Organic magnetoresistance under resonant ac drive

R. C. Roundy and M. E. Raikh
Department of Physics and Astronomy, University of Utah, Salt Lake City, UT 84112

We study the spin dynamics of an electron-hole polaron pair in a random hyperfine magnetic field and an external field, $B_0$, under a resonant drive with frequency $\omega_0 = \gamma B_0$. The fact that the pair decays by recombination exclusively from a singlet configuration, $S$, in which the spins of the pair-partners are entangled, makes this dynamics highly nontrivial. Namely, as the amplitude, $B_1$, of the driving field grows, mixing all of the triplet components, the long-living modes do not disappear, but evolve from $T_+T_- \rightarrow \frac{1}{2}(T_+ \pm \sqrt{2} T_0 + T_-)$. Upon further increase of $B_1$, the lifetime of the $S$-mode is cut in half, while the $T_0$-mode transforms into an antisymmetric combination $\frac{1}{\sqrt{2}}(T_+ - T_-)$ and acquires a long lifetime, in full analogy to the superradiant and subradiant modes in the Dicke effect. Peculiar spin dynamics translates into a peculiar dependence of the current through an organic device on $B_1$. In particular, at small $B_1$, the radiation-induced correction to the current is linear in $B_1$.

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Introduction. Experimental finding that the intensity of room-temperature exciton luminescence in anthracene crystal changes by several percent in a weak magnetic field $B \sim 0.1$ T was reported more than four decades ago. Such a small scale of $B$ is set by the magnitude of zero-field splitting which controls the spin states of a pair of annihilating carriers forming an exciton. Organic magnetoresistance (OMAR) is an effect of a similar physical origin, where the external magnetic field causes a change of annihilating carriers forming an exciton. Organic magnetoresistance (OMAR) is an effect of a similar physical origin, where the external magnetic field causes a change of current through an organic layer by affecting the rate of spin-dependent processes, either recombination or bipolaron formation. It is commonly accepted that, in OMAR, the scale of $B$ is set by random hyperfine fields with rms $b_0 \sim 10$ mT. This fundamental origin of OMAR explains why the effect itself is robust, while its magnitude and even the sign are sensitive to technological details.

To capture the fundamental nature of OMAR quantitatively, it is sufficient to adopt the simplest assumption that bipolaron formation or recombination proceed only when the pair-partners are in the singlet state, $S$. With equal probabilities of all initial states, the recombination time of a pair is determined by the degree of admixture of the singlet to three other spin eigenstates caused by the hyperfine field. For external field $B \sim b_0$ the current response, $I(B)$, is governed by blocking configurations in which hyperfine fields “conspire” to protect the pair from crossing into $S$ after its creation. As the field increases and exceeds $b_0$, these long-living states evolve into $T_+$ and $T_-$ components of a triplet, and the current saturates.

A recent experiment, Ref. [12], has demonstrated that saturated OMAR exhibits a lively response to the external resonant ac drive at frequency $\omega_0 = \gamma B_0$, where $\gamma$ is the gyromagnetic ratio. The experiment was performed on a bipolar organic-semiconductor diode placed on the top of a conducting stripline through which the ac current was passed. To the first approximation, this fascinating finding can be accounted for by considering the ac field as a mixing agent, which tends to scramble all three triplet states and, thus, to limit the trapping ability of $T_+, T_-$, see Fig. 1. In this way, the ac field tends to change the current towards its value at zero magnetic field, which is what was observed in Ref. [12]. From the above picture one would expect that the radiation-induced change of current, $\delta I$, is due to the change of the recombination rate, which, in turn, is proportional to $B_1^2$, i.e. to the power of the driving field.

In the present paper we demonstrate that the dependence of $\delta I$ on $B_1$ is much more intricate. In particular, it is linear for weak $B_1$. This effect stems from pairs in which one of the partners is on-resonance, see Fig. 1. It appears that for these particular pairs the radiation-induced correction to the current is linear in $B_1$. (Color online). (a) Current passage through a bipolar device involves recombination of electron (red) and hole (blue) which occupy the neighboring sites; (b) Example of a pair in which electron is on-resonance and hole is off-resonance. The bubble illustrates the efficient mixing of the triplet components by the ac field, which, in turn, affects the crossing rate $T_0 \Rightarrow S$. The gray arrow indicates that recombination occurs exclusively from $S$.
induced suppression of trapping by $T_+$ and $T_-$ is especially efficient. However, such pairs determine $\delta I(B_1)$ only for weak driving fields, namely, for fields in which the nutation frequency is much smaller than $\Gamma$. As we demonstrate below, a very nontrivial physics unfolds for higher $B_1$. Quite unexpectedly, a new long-living mode, $\frac{1}{\sqrt{2}}(T_+ - T_-)$, emerges in strong enough driving fields, see Fig. 2. This mode, in which both pair-partners are on resonance, is fully analogous to subradiant state in the Dicke effect.\(^{16}\) Trapping by this state also yields a linear correction to the current, but with opposite slope.

\textit{Driven spin-pair without recombination.} To highlight the physics, we first neglect recombination. The Hamiltonian of the driven pair has a form

$$\hat{H} = \omega_e S_e^z + \omega_h S_h^z + 2\Omega_R (S_e^+ S_h^- + S_e^- S_h^+) \cos \omega t,$$

where $\omega_{e,h} = \omega + \delta_{e,h}$, $\Omega_R = \gamma B_1$ is the Rabi frequency, and $\delta_{e,h}$ are the $z$-components of the hyperfine fields acting on the electron and hole, respectively, i.e. the detunings of the pair-partners from the resonance. By retaining only $z$-components, we assumed that $B_o \gg b_0$. We will also assume that $\gamma B_o \gg \Omega_R$, which allows us to employ the rotating wave approximation. In the rotating frame, the amplitudes of $T_e$, $T_h$, $T_0$, and $S$-components of the wave function are related as

$$(\chi - \delta)A_{T_e} = \frac{\Omega_R}{\sqrt{2}} A_{T_0}, \quad (\chi + \delta)A_{T_h} = \frac{\Omega_R}{\sqrt{2}} A_{T_0},$$

$$\chi A_S = -\delta A_{T_0}, \quad \chi A_{T_0} = -\delta A_S + \frac{\Omega_R}{\sqrt{2}} (A_{T_+} + A_{T_-}),$$

where $\chi$ is the quasienergy, see Fig. 3 while parameters $\delta_0$ and $\delta$ are defined as

$$\delta_0 = \frac{1}{2}(\delta_e - \delta_h), \quad \delta = \frac{1}{2}(\delta_e + \delta_h).$$

The quasienergies satisfy the equation

$$\chi^2(\chi^2 - 2^2 - \Omega_R^2) - \delta_0^2(\chi^2 - 2^2) = 0 \quad (5)$$

with obvious solutions $\chi = \pm \frac{1}{2}\left[(\delta_0 + \delta)^2 + \Omega_R^2\right]^{-1/2} \pm \frac{1}{2} \left[(\delta_0 - \delta)^2 + \Omega_R^2\right]^{-1/2}$. It follows from Eqs. (2), (5) that for large $\Omega_R \gg \delta_0$, the pair of quasienergies, which approaches $\chi = 0$, corresponds to the modes $S$ and $\frac{1}{\sqrt{2}}(T_+ - T_-)$, while the quasienergies that approach $\chi = \pm \Omega_R$ correspond to the combinations $\frac{1}{\sqrt{2}}(T_+ \pm \sqrt{2}T_0 + T_-)$, respectively.

\textit{Driven spin-pair with recombination.} Including recombination from $S$ requires the analysis of the full equation for the density matrix, $i\dot{\rho} = [\hat{H}, \rho] - \frac{i}{\tau} \{\Pi_s, \rho\}$, where $\tau$ is the recombination time, and $\Pi_s$ is the projector onto the singlet subspace. The matrix corresponding to this equation is $16 \times 16$. The 16 eigenvalues can be cast in the form $\chi_i - \chi_j^*$, where $\chi_i$ and $\chi_j$ satisfy the quartic equation

$$\chi \left(\chi + \frac{i}{\tau}\right)(\chi^2 - 2^2 - \Omega_R^2) - \delta_0^2(\chi^2 - 2^2) = 0, \quad (6)$$

which generalizes Eq. (5) to the pair with decay. For slow recombination, $b_0\tau \gg 1$, the quasienergies acquire small imaginary parts, which can be found perturbatively from Eq. (6)

$$\delta \chi = -\frac{i}{4\tau} \left(1 \pm \frac{|\delta_0^2 - 2^2 - \Omega_R^2|}{\sqrt{(\delta_0^2 - 2^2 + \Omega_R^2)^2 - 4\delta_0^2 \delta^2}}\right). \quad (7)$$

Naturally, in the limit $\Omega_R \to 0$, Eq. (7) yields either $\delta \chi = -i/2\tau$ for $S$ and $T_0$ states, and $\delta \chi = 0$ for the trapping states $T_+$ and $T_-$. Less trivial is that at large $\Omega_R \gg \delta_0, \delta$ the values $\delta \chi$ again approach $\delta \chi = -i/2\tau$.\(\)
and $\delta \chi = 0$. The evolution of the imaginary parts of the quasienergies with $\Omega_R$ is illustrated in Fig. 2.

**Current at a weak drive.** Finite $\Omega_R \ll \delta, \delta_0 \sim b_0$ leads to finite lifetimes of the trapping modes. Expanding Eq. (7), we get

$$\tau_{tr} = \frac{1}{2|\chi|} = \frac{4\tau (\delta^2 - \delta_0^2)^2}{\Omega_R^2 \delta_0^2}. \tag{8}$$

Once $\tau_{tr}$ is known, we can employ the simplest quantitative description of transport based on the model Ref. 6 to express the correction, $\delta I(\Omega_R)$, to the current caused by the ac drive. Within this description, a pair at a given site is first assembled, then undergoes the pair-dynamics and either recombines or gets disassembled depending on which process takes less time, see Fig. 1 (a). These three steps are then repeated, so that the passage of current proceeds in cycles. Then the current associated with a given pair is equal to $1/\tau$, where $\langle t \rangle$ is the average cycle duration. Importantly, all the initial spin configurations of the pair have equal probabilities. For simplicity, it is assumed that, on average, the times of assembly and disassembly are the same $\tau_D \gg \tau$. This input is sufficient to derive the following expression for $\delta I(\Omega_R)$

$$\frac{\delta I(\Omega_R)}{I(0)} = \frac{\tau_{tr}^{-1}}{\tau_{tr}^{-1} + 2\tau_D} = \frac{\Omega_R^2 \delta_0^2}{\Omega_R^2 \delta_0^2 + 8(\delta^2 - \delta_0^2)^2 \tau_D}, \tag{9}$$

where $I(0) = \frac{1}{\tau_D}$. The remaining task is to average Eq. (9) over the distributions of the hyperfine fields, or equivalently, over $\delta$ and $\delta_0$. Since we consider a weak drive, this averaging is greatly simplified. Indeed, the major contributions to the average come from narrow domains $|\delta - \delta_0| \sim \Omega_R (\tau_D^0)^{1/2}$ and $|\delta + \delta_0| \sim \Omega_R (\tau_D^0)^{1/2}$, much narrower than $b_0$. On the other hand, these domains are wider than $\Omega_R$, which justifies the expansion Eq. (9). Replacing the distribution functions of $(\delta + \delta_0)$ and $(\delta - \delta_0)$ by $\frac{1}{\sqrt{\pi b_0}}$, we get

$$\frac{\langle \delta I(\Omega_R) \rangle}{I(0)} = \frac{\Omega_R^2}{(2\pi)^{1/2} b_0} \frac{1}{\Omega_R^2 + \frac{8\Omega_R^2}{\tau_D^0} (\delta - \delta_0)^2} \int d(\delta - \delta_0) \frac{d(\delta + \delta_0)}{\Omega_R^2 + \frac{8\Omega_R^2}{\tau_D^0} (\delta + \delta_0)^2} = \left( \frac{\tau_D^0}{2\tau} \right)^{1/2} \frac{\Omega_R}{b_0}, \tag{10}$$

i.e. the radiation-induced correction is linear in $\Omega_R$. To understand this anomalous behavior qualitatively, notice that small $\delta + \delta_0$ and $\delta - \delta_0$ correspond to small $\delta_e$ and $\delta_0$, respectively. Therefore, the linear $\delta I(\Omega_R)$ comes from configurations of hyperfine fields in which one of the pair-partners is on-resonance $17.18$, this partner responds strongly to the ac drive. The ratio $\Omega_R/b_0$ is the portion of such configurations. The upper boundary of the weak driving domain is set by the condition $\Omega_R \sqrt{\tau_D/\tau} \lesssim b_0$, which allowed us to replace the distribution functions of $\delta - \delta_0, \delta + \delta_0$ by a constant. It is also seen from Eq. (9) that for $\Omega_R \gg b_0 \sqrt{\tau_D/\tau}$ that the correction saturates at $\langle \delta I \rangle/I(0) = 1$. This saturation applies as long as $T_+$ and $T_-$ are the trapping eigenmodes. As was mentioned above, upon increasing $\Omega_R$, the trapping eigenmodes evolve into $\frac{1}{2} (T_+ \pm 2T_0 + T_-)$ and we enter the strong-driving regime. **Strong drive.** Expanding Eq. (7) in the limit $\Omega_R \gg \delta, \delta_0$ yields the expression $\tau_{tr} \approx \tau \Omega_R^2 / \delta_0^2$ for the lifetime of the trapping eigenmodes. The same steps that led to Eq. (9) give rise to the following negative correction to the current

$$\frac{\delta I(\Omega_R)}{I(0)} = 1 - \left( \frac{\tau}{\tau_D} \right) \frac{\Omega_R^2}{\delta_0^2 + \frac{8\Omega_R^2}{\tau_D^0} \Omega_R^2}. \tag{11}$$

We see from Eq. (11) that at $\Omega_R \gg (\tau_D)^{1/2}/b_0$ the current is the same as it was in the absence of the ac drive. This is due to the fact that both in the absence of drive and in this domain the number of long-living modes is two. The return of $\delta I(\Omega_R)$ to zero takes place over a parametrically broad interval $\sqrt{\tau_D} < \frac{\Omega_R}{b_0} < \sqrt{\pi b_0}$. The slope is calculated upon averaging Eq. (10) over $\delta_0$, which again can be carried out after replacing the distribution function by $\frac{1}{\sqrt{\pi b_0}}$ and yields

$$\frac{1}{\tau_D} \frac{\partial \langle \delta I \rangle}{\partial \Omega_R} = - \left( \frac{\tau}{\tau_D} \right)^{1/2} \frac{1}{b_0}. \tag{12}$$

This result shows a slope which is $\tau_D/\tau$ times smaller than that given by Eq. (11); this is consistent with the fact that the domain of the current drop is $\tau_D/\tau$ times broader than the domain of current growth.

In fact, the saturation predicted by Eq. (11) precedes another domain of change of current, which stems from bifurcation in lifetimes of $S, T_0$ modes at large $\Omega_R$, see Fig. 3. To capture this bifurcation analytically, notice that for large $\Omega_R$ Eq. (7) predicts for $\delta \chi = -\frac{i}{\tau} \chi$ for the $\frac{1}{2} (T_+ - T_-)$-mode, while the zero-order value of quasienergy falls off with $\Omega_R$ as $\delta_0 \delta / \Omega_R$. When $\Omega_R \gg \delta_0 \delta / \tau$, the correction exceeds the zero-order value and the perturbative treatment becomes inapplicable. Instead, we must make use of the fact that quasienergy is small, which allows us to simplify the quartic equation Eq. (9) to

$$\chi^2 + \frac{i}{\tau} \chi - \frac{\delta \chi^2}{\Omega_R^2} = 0. \tag{13}$$

The bifurcation of the lifetimes is revealed in the imaginary parts of the quasienergies, which are given by

$$\chi = -\frac{1}{2\tau} \left[ 1 \pm \sqrt{1 - 4\delta \chi^2 / \Omega_R^2} \right], \tag{14}$$

see Fig. 3. For large $\Omega_R$, solution $\chi_+ \approx -i/\tau$ corresponds to the $S$-mode, while the solution $\chi_- \approx -i\delta / \tau / \Omega_R^2$ evolves into a long-living mode $\frac{1}{2} (T_+ - T_-)$. In other
words, strong ac drive induces a third long-living mode which decouples from $S$, and therefore, cannot recombine. At the same time, the decoupling of $S$ from all other triplet states makes its lifetime two times shorter than in the absence of drive. Note, that there is a full formal correspondence between the solutions $\chi_+ , \chi_- \text{ and the superradiant and subradiant modes in the Dicke effect}^{16}$. On the physical level, in the Dicke effect, the subradiant mode acquires a long lifetime due to weak overlap with a photon field, while the long lifetime of the mode $1/\sqrt{2}(T_+ - T_-)$ is due to weak overlap with the recombinating state $S$. With trapping by the subradiant mode incorporated, the correction to current takes the form

$$\frac{\delta I(\Omega_R)}{I(0)} = - \frac{\Omega_R^2}{\delta^2 \delta^2 \tau \tau_D + \Omega_R^2},$$

(15)

It can be seen that the denominator in Eq. (15) defines a narrow domain $\delta_0 \sim \delta \sim \Omega_R^{1/2}/(\tau \tau_D)^{1/4}$, which yields the major contribution to $\langle \delta I(\Omega_R) \rangle$. Physically, this corresponds to configurations of the hyperfine fields in which both pair-partners are on-resonance. This again leads to the linear correction to $\langle \delta I(\Omega_R) \rangle$, which can be rewritten in dimensionless units as

$$\frac{\langle \delta I(\Omega_R) \rangle}{I(0)} = - \frac{\Omega_R}{\pi b_0^2 \sqrt{\tau_D}} \int dx \int dy \frac{1}{x^2 y^2 + 1}.$$  

(16)

The double integral in Eq. (16) diverges, but only logarithmically, as $\ln b_0^2 (\tau \tau_D)^{1/4}/\Omega_R$. In performing the averaging Eq. (16) we again replaced the distribution functions of $\delta, \delta_0$ by $1/\tau_D$. This replacement is justified provided the characteristic $\delta, \delta_0$ are much smaller than $b_0$. The latter condition is equivalent to the condition that the argument of the logarithm is big. We should also check the validity of the expansion of the square root in Eq. (14). For characteristic $\delta, \delta_0$ the combination $\delta^2 \delta^2 \tau \tau_D / \Omega_R^2 \sim \tau / \tau_D \ll 1$, i.e. the expansion is valid. Overall dependence of $\langle \delta I \rangle$ on $\Omega_R$ exhibiting three prominent domains, Eqs. (10), (11) and (16) is sketched in Fig. 4.

**Discussion.** The prime experimental finding reported in Ref. [15] which motivated the present paper, is that the current blocking responsible for the OMAR effect is effectively lifted under magnetic-resonance conditions. We demonstrated that this lifting is a natural consequence of developing of the Rabi oscillations in one of the spin-pair partners. It is also known$^{17,18}$ that Rabi oscillations in organic semiconductors, detected by pulsed magnetic resonance techniques, are also dominated by pairs in which one partner is on-resonance. The reason why both effects are due to the same sparse objects is that these objects are more responsive to the ac-drive than non-resonant pairs. At the same time, the phase volume of such pairs is linear in $\Omega_R$.

Besides the physical picture in the weak-driving domain, we also predict that the overall evolution of current with increasing $B_1$ is much more complex, and involves a maximum followed by a drop and subsequent saturation, see Fig. 4. Note that strong deviation from linear dependence of $\delta I$ sets in already at weak driving fields, $B_1 \lesssim b_0$. The non-monotonic behavior of current with ac drive is very unusual; its experimental verification would be a crucial test of radiation-induced trapping, which we predict.

Throughout the paper we assumed that the driving frequency exactly matches the Zeeman splitting $\gamma B_0$. In fact, in Ref. [15] the sensitivity of OMAR to the ac drive extended over a sizable interval of applied dc fields centered at $B_0$. It is straightforward to generalize our consideration to a finite detuning $\Delta = \gamma B_0 - \omega_0$. It enters the theory as a shift of the center of the gaussian distribution of parameter $\delta$ from $\delta = 0$ to $\delta = \Delta$. Below we simply list the changes in the correction $\delta I$ caused by strong detuning $\Delta \gg \gamma b_0$. These changes are different in different domains of the driving field shown in Fig. 4. For weak driving the correction $\delta I$ is given by

$$\frac{\delta I(\Omega_R)}{I(0)} = \frac{\Omega_R^2 b_0^2 \tau_D}{8 \Delta^2 \tau}.$$  

(17)

It emerges upon neglecting the $\Omega_R^2$ term in the denominator of Eq. (9) and applies in the domain $\Omega_R \lesssim \Delta$ if $\Delta$ exceeds not only $b_0$ but also $b_0 \sqrt{\tau_D / \tau}$. Then, unlike Fig. 4, the change $\frac{\delta I}{I(0)}$ does not reach one. The maximal change is $\sim b_0^2 \tau_D / \Delta^2 \tau \ll 1$. Interestingly, the domain (c) in Fig. 4 is affected much weaker by the detuning, $\Delta$. Instead of Eq. (10) we have

$$\frac{\delta I(\Omega_R)}{I(0)} = - \frac{\Omega_R}{\Delta b_0 \sqrt{\tau \tau_D}},$$  

(18)

which amounts to the suppression of the linear slope by $\Delta/b_0$.

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