thus, the Berry-phase blockade is experimentally accessible since recent experiments have achieved near 100% spin polarization [23]. Sequential and cotunneling calculations provide exactly the same features at 0.01 K, but the cotunneling current is very small since it involves a second-order process in which electrons tunnel over virtual states. If the temperature is increased, then, at thermal equilibrium, the population of the excited states of the SMM will satisfy $\rho_{\pm m'} = \rho_{\pm s'} \exp[-\beta(E_{\pm m'} - E_{\pm s'})]$, and thus V_{gate} can tune also the excited states of the SMM in resonance with the leads, i.e., $\mu_L \geq E_{m'} \geq \mu_R$. Consequently, the stationary current involving the states $|\pm m'\rangle$ is suppressed by the Boltzmann factor $\exp[-\beta(E_{\pm m'} - E_{\pm s'})]$.

In summary, we have shown the Berry-phase blockade for a SMM placed between polarized leads. This behavior is due to Berry-phase interference of the SMM spin between different tunneling paths. We have shown that, in the MQT regime, it is essential to use polarized leads in order to observe the Berry-phase blockade.

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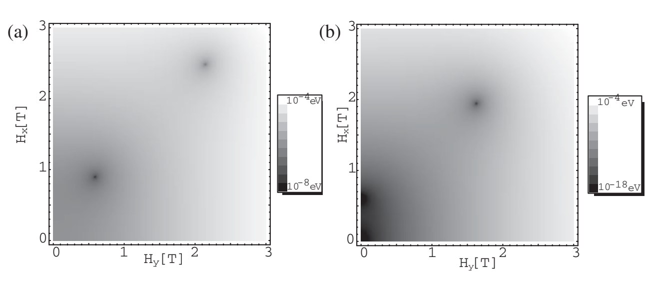

FIG. 4. The graphs show (a) $\log_{10}(\Delta E_{4,-4})$ and (b) $\log_{10}(\Delta E_{7/2,-7/2})$ versus transverse magnetic field $H_\perp$. These zeros correspond to those displayed in Fig. 3.

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