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A two-site bipolaron model for organic magnetoresistance

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The recently proposed bipolaron model for large “organic magnetoresistance” (OMAR) at room temperature is extended to an analytically solvable two-site scheme. It is shown that even this extremely simplified approach reproduces some of the key features of OMAR, viz., the possibility to have both positive and negative magnetoresistance, as well as its universal line shapes. Specific behavior and limiting cases are discussed. Extensions of the model, to guide future experiments and numerical Monte Carlo studies, are suggested. © 2008 American Institute of Physics.

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An entirely novel organic magnetoresistance (OMAR) phenomenon has started to puzzle the scientific community: magnetoresistance (MR) values up to 10% at room temperature and at fields of only a few millitesla have recently been reported in various organic materials.^{1–5} OMAR can be both positive and negative, and displays universal line shapes of approximately the same width B_0 for many small molecules and polymers. The magnetoconductance, $MC(B)=[J(B)-J(0)]/J(0)$, where J is the current density and B is the applied field, is described by either a Lorentzian $B^2/(B_0^2+B^2)$ or a specific non-Lorentzian $B^2/(|B|+B_0)^2$.⁶ A number of models have been suggested to account for this intriguing behavior. One class of models assigns OMAR to spin-related excitonic effects.^{2,3} Such a mechanism would only explain finite MC in bipolar devices where both types of carriers are present. However, this interpretation is in conflict with reports that claim the observation of a finite OMAR in unipolar devices.⁶ Bobbert *et al.* proposed a *bipolaron model*⁷ that does not rely on electron-hole recombination. A Monte Carlo scheme was implemented to describe hopping conductance on a large grid of molecular sites displaying energetic disorder. Thus, both positive and negative MC, as well as the particular line shapes, were reproduced.

In this paper, we calculate the MC analytically by mapping the bipolaron model on two “characteristic sites” out of a random distribution of molecular energy levels; a simplification which was already briefly outlined in Ref. 7. It will be shown that such an approach is sufficient to capture all the characteristics of OMAR in a qualitative way. We will successively discuss the basic ingredients of the bipolaron model, the definition of the two-site version of it, the derivation of the associated set of rate equations resulting in ana-

lytical expressions for $J(B)$, and, finally, the generic line shapes and the sign changes of OMAR. We conclude by suggesting possible extensions of the model.

The key ingredient of the bipolaron model is the effect of an applied field on the probability of forming bipolarons (doubly occupied molecular sites). The formation of a bipolaron by hopping to a singly occupied site is only possible when the two electrons involved have a finite singlet component. Thus, two electrons on different sites, originally in a parallel (P) state, will have a lower probability to form a bipolaron than electrons in an antiparallel (AP) state. The restriction can be (partially) lifted by the presence of different local magnetic fields at the two sites. Then, the bipolaron formation probability ($P_{AP/P}$) scales with the time averaged singlet component of the two particle wave function, $P_{AP/P} = \frac{1}{4}(1 \pm \hat{h}_1 \cdot \hat{h}_2)$, where the plus (minus) sign is for the AP (P) orientation and \hat{h}_i is a unit vector along the local magnetic field at site i .⁷ The magnitude $B_0 \sim 10$ mT observed in experiments supports the conjecture that the random field is the local hyperfine field ($\vec{B}_{hf,i}$) of hydrogen atoms surrounding the respective molecular sites i . At applied fields $B \gg |\vec{B}_{hf,i}|$, the local fields are aligned: $\hat{h}_i \parallel \vec{B}$. In the Monte Carlo calculations of Ref. 7, the resulting MC was calculated as a function of temperature T and relevant model parameters, such as the on-site Coulomb repulsion U within a bipolaron state, the long-range Coulomb interaction V , and the Gaussian energy disorder σ .

In the present work, we select two neighboring critical sites, α and β , situated upstream and downstream, respectively, extending the approach of Ref. 7. The two sites are considered to be bottlenecks in the carrier transport with α at most and β at least singly occupied, thereby strongly affecting the MC. To account for blocking effects to the current, it

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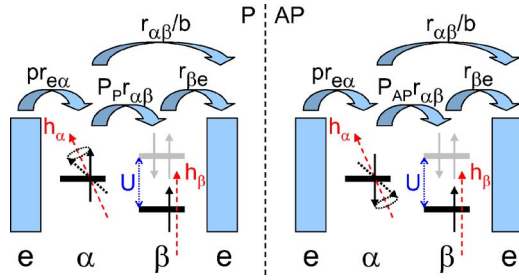


FIG. 1. (Color online) Schematic representation of the transport rates and electron spins in the P and AP configurations. The symbols are explained in the text.

is crucial to work out the model in terms of many-electron states. Within the aforementioned restrictions and excluding time-reversed states,⁸ we have five of them: $|01\rangle$, $|11_P\rangle$, $|11_{AP}\rangle$, $|02\rangle$, and $|12\rangle$, where $|nm\rangle$ denotes an $n(m)$ -fold occupation at site α (β) and P/AP describes the spin orientation in case both sites are singly occupied. We consider only a downstream flow of electrons (Fig. 1); from upstream in the environment e (not further specified in the model) to α at rate $pr_{e\rightarrow\alpha}$ (where p is a measure of the electron density in the environment), from site α to β at rate $P_{P/AP}r_{\alpha\rightarrow\beta}$, and from site β to downstream e at rate $r_{\beta\rightarrow e}$. Furthermore, we introduce two routes that can release a blocking situation: (i) from site α bypassing β directly to the downstream environment, at a rate $r_{\alpha\rightarrow e} = r_{\alpha\rightarrow\beta}/b$, where b is the *branching ratio*, and (ii) a spin-orbit induced spin-flip process between states $|11_P\rangle$ and $|11_{AP}\rangle$ at a rate $r_{\alpha\rightarrow\beta}/a$, where a is the *spin flip coherence ratio*. Increasing a and b tends to make blocking effects more pronounced and thereby increases the MC.

Next, we define occupation probabilities A_{nm} for the respective many-electron states $|nm\rangle$, with $\sum_{nm} A_{nm} = 1$, and construct a set of rate equations. In a stable solution, the time derivative of all probabilities should vanish. As an example, $dA_{11_P}/dt = 0$ yields

$$0 = A_{01}pr_{e\rightarrow\alpha} + A_{11_{AP}}r_{\alpha\rightarrow\beta}/a + A_{12}r_{\alpha\rightarrow e} - A_{11_P}(P_P r_{\alpha\rightarrow\beta} + r_{\alpha\rightarrow\beta}/a + r_{\alpha\rightarrow\beta}/b), \quad (1)$$

while the other equations can be constructed in a similar way. Solving the set of equations results in analytical expressions for A_{nm} . The current through the system equals the total rate from the upstream environment to α ,

$$I/e = \langle (2A_{01} + A_{02}) \rangle pr_{e\rightarrow\alpha}, \quad (2)$$

where $\langle \dots \rangle$ denotes the ensemble average over $\vec{B}_{\text{hf},i}$ and e is the electron charge. The explicit expression for I is lengthy but can be rewritten in a generic form,

$$I = I_\infty + I_B \left\langle 1 - \frac{1}{1 + \Gamma P_P P_{AP}} \right\rangle = I_\infty + I_{BG} \left(\Gamma, \frac{B}{B_{\text{hf}}} \right), \quad (3)$$

where I_∞ , I_B , and Γ are straightforward analytical expressions in terms of the model parameters, and B_{hf} is the hyperfine field scale. All field dependencies are described by the model function $g(\Gamma, B/B_{\text{hf}})$; i.e., the line shape is fully described by a single parameter Γ , with $g(\Gamma, \infty) = 0$ and $g(\Gamma, 0) \rightarrow 1$ for $\Gamma \gg 1$ and $g(\Gamma, B) \propto \Gamma$ for $\Gamma \ll 1$. Thus, the shape and magnitude (including sign) of the OMAR are, respectively,

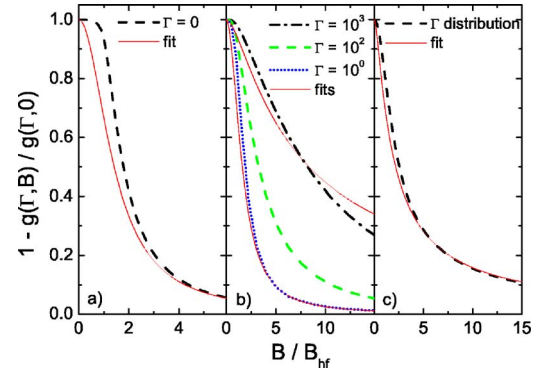


FIG. 2. (Color online) Modeled magnetic response for (a) $\Gamma=0$, (b) $\Gamma = 10^0, 10^2, 10^3$ compared to a Lorentzian and non-Lorentzian fit, and (c) a distribution of Γ values, with average value $\log_{10} \Gamma = 1.4$ and half-width $\Delta \log_{10} \Gamma = 2.1$.

$$\frac{MC(B)}{MC(\infty)} = 1 - \frac{g(\Gamma, B/B_{\text{hf}})}{g(\Gamma, 0)}, \quad (4)$$

$$MC(\infty) = - \frac{I_B g(\Gamma, 0)}{I_\infty + I_B g(\Gamma, 0)}. \quad (5)$$

In order to calculate the line shape, it is required to specify the distribution of hyperfine fields. Assuming a fixed magnitude $|\vec{B}_{\text{hf},i}| = B_{\text{hf}}$ but a random orientation, it is possible to derive a (rather lengthy) analytical expression for $g(0, B/B_{\text{hf}})$.⁹ As illustrated in Fig. 2(a), at large B the function converges to a Lorentzian with width $B_0 = \sqrt{2}B_{\text{hf}}$ and normalized to 1 at $B=0$. However, a plateau up to around $B/B_{\text{hf}} = 1$ is obtained using this averaging procedure. Numerical results for a more realistic average over a three dimensional Gaussian distribution of $\vec{B}_{\text{hf},i}$ (defining $\langle |\vec{B}_{\text{hf},i}| \rangle = B_{\text{hf}}$) are collected in Fig. 2(b) for several values of Γ . It is found that MR(B) broadens as a function of Γ and resembles a Lorentzian reasonably well for small Γ , while for large Γ a reasonable agreement with the empirical non-Lorentzian line shape (as seen in many of the experiments) is obtained. Nevertheless, it is not possible to achieve a perfect agreement for large fields in the latter case. In order to link the shape parameter Γ to the model parameters, we first consider analytical results in lowest order of p , i.e., a low electron density,

$$\Gamma = 2/[a^{-1} + b^{-1} + 4(ab)^{-1} + 2b^{-2}]. \quad (6)$$

Thus, it is found that reducing b^{-1} —which corresponds to enhancing bipolaron formation—broadens the MC(B). This means that higher magnetic fields are required to quench the bipolaron formation and to saturate the MC, in agreement with the full Monte Carlo calculations.⁷ A similar trend is found for lowering a^{-1} . For general values of p , an example of Γ as a function of both p and b^{-1} (and setting $a^{-1} = 0$) is displayed in Fig. 3(b).

In order to calculate the magnitude of OMAR, $MC(\infty)$, one can follow two routes. Treating Eq. (5) in an exact way requires the numerical evaluation of $g(\Gamma, 0)$. Alternatively, one can average over a discrete number of orientations, rather than integrate over all orientations of $\vec{B}_{\text{hf},i}$ at the two

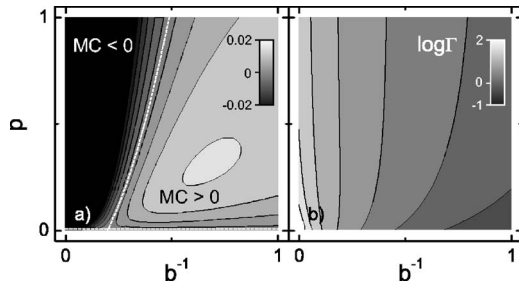


FIG. 3. (a) Magnetoconductance $MC(\infty)$ as a function of b^{-1} and p for $r_{e \rightarrow \alpha} = r_{\alpha \rightarrow \beta} = 1$, $r_{\beta \rightarrow e} = 0.1$, and $a^{-1} = 0$. The dashed lines indicate $MC = 0$, where the transition from negative to positive magnetoconductance occurs. (b) $\log \Gamma$ as a function of b^{-1} and p .

sites. As an example of such a calculation, $MC(\infty)$ is plotted as a function of p and b^{-1} in Fig. 3(a). Interestingly, it is found that *even this extremely simple model reproduces both positive and negative MC*. As a general trend at a large branching ratio (small b^{-1}), a negative MC is obtained, as expected according to the “blocking mechanism.” Actually, one can show analytically that $MC(\infty) = -1$ for $a^{-1} = b^{-1} = 0$, i.e., a fully blocked situation. At a smaller branching ratio, however, a sign change to a positive MC is witnessed. Within the two-site model, positive MC is a consequence of a doubly occupied β site that blocks other electrons to pass it. Interestingly, the line separating negative and positive MC is given by a simple expression (for arbitrary a),

$$p = (b^{-2}r_{\alpha \rightarrow \beta}^2 - 4r_{\beta \rightarrow e}^2)/(2r_{e \rightarrow \alpha}r_{\beta \rightarrow e}). \quad (7)$$

Thus, although the inclusion of spin-flip scattering (finite a) decreases the magnitude of the MC, the sign of MC is totally independent of a . Moreover, we found that Eq. (7) is unaffected by details of the $\vec{B}_{\text{hf},i}$ distribution.

Comparing $MC(\infty)$ and Γ [Figs. 3(a) and 3(b), respectively], a one-to-one relation is found to be absent. However, there is some trend that the negative MC has a larger width (Γ). It would be challenging to unambiguously correlate this outcome with experiments. Actually, in recent experiments on Alq_3 devices we measured a trend that upon a transition from positive to negative MC, B_0 is significantly increased.⁵ However, care has to be taken in drawing too strong conclusions from experiments on a single system. Moreover, our limited understanding of OMAR does not allow us to fully correlate experiments and theory yet.

Finally, we sketch a number of extensions of the present work that could lead to a closer agreement with the Monte Carlo studies and maybe even provide predictive power with respect to experiments. First of all, the rate parameters within our model as well as p , a , and b should be expressed in terms of the more generic system parameters (U , V , σ , E_F), electrical bias, and temperature. Second, rather than specifying two levels with fixed rate parameters, it might be necessary to model an ensemble of two-level systems with different relative energy alignments. As one of the outcomes, the final line shape would not be defined by a single Γ but rather be described by a distribution of values. Doing so in an *ad hoc* way, we found this to be a promising route. As an example, Fig. 2(c) displays the line shape resulting from a Gaussian distribution of $\log \Gamma$. This way, contrary to using a single component [Fig. 2(b)], perfect agreement is achieved with the phenomenological non-Lorentzian line shape (as also reproduced by Monte Carlo calculations) and up to large B .

In summary, we have introduced a simple two-site bipolaron model that reproduces the main features of OMAR, viz., the occurrence of sign changes and the characteristic line shapes. By producing simple analytical expressions, the approach could be valuable in guiding further numerical (Monte Carlo) and experimental efforts aimed at improving our understanding of this new phenomenon.

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⁸Time-reversed states are implicitly included in the occupation and rate parameters.

⁹ $g(0, s) = [16s^2(s^2 + 1)(13s^2 - 3) - (s^2 - 1)^2 \times (\log[(s - 1)^2] - \log[(s + 1)^2])] \times (3 \log[(s - 1)^2](s^2 - 1)^2 - 3 \log[(s + 1)^2](s^2 - 1)^2 + 8s(3 - 5s^2)) / [4096s^6]$, with $s = B/B_{\text{hf}}$