

Hopping Magnetotransport via Nonzero Orbital Momentum States and Organic Magnetoresistance

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In hopping magnetoresistance of doped insulators, an applied magnetic field shrinks the electron (hole) s -wave function of a donor or an acceptor and this reduces the overlap between hopping sites resulting in the positive magnetoresistance quadratic in a weak magnetic field, B . We extend the theory of hopping magnetoresistance to states with nonzero orbital momenta. Different from s states, a weak magnetic field *expands* the electron (hole) wave functions with positive magnetic quantum numbers, $m > 0$, and shrinks the states with negative m in a wide region outside the point defect. This together with a magnetic-field dependence of injection/ionization rates results in a *negative* weak-field magnetoresistance, which is linear in B when the orbital degeneracy is lifted. The theory provides a possible explanation of a large low-field magnetoresistance in disordered π -conjugated organic materials.

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As is well known the magnetoresistance (MR) in the hopping regime is caused by a strong magnetic-field dependence of the exponential asymptotic of the bound state wave function at a remote distance from a donor (or an acceptor) [1]. In the case of the Coulomb potential, when the wave function is spherically symmetric in the absence of the magnetic field, it becomes cigar-shaped squeezed in the transverse direction to the field [1,2]. This leads to a significant decrease in the overlap of the wave-function tails of two neighboring donors, and hence to a significant increase of resistivity (positive MR). An exponential positive MR in sufficiently strong magnetic fields is used to be a hallmark of the hopping conduction. On the other hand, there is anomalous (negative) MR observed in some hopping systems, for instance in amorphous germanium and silicon. It has been attributed to magnetic-field dependence of spin-flip transitions between sites when some fraction of them has a frozen spin [3], and/or to an increase of the density of localized states due to the Zeeman energy shift, $\mu_B B$ [4]. This negative MR is used to be small (much less than 1%) even in relatively high magnetic fields of about 1 Tesla.

In inorganic and organic insulators, lattice defects such as vacancies, interstitials, excess atoms or ions, and other “impurity” centers quite often localize carriers with a finite momentum rather than in the zero-momentum s states. A simple example of such centers is the transition-metal impurities in semiconductors studied in great detail in the 1980s, when the growth methods produced ultra-dilute samples [5]. In particular, a number of intriguing physical phenomena were revealed due to localized $3d$ impurity states. Importantly increasing concentrations of magnetic ions in semiconductors, such as GaAs:Mn leads to superpara and ferro-magnetism. The formation of a

substitutional $3d$ impurity can be thought of as a two-step process, involving first the removal of a host Ga atom, and second, the placement of a $3d$ impurity atom in its place. The combined impurity or host orbitals simply result from coupling between the host-crystal cation vacancy state and the impurity orbital of the $3d$ atom filling this vacancy. Also the conventional nonmagnetic donors and acceptors have nonzero orbital momentum states along with s states, which are accessible for the hopping conduction.

Here we develop the theory of hopping magnetoresistance via non-zero-momentum orbitals. Quite remarkably this renders a giant weak-field magnetoresistance, which is negative. Moreover, if the orbital degeneracy is lifted due to a broken time-reversal symmetry with or without net magnetization, the negative MR is linear in B .

The Schrödinger equation for the impurity-localized carrier wave function $\psi(\mathbf{r})$ can be written in the integral form using the Green function (GF), $G(\mathbf{r}, \mathbf{r}'; E)$, of the Bloch electron in a magnetic field,

$$\psi(\mathbf{r}) = - \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}'; E) V_{\text{imp}}(\mathbf{r}') \psi(\mathbf{r}'), \quad (1)$$

where E is the energy and $V_{\text{imp}}(\mathbf{r})$ is the impurity potential. We consider first a two-dimensional (2D) system, such as a thin film in the magnetic field, \vec{B} perpendicular to the surface of the film. Generally GF is expressed as a sum over wave functions of the 2D Bloch electron in a rational or irrational magnetic field with the Hofstadter’s butterfly eigenvalues [6]. In a weak magnetic field with $\hbar\omega_c = \hbar eB/m_b$ much smaller than the bandwidth, the effective band mass (m_b) approximation is sufficient, so that one can use the 2D free-electron GF in the magnetic field [7]

$$G_{2D}(\vec{\rho}, \vec{\rho}'; E) = \frac{m_b}{2\pi\hbar^2} \exp\left[i\frac{\rho\rho' \sin(\phi' - \phi)}{2l^2}\right] \times e^{-(\vec{\rho}-\vec{\rho}')^2/4l^2} \Gamma(a) U[a, 1, (\vec{\rho} - \vec{\rho}')^2/2l^2], \quad (2)$$

where ϕ and ϕ' are azimuth angles of $\vec{\rho}$ and $\vec{\rho}'$, respectively, $l = (\hbar/eB)^{1/2}$ is the magnetic length, $\Gamma(a)$ is the gamma function, and $U(a, b, z)$ is the Tricomi's confluent hypergeometric function well behaved at infinity, $z \rightarrow \infty$, for negative E [8]. Here $a = 1/2 - (E \mp \mu_B B)/\hbar\omega_c$, where \mp corresponds to spin up/down, respectively. Using Eqs. (1) and (2) one finds the wave function, $\psi(\mathbf{r}) = F_m(\rho) \exp(im\phi)$, at $r_0 \ll \rho \ll l^2/r_0$ as

$$F_m(\rho, b) \propto \rho^{|m|} e^{-(\kappa\rho)^2 b/8} \Gamma(a) U[a, 1, (\kappa\rho)^2 b/4], \quad (3)$$

where r_0 is the radius of the impurity potential, $\kappa = (2m_b\epsilon_0)^{1/2}/\hbar$ is the inverse localization length of the zero-field state with the ionization energy ϵ_0 , $b = B/B_0$ is the reduced magnetic field with $B_0 = \hbar\kappa^2/2e$, and ρ is the distance from the impurity. While $F_m(\rho) \propto \rho^{|m|} G(\rho, 0; E)$ is strictly applied to any finite-range $V_{\text{imp}}(\rho)$, it works for the infinite-range Coulomb potential at large distances as well [1]. Neglecting a small diamagnetic correction (quadratic in $b \ll 1$) yields $E = -\epsilon_0 + \hbar\omega_c m/2 \pm \mu_B B$ where $m = 0, \pm 1, \pm 2, \dots$ is the magnetic quantum number of the localized state, so that

$$a = \frac{1}{b} + \frac{1-m}{2}. \quad (4)$$

To elucidate the magnetic-field dependence of the bound state, we expand the solution, Eq. (3), in powers of b making use of the integral representation of $U(a, b, z)$ [8],

$$U(a, 1, z) = \Gamma(a)^{-1} \int_0^\infty e^{-zt} \frac{t^{a-1}}{(1+t)^a} dt. \quad (5)$$

Replacing t with $x = t/a$ and $(1+ax)^a$ with $(ax)^a \times \exp[1/x - 1/(2ax^2) + 1/(3a^2x^3) - \dots]$ yields

$$\frac{F_m(\rho, b)}{\rho^{|m|}} \propto 2K_0(\kappa\rho) + b(m-1) \frac{\kappa\rho}{2} K_1(\kappa\rho) + b \frac{(\kappa\rho)^2}{4} [K_2(\kappa\rho) - K_0(\kappa\rho)] + O(b^2), \quad (6)$$

where $K_n(x)$ is the modified Bessel function. Equation (6) is applicable in weak magnetic fields, $b \ll 1$ far enough but not too far from the point defect ($\kappa\rho \lesssim 1/b$). In a wide region $1 \ll \kappa\rho \lesssim 1/b$ one can use the asymptotic [8] of $K_n(x) \approx (\pi/2x)^{1/2} \exp(-x) [1 + (4n^2 - 1)/8x]$ to get a leading magnetic-field correction to the wave function,

$$\frac{F_m(\rho, b) - F_m(\rho, 0)}{F_m(\rho, 0)} = mb \frac{\kappa\rho}{2}. \quad (7)$$

Remarkably, the correction is *linear* in B for any nonzero m and could be large, if the bound state is sufficiently shallow and/or the hopping distance is large enough. It is positive for positive m and negative for negative m . The unusual expansion of the wave function with the positive m originates in the linear lowering of the ionization energy due to the orbital magnetic moment in weak magnetic fields. On the contrary, the states with negative m shrink because their ionization energy increases with the magnetic field. As shown below the state expansion or shrinking in the region $\kappa\rho \lesssim 1/b$ causes a *linear* MR in the weak magnetic field, which is negative or positive depending on the particular orbitals involved in the hopping.

In the case of a finite-range impurity potential, $V_{i,j}$, the standard expression for the hopping integral [1], $t_{ij} = \langle i | V_j | j \rangle - \langle i | j \rangle \langle i | V_j | i \rangle$, yields $t_{ij} \propto F_m(\rho)$, where ρ is the distance between two hopping sites i and j , which is assumed to be much larger than the localization length. The hopping conductance is proportional to the hopping integral squared. Hence, the magnetoresistance to the hopping transport via particular m orbitals is found as

$$\text{MR}_m \equiv \frac{R(B) - R(0)}{R(0)} = \frac{qK_0(\kappa\rho)^2}{pF_m(\rho, b)^2} - 1, \quad (8)$$

where $p = \int_0^\infty dx x^{2m+1} K_0(x)^2$ and $q = \int_0^\infty dx x^{2m+1} F_m(x, b)^2$ accounts for some weak-field dependence of the norm of the wave function. The same expression is also applied when hops take place between deep donor (acceptor) levels and shallow levels with the emission or absorption of phonons, as in the resistor network model of Ref. [9].

Here and below we take ρ as an average distance between defects. Figure 1 represents hopping MR in the d -wave orbital state with $m = 2$ as a function of the reduced magnetic field for a few distances between defects.

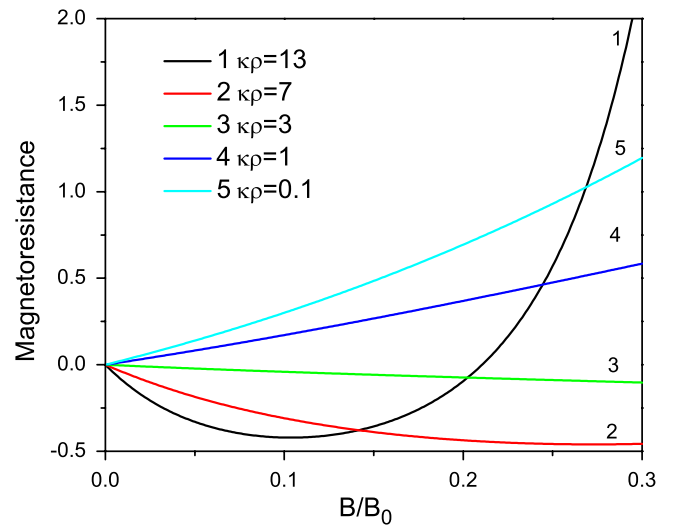


FIG. 1 (color online). Hopping magnetoresistance in $m = 2$ channel as a function of the reduced magnetic field B/B_0 for a few hopping distances.

As one can see from the figure, the anomalous expansion of the bound state results in the negative MR in weak magnetic fields, $b \lesssim (\kappa\rho)^{-1}$, followed by the positive MR in stronger fields. The absolute value of the negative MR could be in excess of 50%. The negative (for $m > 0$) and positive (for $m < 0$) MRs are linear in B at relatively low B .

Let us now extend the theory to a 3D system. To incorporate the free motion in the z direction, one can replace E with $E - p_z^2/2m_b$ and perform the Fourier transformation in Eq. (2), $G_{3D}(\mathbf{r}, \mathbf{r}'; E) = (1/2\pi\hbar) \times \int_{-\infty}^{\infty} dp_z e^{ip_z(z'-z)} G_{2D}(\vec{\rho}, \vec{\rho}'; E - p_z^2/2m_b)$. Replacing t in the integral representation of the confluent hypergeometric function, Eq. (5), with $t = 1/(\exp(x) - 1)$ and integrating over p_z one obtains

$$G_{3D}(\mathbf{r}, 0; E) = \frac{m_b}{(2\pi)^{3/2}\hbar^2 l} \int_0^{\infty} dx \frac{e^{mx}}{\sqrt{x} \sinh(x/2)} \times \exp\left\{-\left[\frac{(\kappa\rho)^2 b}{8} + \frac{x}{b} + \frac{(\kappa z)^2 b}{4x} + \frac{(\kappa\rho)^2 b}{4(e^x - 1)}\right]\right\}. \quad (9)$$

Expanding the exponent in the square brackets in Eq. (9) up to the third power in x and performing the integration by the saddle-point method, we finally obtain the asymptotic of the 3D wave function, $\psi(\mathbf{r}, b) \propto \rho^{|m|} G_{3D}(\mathbf{r}, 0; E)$ at $1 \ll \kappa r \lesssim 1/b$ as

$$\psi_m(\mathbf{r}, b) \propto \psi_m(\mathbf{r}, 0) \frac{\kappa r b/2}{\sinh(\kappa r b/2)} \exp\left[\frac{m\kappa r b}{2} - \frac{\kappa^3 \rho^2 r b^2}{96}\right] \quad (10)$$

with $r^2 = \rho^2 + z^2$. For the s -wave bound state with $m = 0$ this is the textbook asymptotic [1,2] accounting for the conventional positive MR quadratic in small B . On the contrary, for orbitals with nonzero orbital momentum, the wave function, Eq. (10), is linear in small B .

If there is no time-reversal symmetry breaking, the states with the opposite direction of the orbital angular momentum, m and $-m$, are degenerate, so that the linear term in the conductivity, $\sigma = \sigma_m + \sigma_{-m}$ cancels,

$$\sigma(b) = \sigma(0) \left[\frac{\kappa r b/2}{\sinh(\kappa r b/2)}\right]^2 \cosh(m\kappa r b) e^{-\kappa^3 \rho^2 r b^2/48}. \quad (11)$$

But even in this case the hopping conductivity, $\sigma(b)$, first *increases* with the magnetic field (negative quadratic MR) and only then decreases with B (positive quadratic MR), if $\kappa\rho^2/r < 24m^2 - 4$. Because of a large numerical factor (24), this negative quadratic MR dominates in the whole region of realistic impurity densities for any nonzero m . Ions that carry a magnetic moment break the time-reversal symmetry and split m and $-m$ states. Such zero-field splitting gives preference to the hopping via orbitals with

a lower ionization energy (positive m) providing the *negative linear* MR. In the extreme case of a ferromagnet with a frozen magnetization, magnetoresistance to hopping via nonzero momentum orbitals should be highly anisotropic changing from linear and negative in the field applied parallel to the magnetization to linear but positive in the opposite field, if the splitting due to exchange field is large enough compared with the temperature.

At high electric fields the conduction in organic and inorganic insulators is often injection and/or ionization limited where carriers tunnel from extended states to a bound impurity level or visa versa under a potential barrier shaped by the electric field [10]. The tunnelling ionization/injection rate, W , can be described by a modified tunnelling ionization formula [11] fitting the numerically calculated ionization rates of atoms and ions over a large region of the electric field, F ,

$$W_m \propto F^{-\beta} \exp\left(-\frac{F_i}{F} - \frac{\alpha F}{F_i}\right), \quad (12)$$

where α and β are numerical constants, depending on a particular ion, and $F_i \propto |\epsilon_0 - \hbar\omega_c m/2|^{3/2}$ is the characteristic ionization electric field depending on the magnetic field in our case. Expanding F_i in powers of B yields

$$W_m(F, b) \approx W(F, 0) e^{mb}, \quad (13)$$

where $W(F, 0) \propto F^{-\beta} \exp(-F_{i0}/F - \alpha F/F_{i0})$ is the ionization/injection rate without the magnetic field, $F_{i0} \propto \epsilon_0^{3/2}$, and $b = B/B_{i0}$ is the reduced magnetic field with $B_{i0} = 4B_0 F F_{i0}/3(F_{i0}^2 - \alpha F^2)$, which is a superlinear function of the electric field. Like in the case of the hopping conduction the injection/ionization conduction is a linear function of the weak magnetic field, resulting in the linear negative MR, if the orbital degeneracy is lifted.

Finally, let us address puzzling experimental observations of negative and positive low-field MR in a number of organic materials [12–14]. Organic magnetoresistance (OMAR) reaches 10% at fields on the order of only 10 mT and can be either positive or negative, depending on operating conditions. The Zeeman energy does not account for the observed OMAR at ambient temperatures since it is too small, $\mu_B B \approx 10$ mK, at a field of 10 mT. OMAR in hole-only devices [12,13] rules out exciton-based mechanisms as an explanation. An alternative model involving spin-dependent bipolaron formation in deep potential wells has been proposed [13]. Nevertheless, the origin of OMAR is still debated. Finding a convincing explanation of OMAR is important for understanding the basic transport mechanism of organic insulators, which are used in molecular spintronics [15,16].

Here we propose a more general model describing various classes of materials characterized by hopping transport regime, which accounts also for OMAR. We suggest that the hopping conductance could be a combination of hoppings via conventional s -wave centers and via nonzero

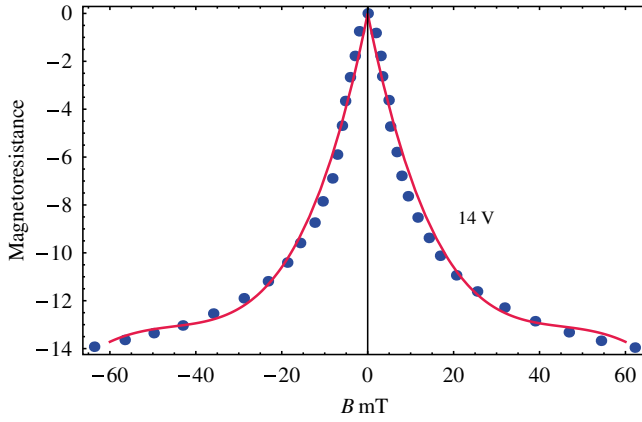


FIG. 2 (color online). Negative OMAR (%) at room temperature in ITO/PEDOT/Alq3/Ca device at bias voltage 14 V (symbols, Ref. [12]) described with Eq. (14) with $\eta = 1.8$, $B_s = 64$ mT, and $B_m = 40$ mT (solid line).

angular momentum orbitals. There is experimental evidence for paramagnetic centers and zero-field splitting in polymers, in particular, in Alq3 [17]. More recently (super) paramagnetic susceptibility and ferromagnetic nanoclusters have been reported in Alq3 [18]. The conventional hopping magnetoconductivity is described by the familiar exponential law [1], $\sigma_s = \sigma_{s0} \exp[-(B/B_s)^2]$, where B_s depends on the localization radius and the density of s -wave centers, and σ_{s0} is the zero-field conductivity [see also Eq. (11) with $m = 0$]. The conductivity via non-zero angular momentum orbitals split in zero field is linear, Eqs. (10) and (13), and Fig. 1, so one can approximate it as $\sigma_m = \sigma_{m0}(1 + B/B_m)$, where σ_{m0} and $B_m = B_0/(2|m|\kappa\rho)$ or $B_m = B_{i0}/|m|$ do not depend on the magnetic field. As a result, the combined weak-field MR is described by the following simple expression:

$$\text{MR} = \frac{-B/B_m + \eta[1 - \exp(-B^2/B_s^2)]}{1 + B/B_m + \eta \exp(-B^2/B_s^2)}, \quad (14)$$

which can be readily compared with experimental data for sufficiently weak magnetic fields, $B \lesssim B_m$ (here $\eta = \sigma_{s0}/\sigma_{m0}$). As one can see in Fig. 2, the theory describes reasonably well the large negative OMAR measured at room temperature in ITO/PEDOT/Alq3/Ca device at the bias voltage 14 V (and other voltages in Fig. 11 of Ref. [12]) using η , B_s , B_m as fitting parameters in the weak-field region, $B \lesssim B_m$. The low value of B_m points to a dominating role of hoppings via defects with rather shallow bound states (the binding energy on the order of a few Kelvin) in this device. Some empirical laws [12], in particular $\propto -[B/(B + \text{constant})]^2$, also gives accurate agreement, so that the good fit might be coincidental. However, as noticed in Ref. [12] simple fitting functions can fit the data only if one stays away from the transition region between negative and positive OMAR. Remarkably, as illustrated in Fig. 3, simplified Eq. (14) accounts for the cumbersome MR also in those organic structures, which

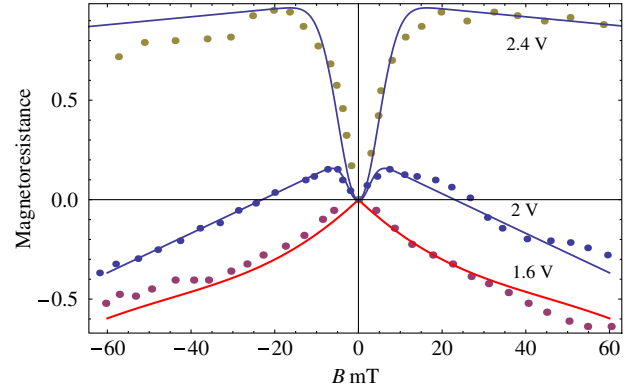


FIG. 3 (color online). Transition from negative to positive OMAR (%) at room temperature in ITO/PEDOT/pentacene/Ca device at different bias voltages (symbols, Ref. [12]) described by Eq. (14) with $\eta = 0.01$, $B_s = 6.7$ mT, $B_m = 50$ T (upper solid line), $\eta = 0.0023$, $B_s = 3.5$ mT, $B_m = 10$ T (middle solid line), and $\eta = 0.01$, $B_s = 63$ mT, $B_m = 5$ T (lower solid line).

show the transition from negative to positive MR. Compared with ITO/PEDOT/Alq3/Ca device, the ITO/PEDOT/pentacene/Ca device in Fig. 14 of Ref. [12] has deeper bound states, and much smaller relative contribution of the conventional hopping conductance. The electric-field behavior of B_m and η are in agreement with the injection/ionization conduction, Eq. (13) with a positive β .

In conclusion, we developed the theory of hopping magnetoconductivity via nonzero orbital momentum states. The asymptotic 2D and 3D solutions of the Schrödinger equation show unusual linear expansion/shrinking of the bound state with positive/negative magnetic quantum numbers far away but not too far from the point defect in the magnetic field. Our theory accounts for an extraordinary negative OMAR and for the transition to a more ordinary positive MR in disordered π -conjugated organic materials. Negative MR in some inorganic semiconductors may be also reanalyzed in the framework of the theory.

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