

## Magnetic-Field Dependence of the Electroluminescence of Organic Light-Emitting Diodes: A Competition between Exciton Formation and Spin Mixing

S. P. Kersten,<sup>\*</sup> A. J. Schellekens, B. Koopmans, and P. A. Bobbert<sup>†</sup>

*Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

(Received 15 October 2010; published 13 May 2011)

We explore the magneto-electroluminescence (MEL) of organic light-emitting diodes by evaluating the magnetic-field dependent fraction of singlet excitons formed. We use two- and multisite polaron-hopping models with spin mixing by hyperfine fields and different singlet and triplet exciton formation rates  $k_S$  and  $k_T$ . A huge MEL is predicted when exciton formation is in competition with spin mixing and when  $k_T$  is significantly larger than  $k_S$ . This competition also leads to a low-field structure in the MEL that is in agreement with recent experiments.

DOI: 10.1103/PhysRevLett.106.197402

PACS numbers: 78.55.Kz, 73.50.Jt, 78.20.Ls, 78.60.Fi

Surprisingly large magnetic field effects (MFEs) of several percent on the electroluminescence and current in organic light-emitting diodes (OLEDs) have been found in recent years [1–5]. Intensive experimental and theoretical research is presently going on to unravel the mechanism behind these effects. The small field scale of a few milli-Tesla at which the effects occur points at the role of hydrogen hyperfine fields. Several mechanisms to explain the effects were proposed, involving excitons [3,4] or bipolarons [6]. These mechanisms rely on the suppression by an applied magnetic field of the hyperfine-induced spin mixing within a pair of polarons prior to exciton or bipolaron formation. Magnetocurrent measurements on organic donor-acceptor and single-carrier devices suggest that both exciton and bipolaron mechanisms can be operative [7].

The importance of hyperfine coupling for spin mixing in organic semiconductors was demonstrated explicitly by experiments in which MFEs occurring in a deuterated conjugated polymer were compared to those in the undeuterated polymer [8]. In identical OLEDs, the deuterated polymer yields a narrower line shape of the magneto-electroluminescence (MEL), i.e., the magnetic-field dependence of the electroluminescence. This is in agreement with the smaller magnetic moment of a deuteron as compared to a proton. Interestingly, the MEL curves of Ref. [8] show an additional structure at low field. Finding the cause of this structure is important for establishing the precise mechanism responsible for the MEL and possibly other MFEs.

Closely related to the discussion about MFEs is the question if the quantum-statistical 1:3 ratio for the formation of singlet ( $S$ ) vs triplet ( $T$ ) excitons in OLEDs is violated. There are experimental claims of either a larger [9–13] or smaller [14–16] ratio. This question has great technological relevance, since a larger than statistical ratio would break the 25% efficiency limit of OLEDs based on fluorescence. Establishing the origin of MFEs in OLEDs is expected to provide an answer to this question. Since the MEL of OLEDs quantifies the change in the number of  $S$

excitons formed when a magnetic field is applied, it is an important tool to address this question.

In this Letter we investigate the effects of spin mixing by hyperfine coupling on the fraction of  $S$  excitons formed in OLEDs. These effects have until now only been described in qualitative terms [1,3,4,15]. Moreover, only the case was considered where exciton formation from a pair of polarons is slow as compared to spin mixing by hyperfine coupling [15]. However, modeling of charge transport in two derivatives of poly( $p$ -phenylene vinylene) (PPV) [17] shows that the rate of polaron hopping is larger than the rate of spin mixing [18]. Since exciton formation is essentially a process in which one charge hops to the site of an opposite charge, exciton formation is not expected to be slow compared to spin mixing. We therefore consider general exciton formation and spin mixing rates. We demonstrate that unexpected effects occur when there is competition between exciton formation and spin mixing. We predict that huge MEL effects can then occur. Furthermore, we show that this competition leads to a low-field structure in the MEL curves comparable to that of Ref. [8].

We start our considerations with the two-site model shown in Fig. 1. The two sites  $\alpha$  and  $\beta$  represent localized states in a disordered organic semiconductor. A hole-polaron at site  $\alpha$  and an electron-polaron at site  $\beta$  together form a “polaron pair” (PP), a precursor to an exciton. In the PP state the exchange coupling and the possible dipolar coupling between the spins of the electron and hole are small with respect to the hyperfine and Zeeman coupling, which means that the spins are free to evolve independently.

We treat the hyperfine coupling at both sites within a semiclassical approach, with coupling of each polaron spin to a random hyperfine field  $\mathbf{B}_{\alpha(\beta),\text{hf}}$ . This field is drawn from a three-dimensional Gaussian distribution with a standard deviation  $B_{\text{hf}}$ . This treatment is correct for the typical situation that coupling of the  $\pi$ -electron spin to several hydrogen nuclear spins occurs [19]. The total effective magnetic field  $\mathbf{B}_{\alpha(\beta),\text{tot}}$  at each site is the sum of

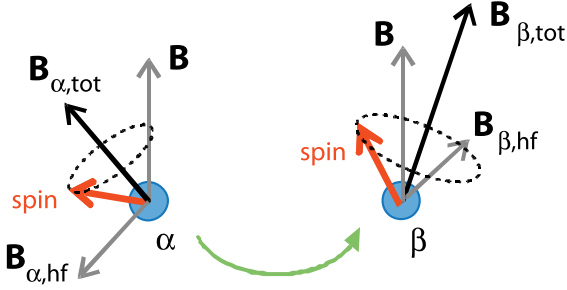


FIG. 1 (color online). Two-site model, with an electron at site  $\beta$  at which an exciton will be formed by hopping of a hole at site  $\alpha$  to  $\beta$ . The total effective magnetic field  $\mathbf{B}_{\alpha(\beta),\text{tot}}$  is the sum of a random hyperfine field  $\mathbf{B}_{\alpha(\beta),\text{hf}}$  and an applied field  $\mathbf{B}$ . Spin mixing occurs by precession of the spins around  $\mathbf{B}_{\alpha(\beta),\text{tot}}$ .

its hyperfine field and an externally applied magnetic field  $\mathbf{B} = B\hat{z}$ . The corresponding Hamiltonian is

$$H = g\mu_B(\mathbf{B}_{\alpha,\text{tot}} \cdot \mathbf{S}_\alpha + \mathbf{B}_{\beta,\text{tot}} \cdot \mathbf{S}_\beta)/\hbar. \quad (1)$$

Here,  $\mathbf{S}_{\alpha(\beta)}$  is the spin operator for the hole (electron) and  $\mu_B$  the Bohr magneton. Because of the small spin-orbit coupling in organic materials we have for the  $g$  factor  $g \approx 2$ ; we take this factor equal for electrons and holes.

Exciton formation in this model takes place by hopping of the hole to site  $\beta$ , resulting in the formation of an  $S$  or one of the  $T$  ( $T_0, T_+, T_-$ ) excitons. We assume that in the exciton states the exchange coupling is dominant with respect to the coupling to  $\mathbf{B}_{\alpha(\beta),\text{tot}}$ . Because of the steep exponential decay of the exchange coupling with distance one should expect that there is always a step in the exciton formation process where this coupling changes from subdominant in the PP state to dominant in the exciton state. We note that the exciton states after the hopping are not necessarily the states with the lowest energy. Further relaxation within the  $S$  or  $T$  exciton manifold can take place, but we assume that the exchange splitting prevents spin mixing during this process.

Because of their different energies and wave functions, the formation of  $S$  and  $T$  excitons occurs with different rates  $k_S$  and  $k_{T_0, T_+, T_-} = k_T$ , with a ratio  $\gamma \equiv k_S/k_T$ . The rates  $k_S$  and  $k_T$  are determined by material-specific details of the exciton formation process that go beyond the present work. We therefore treat  $\gamma$  as a parameter. We also introduce the ratio  $r \equiv k_S/\omega_{\text{hf}}$  as a parameter, with  $\omega_{\text{hf}} = g\mu_B B_{\text{hf}}/\hbar$  the typical hyperfine precession frequency;  $r \gg 1$  ( $r \ll 1$ ) corresponds to “fast” (“slow”) singlet exciton formation, as compared to the hyperfine precession time  $2\pi/\omega_{\text{hf}}$  ( $\approx 35$  ns for  $B_{\text{hf}} \approx 1$  mT). We will assume that unbinding of the excitons is prevented by a large energy difference between the PP and exciton states.

The combination of the coherent time evolution of the spin state of the PP and the incoherent formation of an exciton on site  $\beta$  is described by a stochastic Liouville equation [20] for the PP and exciton density operators  $\rho_{\text{PP}}$  and  $\rho_X$ :

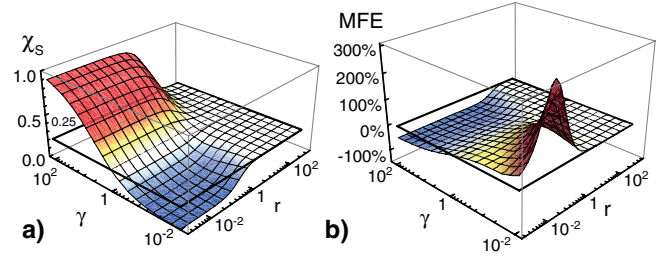


FIG. 2 (color online). (a) Fraction of formed singlet excitons  $\chi_S$  and (b) magnetic-field effect (MFE) of  $\chi_S$  as a function  $\gamma$  and  $r$  for the two-site model.

$$\begin{aligned} \frac{\partial \rho_{\text{PP}}}{\partial t} &= -\frac{i}{\hbar}[H, \rho_{\text{PP}}] - \frac{1}{2}\{\Lambda, \rho_{\text{PP}}\}, \\ \frac{\partial \rho_X}{\partial t} &= \sum_{\lambda} k_{\lambda} P_{\lambda} \rho_{\text{PP}} P_{\lambda}, \end{aligned} \quad (2)$$

where  $\{\cdot, \cdot\}$  denotes the anticommutator and  $\Lambda = \sum_{\lambda} k_{\lambda} P_{\lambda}$  for  $\lambda = S, T_-, T_0, T_+$ .  $P_{\lambda} = |\lambda\rangle\langle\lambda|$  is the projection onto  $|\lambda\rangle$ , with  $|S\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ ,  $|T_0\rangle = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$ ,  $|T_+\rangle = |\uparrow\uparrow\rangle$ , and  $|T_-\rangle = |\downarrow\downarrow\rangle$ . We take  $\rho_X(t=0) = 0$  and for  $\rho_{\text{PP}}(t=0)$  we take a density operator corresponding to equal populations of the PP spin states. The final  $S$  and  $T$  exciton fractions  $\chi_S$  and  $\chi_T = 1 - \chi_S$  are obtained from  $\rho_X(t \rightarrow \infty)$  by solving Eq. (2) with these initial conditions and by performing a numerical average over the hyperfine fields.

Figure 2(a) shows the dependence of the singlet fraction  $\chi_S(B=0)$  on  $\gamma$  and  $r$ . For simplicity, the standard deviations  $B_{\text{hf}}$  were taken equal for electrons and holes. A clear deviation from the statistical value of 1/4 is observed. The deviation disappears in the fast-hopping limit  $r \rightarrow \infty$ , where the effect of the hyperfine fields is quenched. As expected, the largest deviation occurs in the slow-hopping limit  $r \rightarrow 0$ . We conjecture that the mechanism presented here is the generic mechanism behind violations of the statistical  $S:T$  ratio in OLEDs.

Figure 2(b) shows the dependence of the magnetic-field effect  $\text{MFE}(B) = [\chi_S(B) - \chi_S(0)]/\chi_S(0)$  for  $B \rightarrow \infty$  (MFE for short) on  $\gamma$  and  $r$ . We see that in the slow-hopping limit  $r \rightarrow 0$  also a substantial MFE occurs. In this limit the following analytical result can be derived [21]:

$$\begin{aligned} \chi_S(0) &= \frac{\gamma\{\gamma - 1 - \ln[\frac{1}{4}(1 + \gamma)^2]\}}{(\gamma - 1)^2}, \\ \chi_S(\infty) &= \frac{\gamma}{2(\gamma + 1)}. \end{aligned} \quad (3)$$

In the limit  $r \rightarrow 0$  we find from Eq. (3) that  $\text{MFE} \rightarrow -1/2$  for  $\gamma \rightarrow \infty$ , whereas  $\text{MFE} \rightarrow +0.294$  for  $\gamma \rightarrow 0$ .

Quite surprisingly, however, the largest MFE does not occur for  $r \rightarrow 0$ , but for intermediate values of  $r$  and small  $\gamma$  ( $k_T \gg k_S$ ). The reason for this is the competition between exciton formation and spin mixing. For small  $r$  and  $\gamma$  the singlet fraction is small, but increases to the statistical fraction of 1/4 when  $r$  grows to a value where

exciton formation is so fast that it quenches the effects of the hyperfine fields. This increase occurs more abruptly for small than for large  $B$ , leading to a pronounced peak in the MFE that grows indefinitely with decreasing  $\gamma$ . This means that it should be possible to obtain a huge MEL if the parameters of the organic material can be appropriately tuned. As an example, for  $\gamma = 0.1$  and  $r = 0.3$  an MFE of 75% can be obtained, with an  $S$  exciton fraction of 10% at large field.

In order to study situations closer to reality, we simulated recombination in  $3 \times 3 \times 3$  and  $5 \times 5 \times 5$  cubic multisite boxes with an electron fixed in the middle. A hole in the box is attracted to the electron by the Coulomb interaction and will eventually recombine with it. It is straightforward to generalize the Hamiltonian equation (1) and the stochastic Liouville equation (2) to this case. To be specific, we took parameters representative of room-temperature hole transport in PPV derivatives, with random site energies drawn from a Gaussian distribution with a standard deviation of 0.14 eV, a lattice constant of 1.8 nm, and a relative dielectric constant of 3 [17]. Since hole transport in PPV is dominant with respect to electron transport it is indeed reasonable to assume that the electron remains fixed. We assumed hopping by thermally assisted tunneling [22] from site  $i$  to  $j$  with a rate  $k_{ij} = k_{\text{hop}} \exp[-(\varepsilon_j - \varepsilon_i)/k_B T]$  for  $\varepsilon_j \geq \varepsilon_i$  and  $k_{ij} = k_{\text{hop}}$  for  $\varepsilon_j < \varepsilon_i$ . Here,  $T$  is temperature,  $k_B$  is Boltzmann's constant, and  $\varepsilon_i$  and  $\varepsilon_j$  are the site energies of  $i$  and  $j$ , which include the contribution of the Coulomb energy due to the electron. A hole with a random spin is introduced with a Boltzmann probability at one of the boundary sites. Since exciton formation is an energetically downward process that occurs by hopping of a hole to the electron, it is reasonable to assume that  $k_S$  and  $k_T$  are comparable in magnitude to  $k_{\text{hop}}$ . For definiteness we took  $k_S = k_{\text{hop}}$  and  $k_T = k_{\text{hop}}/\gamma$ .

Figures 3(a) and 3(b) show the result for  $\chi_S$  and its MFE, respectively, of the simulations for the two boxes with  $\gamma = 0.1, 0.7$  (see below for this choice) and 10.

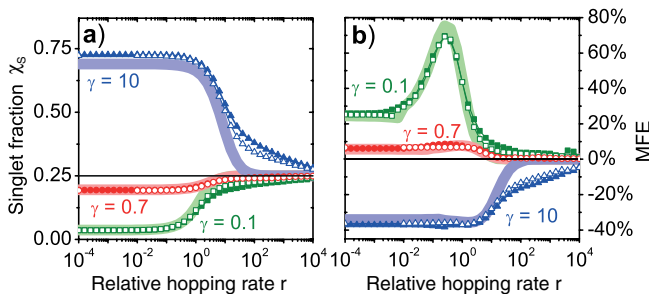


FIG. 3 (color online). (a)  $\chi_S$  and (b) MFE of  $\chi_S$  at different  $\gamma$  as a function of  $r$  for the  $3 \times 3 \times 3$  (open symbols) and  $5 \times 5 \times 5$  (closed symbols) multisite models representative of PPV. The results of the two-site model are included for comparison (thick shaded lines). The value  $\gamma = 0.7$  is compatible with the  $\chi_S = 20 \pm 4\%$  reported in Ref. [14].

Averages were taken over different energetic and hyperfine disorder configurations until the statistical error was of the order of the size of the symbols shown. The results of the two-site model are included for comparison. The huge MFE is again visible in Fig. 3(b) for  $\gamma = 0.1$ . The results for the  $3 \times 3 \times 3$  and  $5 \times 5 \times 5$  boxes almost fall on top of each other, which means that the results are converged with respect to system size. Interestingly, both the deviations from the statistical singlet fraction as well as the MFE extend to higher values of  $r$  for the multisite boxes than for the two-site model. The reason is that a hole at a site neighboring the electron has, apart from the option to recombine with the electron, the option to hop to another site, leading to further possibilities for randomization of its spin before recombination. Hence, the effect of the extra sites is to enhance the spin randomization by the hyperfine fields. This is an important conclusion, since estimates of  $r$  for two PPV derivatives, obtained by an analysis of measured current-voltage characteristic of hole-only devices [17], are in the order of 10–1000 [18]. Figure 3 shows that even for these high values of  $r$  observable effects should remain.

We also investigated the line shapes of  $\text{MFE}(B)$ . For  $r \rightarrow 0$  we always found Lorentzian line shapes with a width of a few times  $B_{\text{hf}}$ . However, for intermediate  $r$  we generically found an additional low-field structure, as in the MEL experiments of Ref. [8]; see Fig. 4. In Ref. [8] the MEL curves were modeled with a coupling of the spins of the PP to a single nuclear spin at each of the two sites of the PP (spin 1/2 for the undeuterated and spin 1 for the deuterated polymer). However, it should be expected that in reality coupling to many nuclear spins occurs [23], in accordance with our semiclassical treatment. An intuitive explanation for the low-field structure is again based on the

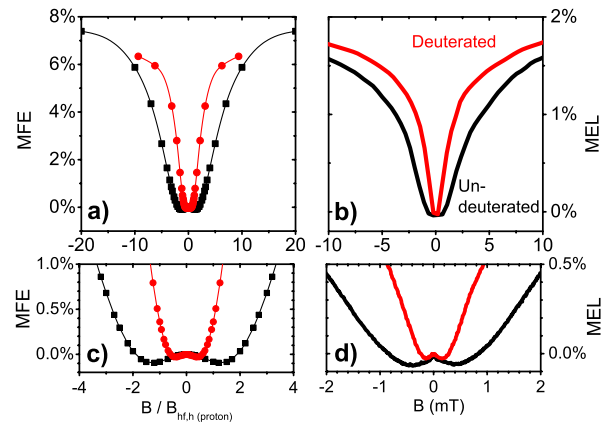


FIG. 4 (color online). (a) Magnetic-field dependence  $\text{MFE}(B)$  of the singlet exciton fraction  $\chi_S$  in the two-site model for  $\gamma = 0.7$  and  $B_{\text{hf},e} = 3B_{\text{hf},h}$ . Black squares:  $r = 1.5$  (protons). Red circles:  $r = 4.886 = 3.257 \times 1.5$  and hyperfine fields divided by 3.257 (deuterons). The field axis is scaled with  $B_{\text{hf},h}$  for protons. (b) Magneto-electroluminescence of OLEDs of a deuterated and undeuterated PPV derivative, reproduced from Ref. [8]. (c) and (d) zoom in to the effects occurring at low field.

competition between exciton formation and spin mixing at finite  $r$ . An increase of  $B$  initially increases spin mixing by increasing the average precession frequencies. With a further increase of  $B$  the alignment of the effective magnetic fields eventually reduces spin mixing.

The experimentally observed increase of the MEL with magnetic field points at a larger  $T$  than  $S$  formation rate, i.e.,  $\gamma < 1$ . This is in agreement with the claim of Segal *et al.* that in PPV the  $S$  fraction is lower than 25% [14]. The result appears to be at odds with theoretical considerations about a faster formation rate of  $S$  than  $T$  excitons [24–26], based on different ionic characters and/or energies of  $S$  and  $T$  excitons. It is our assumption, however, that the step decisive for the final  $S$  fraction occurs in the very early stage of exciton formation, when these considerations may not yet apply. With  $\gamma \approx 0.7$  we can reproduce the value of  $20 \pm 4\%$  reported by these authors [cf. Fig. 3(a)]. Although not essential for obtaining the low-field structure, taking different standard deviations for the hyperfine fields of electrons and holes makes the structure more prominent. The results for the MFE plotted in Figs. 4(a) and 4(c) were obtained with the two-site model [27] by taking  $\gamma = 0.7$  and  $B_{\text{hf},e} = 3B_{\text{hf},h}$ , as found by electrically determined magnetoresonance measurements on a related PPV derivative [28]. We took  $r = k_S/\omega_{\text{hf},h} = 1.5$  and 4.886. The factor  $4.886/1.5 = 3.257$  accounts for the different spins and gyromagnetic ratios (267.51 and 41.07 rad/sT) of the proton and deuteron. With these values of  $r$ , the ratio of the sizes of the low-field structure for the deuterated and undeuterated case is approximately equal for the predicted and measured result. Regarding the large uncertainty in the parameters, the overall agreement with the MEL experiments is quite remarkable. An important conclusion is that our study of MEL curves provides valuable information about the magnitude and ratio of the triplet and singlet exciton formation rates in OLEDs.

Finally, we remark that similar low-field structures as found in the MEL were very recently also found in the magnetoconductance (MC) of OLEDs as well as single-carrier devices [29]. The low-field structure in the MC of OLEDs could very well be related to that in the MEL. However, in the single-carrier devices no exciton formation should take place, leaving the bipolaron mechanism [6] as candidate for the description of the MC. By taking very large values of  $\gamma$  in the two-site model, reflecting suppression of triplet bipolaron formation [6], we checked that the low-field structure for intermediate  $r$  then also appears. This demonstrates the similarity of the physics involved in exciton and bipolaron formation.

In summary, we investigated the effects of hyperfine-induced spin mixing on the magnetoelectroluminescence of organic light-emitting diodes by evaluating the fraction of singlets formed as a function of magnetic field. A huge magnetic-field dependence may be obtained when there is competition between exciton formation and spin mixing.

Low-field structures found in magnetoelectroluminescence experiments were reproduced and explained in terms of this competition. Results obtained with a two-site model for a recombining electron-hole-polaron pair were verified with simulations of a realistic multisite model, in which spin mixing is enhanced by hopping to other sites before recombination.

This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organisation for Scientific Research (NWO). We thank Dr. T.D. Nguyen for providing us with the experimental data in Fig. 4.

\*s.p.kersten@tue.nl

†p.a.bobbert@tue.nl

- [1] J. Kalinowski *et al.*, *Chem. Phys. Lett.* **380**, 710 (2003).
- [2] T.L. Francis *et al.*, *New J. Phys.* **6**, 185 (2004).
- [3] V. Prigodin *et al.*, *Synth. Met.* **156**, 757 (2006).
- [4] P. Desai *et al.*, *Phys. Rev. B* **76**, 235202 (2007).
- [5] B. Hu and Y. Wu, *Nature Mater.* **6**, 985 (2007).
- [6] P. A. Bobbert *et al.*, *Phys. Rev. Lett.* **99**, 216801 (2007).
- [7] F.J. Wang, H. Bässler, and Z. Vally Vardeny, *Phys. Rev. Lett.* **101**, 236805 (2008).
- [8] T.D. Nguyen *et al.*, *Nature Mater.* **9**, 345 (2010).
- [9] Y. Cao *et al.*, *Nature (London)* **397**, 414 (1999).
- [10] M. Wohlgenannt *et al.*, *Nature (London)* **409**, 494 (2001).
- [11] J.S. Wilson *et al.*, *Nature (London)* **413**, 828 (2001).
- [12] A.S. Dhoot *et al.*, *Chem. Phys. Lett.* **360**, 195 (2002).
- [13] C. Rothe, S.M. King, and A.P. Monkman, *Phys. Rev. Lett.* **97**, 076602 (2006).
- [14] M. Segal *et al.*, *Phys. Rev. B* **68**, 075211 (2003).
- [15] Y. Yoshida *et al.*, *Mol. Cryst. Liq. Cryst.* **426**, 19 (2005).
- [16] M. Carvelli, R. A. J. Janssen, and R. Coehoorn, *Phys. Rev. B* **83**, 075203 (2011).
- [17] W.F. Pasveer *et al.*, *Phys. Rev. Lett.* **94**, 206601 (2005).
- [18] P. A. Bobbert *et al.*, *Phys. Rev. Lett.* **102**, 156604 (2009).
- [19] K. Schulten and P. Wolynes, *J. Chem. Phys.* **68**, 3292 (1978).
- [20] R. Kubo, *J. Math. Phys. (N.Y.)* **4**, 174 (1963).
- [21] See supplemental material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.106.197402> for a derivation of the expressions given in Eq. (3).
- [22] A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).
- [23] P. A. Bobbert, *Nature Mater.* **9**, 288 (2010).
- [24] S. Karabunarliev and E.R. Bittner, *Phys. Rev. Lett.* **90**, 057402 (2003).
- [25] K. Tandon, S. Ramasesha, and S. Mazumdar, *Phys. Rev. B* **67**, 045109 (2003).
- [26] W. Barford, *Phys. Rev. B* **70**, 205204 (2004).
- [27] The accuracy we could obtain with the multisite models was not sufficient to resolve the low-field structure, but Fig. 3 demonstrates the equivalence of the two- and multisite models.
- [28] D.R. McCamey *et al.*, *Phys. Rev. Lett.* **104**, 017601 (2010).
- [29] T.D. Nguyen *et al.*, *Phys. Rev. Lett.* **105**, 166804 (2010).