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## Bipolaron Mechanism for Organic Magnetoresistance

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We present a mechanism for the recently discovered magnetoresistance in disordered  $\pi$ -conjugated materials, based on hopping of polarons and bipolaron formation, in the presence of the random hyperfine fields of the hydrogen nuclei and an external magnetic field. Within a simple model we describe the magnetic field dependence of the bipolaron density. Monte Carlo simulations including on-site and longer-range Coulomb repulsion show how this leads to positive and negative magnetoresistance. Depending on the branching ratio between bipolaron formation or dissociation and hopping rates, two different line shapes in excellent agreement with experiment are obtained.

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Organic magnetoresistance (OMAR) is a recently discovered, large (10% or more in some materials), low-field, room-temperature magnetoresistive effect in organic devices with *nonmagnetic* electrodes. The main results obtained up till now are the following: (i) It is associated with the bulk resistance of the organic layer [1]. (ii) It is caused by hyperfine coupling [2]. (iii) It is independent of the magnetic field direction [1,3]. (iv) It obeys empirical laws given by either the non-Lorentzian line shape  $\Delta I(B)/I \propto B^2/(|B| + B_0)^2$  or a Lorentzian  $\Delta I(B)/I \propto B^2/(B^2 + B_0^2)$ , depending on material, for the change in the current  $I$  with magnetic field  $B$ , where  $B_0 \approx 5$  mT in most materials [1]. (v) Its sign can be positive or negative, dependent on material and/or operating conditions of the devices [1,3].

OMAR poses a significant scientific puzzle since it is, to the best of our knowledge, the only known example of large room-temperature bulk magnetoresistance in non-magnetic materials, with the exception of very-high-mobility materials [4,5]. An explanation of OMAR may therefore lead to new insights into magnetoresistance in general. Recently, exciton-based mechanisms have been proposed in terms of  $B$ -dependent mixing of singlet and triplet excitons [3] and trapping of charges by triplet excitons [6]. However, there are strong indications that OMAR is not an excitonic effect: (a) in devices with electrodes of different work functions a dependence on the minority carrier density was measured that is much weaker than the linear dependence expected from an excitonic model [2], (b) Reufer *et al.* showed that in a device of a ladder-type polymer the singlet and triplet exciton density have exactly the same dependence on  $B$  [7]. In this Letter we propose a single carrier-type mechanism.

Conduction in disordered organic materials takes place by hopping of charge carriers between localized sites having a density of states (DOS) that is often assumed to be Gaussian, with a width  $\sigma \sim 0.1$ – $0.2$  eV. Because of strong electron-phonon coupling, charges form polarons and the

energy penalty  $U$  for having a doubly occupied site, i.e., a bipolaron, is modest. Experimental indications are that  $U \sim \sigma$  [8]. Because of strong on-site exchange effects [9,10], we can assume that bipolarons occur only as spin singlets. Two polarons having the same spin component along a common quantization axis have zero singlet probability and cannot form a bipolaron. This “spin blocking” is the basic notion of our mechanism. As will be shown throughout this Letter, it has important consequences for the conduction and can give rise to both positive and negative magnetoconductance, depending on the choice of model parameters. An important aspect of our mechanism is that it is based on correlations between spins in an out-of-thermal-equilibrium situation and not on any net spin polarization. In fact, at the considered temperatures and magnetic fields the Zeeman splitting ( $\sim \mu\text{eV}$ ) is small compared to the thermal energy ( $\sim 10$  meV). We note that various small magnetoresistive effects ( $< 1\%$ ) measured in amorphous semiconductors in the 1970s were attributed to a similar mechanism [11]. However, OMAR is a much larger and more universal effect, and is therefore a much clearer test of this mechanism. We also note that the concept of bipolarons was used in a model for colossal magnetoresistance in doped manganites [12], where the typical field scale is much larger ( $\sim$  Teslas).

To make this mechanism quantitative, we must therefore calculate the singlet probability of a pair of polarons for the situation that pertains to organic materials. Polarons in hydrocarbon molecules are exposed to a local hyperfine field produced by the hydrogen nuclei, which can be treated as a randomly oriented classical field  $\mathbf{B}_{\text{hf}}$  [13]. The total field at a site  $i$  is then  $\mathbf{B}_{\text{total},i} = \mathbf{B} + \mathbf{B}_{\text{hf},i}$ . We assume that two polarons encountering each other to form a bipolaron have a random spin configuration; i.e., the spin density matrix is proportional to the unit matrix. It is then convenient to take the energy eigenstates of the local spin Hamiltonian as a basis and to assume that the electronic

spinor is in one of these states. The hops are therefore taken to occur between energy eigenstates corresponding to the local total magnetic field at the two sites. This is a correct procedure when the spin precession frequency is larger than the hopping frequency, in which case we can treat the hopping perturbatively as a Markov process. At the magnetic field scale under consideration the precession frequency is of the order of  $10^8 \text{ s}^{-1}$  and typical hopping frequencies in organic materials are indeed often smaller. The singlet probability is now given by [13]

$$P = 1/4 - \mathbf{S}_i \cdot \mathbf{S}_j / \hbar^2, \quad (1)$$

where  $\mathbf{S}_{i,j}$  are the classical spin vectors pointing along  $\mathbf{B}_{\text{total},i,j}$ , and  $\hbar$  is Planck's constant. A straightforward analysis of this formula shows that for  $B = 0$  the pairs have an average singlet probability  $P = 1/4$ , whereas for large field this probability is either  $P_P = 0$  or  $P_{AP} = 1/2$  for parallel and antiparallel pairs, respectively. We note that the notion of parallel and antiparallel pairs has its usual meaning only for large  $B$ , whereas for small  $B$  we denote as "parallel" a pair whose spins both point "up" or both "down" along the local field axes, which are randomly oriented.

We start with the consideration of a simple model (see Fig. 1, inset) demonstrating that in an out-of-thermal-equilibrium situation a  $B$  dependence of the bipolaron density is obtained due to the competition between  $B$ -dependent bipolaron formation and  $B$ -independent hopping to empty sites from a "branching" site. Because of the

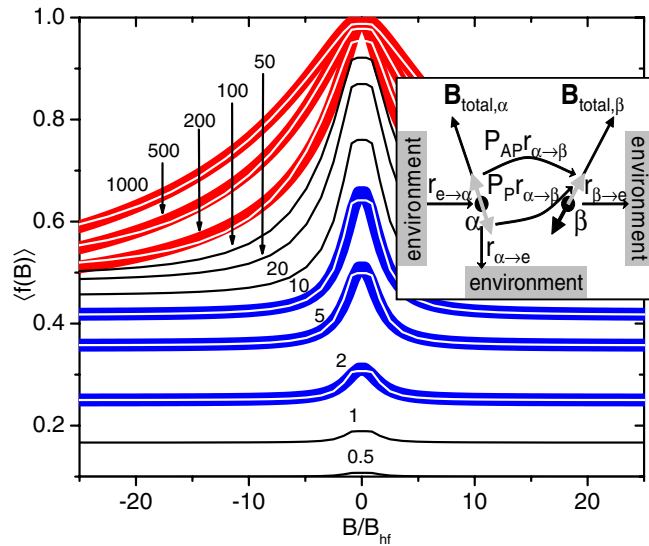


FIG. 1 (color online). Hyperfine field average of the function  $f(B)$  of Eq. (2), determining the bipolaron probability, for various branching ratios  $b = r_{\alpha \rightarrow \beta} / r_{\alpha \rightarrow e}$ . The lower three thick lines show Lorentzian fits, the upper three fits to the non-Lorentzian empirical law. Inset: model as described in the main text, with the black arrow indicating the spin of a polaron present at  $\beta$  (arbitrarily chosen opposite to the local magnetic field) and the gray arrows the spin of a possible additional polaron.

disorder in the site energies, there will be certain sites with a particularly low energy, where bipolarons can be formed. We call one of these sites  $\beta$ . We assume that this site permanently holds at least one polaron. A bipolaron can be formed by hopping of a polaron to  $\beta$  from a site  $\alpha$  next to it, the branching site, with a rate  $P_P r_{\alpha \rightarrow \beta}$  or  $P_{AP} r_{\alpha \rightarrow \beta}$ , depending on the orientation of its spin. We assume that the electric field is large enough such that dissociation does not occur to  $\alpha$  but, with a rate  $r_{\beta \rightarrow e}$ , to other sites, which we consider to be part of the "environment." We assume that polarons enter  $\alpha$  with a rate  $r_{e \rightarrow \alpha}$  by hopping from sites in the environment, with equal "parallel" and "antiparallel" spin, leading to an influx  $r_{e \rightarrow \alpha} p / 2$  into both spin channels, where  $p$  is a measure for the average number of polarons in the environment. We also consider the possibility that a polaron at  $\alpha$  directly hops back to an empty site in the environment with a rate  $r_{\alpha \rightarrow e}$ . Neglecting double occupancy of  $\alpha$  and single occupancy of  $\alpha$  simultaneously with double occupancy of  $\beta$ , the corresponding rate equations can be straightforwardly solved for the probability  $p_\beta$  of double occupancy of  $\beta$ , i.e., the presence of a bipolaron:

$$p_\beta = \frac{r_{e \rightarrow \alpha}}{r_{\beta \rightarrow e}} f(B) p, \quad f(B) \equiv \frac{P_P P_{AP} + 1/(4b)}{P_P P_{AP} + 1/(2b) + 1/b^2}, \quad (2)$$

where the  $B$  dependence has been absorbed in the function  $f(B)$ , and where  $b \equiv r_{\alpha \rightarrow \beta} / r_{\alpha \rightarrow e}$  is the branching ratio. Averaging over the directions of the hyperfine fields, we obtain the results for  $\langle f(B) \rangle$  plotted in Fig. 1 for various values of  $b$ . For not too large  $b$  the line shape is governed by  $\langle P_P P_{AP} \rangle$ , leading to a Lorentzian-like line shape. For increasing  $b$  a strong dependence on  $B$  develops, which now becomes governed by  $\langle (P_P P_{AP})^{-1} \rangle$ . This line shape can be fitted very well with the empirical law  $\propto B^2 / (|B| + B_0)^2$ .

To demonstrate that this mechanism leads to magneto-resistance we employed Monte Carlo simulations of nearest-neighbor hopping on a  $30^3$  cubic grid of sites with lattice constant  $a$  and with periodic boundary conditions. The site energies were drawn randomly from a Gaussian DOS and a randomly oriented hyperfine field of strength  $B_{\text{hf}}$  was attributed to each site. We used the Miller-Abrahams form for the hopping rate  $r$  [14], with  $r \propto \exp[(E_i - E_f)/kT]$  for  $E_i < E_f$  and  $r = 1$  otherwise, with  $T$  temperature, and  $k$  Boltzmann's constant.  $E_i$  and  $E_f$  are the initial and final energies of the configurations before and after hopping, including an energy  $eEa$ , picked up or lost for hops with or against the applied electric field  $E$ , with  $e$  the electronic charge. We also took into account the intrasite Coulomb repulsion  $U$  and a spherical region of long-range Coulomb repulsion around each carrier. For computational reasons we employed a finite-range variant of Coulomb's law, specifically  $V(R) = (a/R - 1/5)V$  for  $R < 5a$ ,  $R \neq 0$ , and zero otherwise. Inserting typical values for organics leads to the expectation  $V \sim U$ . In our

simulation the crucial hops are those for which a bipolaron is formed. In that case the hopping rate  $r$  is multiplied with the singlet probability  $P_P$  or  $P_{AP}$ . Hops that dissociate a bipolaron occur with a rate  $(P_P + P_{AP})r = r/2$ . The simulation proceeds as follows. Randomly picked sites are occupied according to a Fermi-Dirac distribution, taking into account the Coulomb field of all sites already occupied. The system is then propagated in time, keeping track of site occupations, spin, and Coulomb field, until it reaches a steady state. Subsequent hops are then used to calculate the magnetoconductivity (MC). The current is evaluated as the difference in number between downfield and upfield hops divided by the simulation time. This procedure is repeated for different disorder configurations until the average MC value converged to within 1% absolute.

Figure 2 shows a simulated MC trace as a scatter plot for a, not necessarily realistic, choice of the model parameters yielding a particularly large effect. The trace can be fitted very accurately by the Lorentzian law. To investigate the effect of the branching ratio, we multiplied the rates for bipolaron formation and dissociation by a factor  $b' = 10$ . We found that this has almost no effect on the size of the MC, but that the line shape changes to the non-Lorentzian form, in agreement with the prediction of the model. Hence, both experimentally observed line shapes are reproduced by our simulations. Ultimately, the value of  $b'$  must be obtained from realistic quantum-chemical simulations of the hopping and bipolaron formation processes, and we conjecture that this will determine the line shape of a specific material. We note that the *shapes* predicted by the simulations contain no adjustable parameters, other than the described dependence on the branching ratio. We note that  $B_0 \approx 3B_{\text{hf}}$  is obtained by the MC simulations. Therefore, for a typical  $B_{\text{hf}} \approx 1$  mT we obtain  $B_0 \approx 3$  mT in good agreement with experiment.

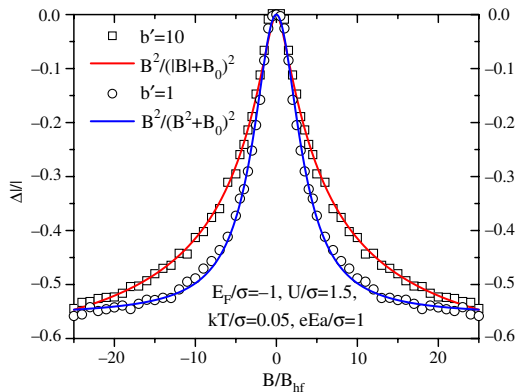


FIG. 2 (color online). Symbols:  $\circ$ , simulated magnetoconductance traces for a particular choice of parameters.  $\square$ , bipolaron formation and dissociation rates multiplied by  $b' = 10$ . Solid lines: fits through  $\square$  and  $\circ$  with the empirical laws  $\propto B^2/(|B| + B_0)^2$  ( $B_0 \approx 2.75B_{\text{hf}}$ ) and  $\propto B^2/(B^2 + B_0^2)$  ( $B_0 \approx 3.5B_{\text{hf}}$ ), respectively.

For the Lorentzian case, we have studied the dependence on some of the model parameters (no significant changes of the line shape and width were observed). Initially, we set  $V = 0$  for simplicity. Figures 3(a) and 3(b) show a negative  $\Delta I/I$  for  $B/B_{\text{hf}} = 100$  as a function of  $U$  for two typical choices of parameters, and several choices for the Fermi energy  $E_F$  ( $E_F = 0$  corresponds to the center of the Gaussian DOS). Although larger at high carrier densities, the effect persists at low carrier densities, i.e., large  $|E_F/\sigma|$ . It is seen that the effect is largest for  $U/\sigma \approx 1$ . For large  $U$  the effect is small because of the high energy cost of creating bipolarons. For small  $U$  the effect is small because of the small number of single polarons, since many of them combine to form bipolarons. Figure 4 shows that the negative MC effect increases with decreasing temperature (for room temperature and below the relevant range is  $\sigma/kT > 4$ ). For smaller electric fields the effect becomes less temperature dependent, in agreement with experimental findings [1].

Inclusion of  $V$  dramatically changes the situation, leading to positive MC; see Fig. 4. We have identified two competing effects contributing to the MC: (i) blocking of transport through bipolaron states (negative MC), and (ii) an increase in polaron population at the expense of bipolarons with increasing  $B$  (positive MC). Apparently, (i) dominates for the parameters used in Fig. 3 and (ii) dominates for large  $V$ . Figure 5(a) shows that the MC changes sign as  $V$  increases. Furthermore, Fig. 5(b) (inset) shows that the number of polarons decreases with increasing Coulomb repulsion, reflecting increased bipolaron formation. The reason for this seemingly contradictory result might be the following. For  $V = 0$  bipolaron formation requires a hop to sites with a particularly low energy to offset the bipolaron formation energy  $U$ , and such sites are

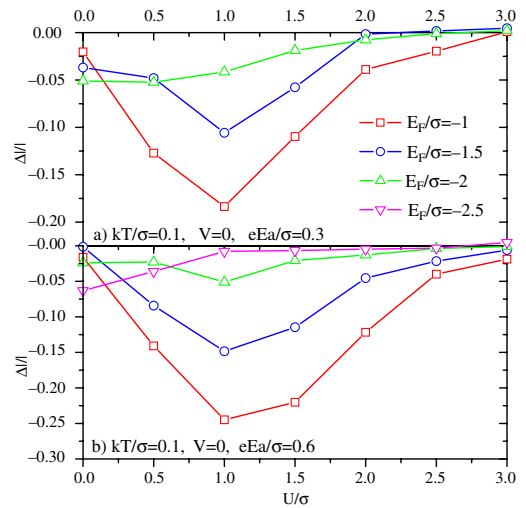


FIG. 3 (color online). Simulated magnetoconductance for  $B/B_{\text{hf}} = 100$  and  $kT/\sigma = 0.1$  as a function of the bipolaron energy  $U$  for (a)  $eEa/\sigma = 0.3$  and (b)  $eEa/\sigma = 0.6$  for several choices of the Fermi level,  $E_F$ . The model parameters are assigned.

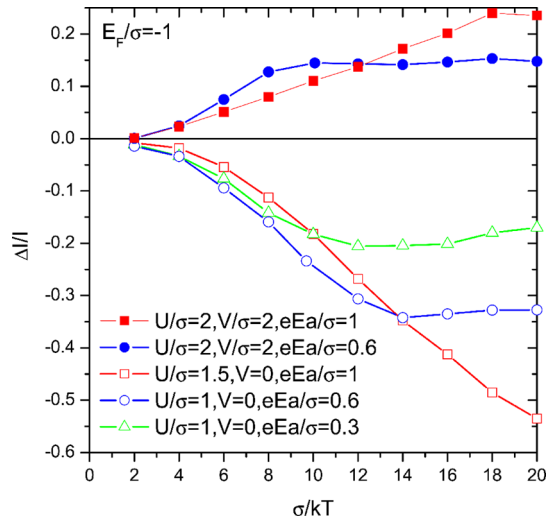


FIG. 4 (color online). Simulated magnetoconductance for  $B/B_{\text{hf}} = 100$  as a function of  $\sigma/kT$  for several choices of the model parameters. The model parameters are assigned.

rare. However, upon inclusion of long-range repulsion the offset energy is reduced to  $U - V$ . Therefore, inclusion of  $V$  leads to enhanced bipolaron formation and to an enhanced sensitivity of the bipolaron population on  $B$ , favoring effect (ii). Figure 5(b) shows that the magnetic field effect on the polaron population increases with  $V$ , reflecting this enhancement. This change in population corresponds to a splitting between the chemical potentials for polarons and bipolarons [this is, therefore, an out-of-thermal-equilibrium effect, which is evidenced in our

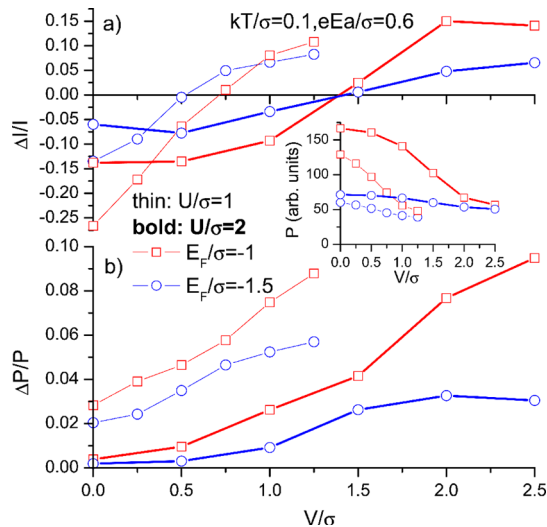


FIG. 5 (color online). (a) Simulated magnetoconductance for  $B/B_{\text{hf}} = 100$  as a function of the long-range Coulomb repulsion strength  $V$  for several choices of the model parameters. (b) Magnetic field induced change,  $\Delta P/P$ , in polaron population,  $P$ , as a function of  $V$ . The inset shows  $P$  vs  $V$ . The model parameters are assigned.

simulations by the observation that this effect is essentially proportional to  $eEa$  (data not shown)]. In particular, the chemical potential of polarons is shifted to higher energy, leading to a smaller activation energy and positive magnetoconductance. Figure 4 shows that the temperature dependence of the positive MC is similar to that of the negative MC.

In summary, we have proposed a mechanism for the recently discovered organic magnetoresistance effect. Our mechanism is based on the dynamics of singlet bipolaron formation in the presence of random hyperfine fields and an external magnetic field. We show that positive and negative magnetoconductance can occur and recover both experimentally observed line shapes. A next challenge is to perform a detailed quantitative analysis and comparison with experiments. The mechanism may also be applicable to other hopping systems.

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