P H Y S I C A L   R E V I E W   L E T T E R S

Exact Solution for Hopping Dissociation of Geminate Electron-Hole Pairs in a Disordered Chain

O. Rubel,* S. D. Baranovskii, W. Stolz, and F. Gebhard

Department of Physics and Material Sciences Center, Philipps-University Marburg, Marburg 35032, Germany

A universal theoretical description of the dissociation problem for electron-hole pair on a one-dimensional chain in the hopping regime is proposed. Widely used results of Frenkel and Onsager theories are obtained as particular cases of the general solution. The application of the analytical theory to disordered chains shows that disorder enhances dissociation of geminate electron-hole pairs at low electric fields and suppresses at high fields.

PACS numbers: 72.80.Ng, 72.20.Jv, 72.80.Le

The problem of the dissociation of geminate electron-hole pairs and the problem of injection of electrons into semiconductor out of a metallic contact are among the most often discussed topics in the field of disordered systems, particularly organic disordered materials [1–4]. The central question in both cases is how electrons escape from the Coulomb potential well via a series of noncoherent hopping transitions between spatially localized states. In the case of pair dissociation, the Coulomb potential is created by the geminate hole, whereas, in the case of electron injection, the potential is created by the image charge within the metallic contact. A solution of the dissociation and injection problems is of vital importance for the physics of molecular solar cells, organic light emitting diodes, polymer field effect transistors, and other optoelectronic molecular devices.

Experimental and theoretical studies are usually focused on the effect of the external electric field on the efficiencies of the dissociation and injection [5–14]. Field dependence of the dissociation efficiency of geminate electron-hole pairs is typically interpreted in terms of Onsager [15] or Frenkel [16] theories. Frenkel [16] treated escape of charge carriers from the Coulomb potential well in a rather simplified way considering a *one-step* process, the rate of which is determined by thermal activation over the Coulomb barrier, which itself is lowered by the external electric field $\mathcal{E}$. In the case of excitons, the escape process competes with the exciton recombination, the rate of which is determined by the inverse exciton lifetime τ_0^{-1}. Such a formalism yields the field dependence of the exciton dissociation efficiency in the form [17]

$$\eta_F(\mathcal{E}) = \left[1 + (\nu_0 \tau_0)^{-1} \exp\left(\frac{E_b - \beta\sqrt{\mathcal{E}}}{k_B T} \right) \right]^{-1}, \quad (1)$$

where ν_0 is the attempt-to-escape frequency, E_b is the exciton binding energy, k_B is the Boltzmann constant, T is the temperature, and $\beta = (e^3/\pi\epsilon\epsilon_0)^{1/2}$ in which e is the elementary charge, ϵ is the dielectric constant, and ϵ_0 is the permittivity of vacuum.

Onsager's theory [15] of geminate pair dissociation offers a more rigorous solution of the problem, in which an electron-hole pair is generated with some initial sepa-

ration x_0, and one of the carriers undergoes subsequent diffusion and drift in the Coulomb potential modified by the external electric field. The disadvantage of the original formulation is that the recombination was assumed to occur instantaneously as soon as the traveling charged particle arrives at the site occupied by the recombination partner. This assumption is, however, not applicable to molecular solids where the exciton recombination time is of the order of nanoseconds. Hong and Noolandi [18] solved the problem with modified boundary conditions in order to account for the partial absorption at the origin and, thus, for the finite recombination time. This yields the following expression for the electron-hole pair dissociation efficiency in the case of one-dimensional systems [18]:

$$\eta_{\rm ON}(\mathcal{E}) = \frac{(D/v)\exp(-E_b/k_B T) + \int_0^{x_0} \exp[E(x,\mathcal{E})/k_B T]dx}{(D/v)\exp(-E_b/k_B T) + \int_0^{\infty} \exp[E(x,\mathcal{E})/k_B T]dx}, \quad (2)$$

where D is the diffusion coefficient, v is the recombination velocity, and the potential profile is given by $E(x, \mathcal{E}) = -e^2/4\pi\epsilon\epsilon_0 x - e\mathcal{E}x$ for $x > 0$.

It is worth noting that the results of Frenkel and Onsager do not include disorder effects. However, charge transport in amorphous organic semiconductors is characterized by disorder in the positions and energy levels of single molecules, which causes the spatial localization of the electron states [19]. As a result, the primary transport mechanism in such solids is the incoherent hopping of localized charge carriers between molecular sites [19,20]. So far, the most reliable approach for modeling dissociation processes in disordered solids is Monte Carlo computer simulations [10,13,21].

In our work we present a general analytical solution for the dissociation problem in the hopping transport mode. The aim is to describe analytically the field-dependent dissociation probability of a geminate electron-hole pair taking into account not only the Coulomb potential but also the disorder leading to the distribution of local transition rates and site energies. The model is solved exactly, and the dissociation probability is obtained as a function of the particular transition rates between hopping sites, of the recombination rate, and of the particular energies of local-
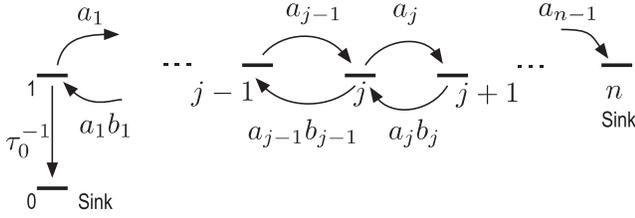
FIG. 1.   One-dimensional chain of n hopping sites with asymmetry in transition rates.

ized states. The results of Frenkel and Onsager [Eqs. (1) and (2), respectively] turn out to be asymptotic forms of the general solution in the absence of disorder. As an example we consider electron-hole dissociation at the interface between donor and acceptor phases and show that the disorder promotes dissociation at low and intermediate electric fields and suppresses at high fields, which is in agreement with results of the computer simulation reported earlier [13,21].

Model.—We treat the following recombination model. An electron executes a nearest-neighbor random walk on a one-dimensional chain of hopping sites as schematically shown in Fig. 1. The transition rate a_j from site j to $j+1$ depends on the spatial separation r_j between the sites and on the site energies according to [22]

$$a_j = \nu_0 \exp\left(-\frac{2r_j}{\alpha} - \frac{E_{j+1} - E_j + |E_{j+1} - E_j|}{2k_BT}\right). \quad (3)$$

The backward transition rate from site $j+1$ to j is given by the product a_jb_j, where $b_j = \exp[(E_{j+1} - E_j)/k_BT]$ is the asymmetry factor. The electron can recombine with the hole fixed at the origin (site 0) only via transition from site 1. The rate of the latter process is τ_0^{-1}, provided there is no separation between sites 0 and 1. Otherwise, τ_0 should additionally include an exponential term responsible for tunneling. The time evolution of the particle density at site j is determined by the set of rate equations

$$\frac{df_j}{dt} = f_{j-1}a_{j-1} - f_j(a_{j-1}b_{j-1} + a_j) + f_{j+1}a_jb_j + G_j$$
$$- \frac{f_j}{\tau_0}\delta_{1j}, \quad (4)$$

where δ_{ij} is Kronecker's symbol and $G_j = g_0\delta_{ij}$ represents the generation rate implying that the electron can start its random walk at an arbitrary site i.

We are searching for the stationary solution of Eq. (4) with the boundary condition corresponding to full absorption on site n. The probability for the recombination is determined by the relative ratio of the recombination and generation fluxes

$$\vartheta = \frac{f_1}{\tau_0 g_0}. \quad (5)$$

Then the probability of recombination is given by

$$\vartheta = \frac{\frac{1}{a_i} + \sum_{j=i+1}^{n-1}\frac{1}{a_j}\prod_{k=1}^{j-1}b_k}{\tau_0 + \frac{1}{a_1} + \sum_{j=2}^{n-1}\frac{1}{a_j}\prod_{k=1}^{j-1}b_k}. \quad (6)$$

According to the definition of the asymmetry factors b_k, the products in Eq. (6) reduce to a simple exponential term

$$\prod_{k=1}^{j-1}b_k = \exp\left(\frac{E_j - E_1}{k_BT}\right). \quad (7)$$

Substituting Eq. (7) into Eq. (6) and using the property $\vartheta + \eta = 1$ we obtain the dissociation probability as a function of transition rates, recombination rate, and energies of localized states

$$\eta(\mathcal{E}) = 1 - \frac{\sum_{j=i}^{n-1}\frac{1}{a_j(\mathcal{E})}\exp\left[\frac{E_j(\mathcal{E})-E_1}{k_BT}\right]}{\tau_0 + \sum_{j=1}^{n-1}\frac{1}{a_j(\mathcal{E})}\exp\left[\frac{E_j(\mathcal{E})-E_1}{k_BT}\right]}. \quad (8)$$

This general equation is the main result of our contribution. It shows that the dissociation probability is determined by the sum of inverse transition rates weighted by the Arrhenius term with the potential value at a particular hopping site taken relative to the potential value at the recombination site. For instance, in the case of the Coulomb potential combined with an external electric field, transitions at the hump of the potential barrier have a dominant impact on the dissociation probability and not transitions in the close proximity to the hole as it is sometimes believed [4].

Asymptotics.—Let us now consider important asymptotic forms of the general solution and compare them with the known theoretical results—Frenkel and Onsager theories. In order to compare our solution with the Onsager theory, we consider electron diffusion on a regular semi-infinite chain of hopping sites with separations r_0. The starting point is chosen at an arbitrary site $i \in \mathbb{Z}^+$ and all forward transition rates between neighboring sites are equal to a_0. To fulfil this condition, one has to assume the spatial separation r_0 between hopping sites as infinitely small, so that energy differences between neighboring sites are much less than k_BT. The potential is assumed to be not divergent with the value E_1 at the origin. The boundary conditions correspond to the partial recombination at the origin with the rate τ_0^{-1} and complete absorption at infinity. Under such circumstances, Eq. (8) yields the dissociation probability

$$\eta_{ON} = \frac{a_0\tau_0\exp(E_1/k_BT) + \sum_{j=1}^{i-1}\exp(E_j/k_BT)}{a_0\tau_0\exp(E_1/k_BT) + \sum_{j=1}^{\infty}\exp(E_j/k_BT)}. \quad (9)$$

This expression is identical to the Onsager dissociation probability given by Eq. (2), provided the diffusion coefficient and the recombination velocity are replaced by $D = a_0r_0^2$ and $v = r_0/\tau_0$, respectively, and the summation in Eq. (9) is replaced by integration.

In order to compare our general solution with the Frenkel theory of exciton dissociation, we consider the situation where an electron starting at the origin executes a random walk in the combined potential created by the hole and by the external electric field. The corresponding dissociation probability determined by Eq. (9) reduces to the form

$$\eta_F = \left[1 + (a_0\tau_0)^{-1} \exp(-E_1/k_B T) \sum_{j=1}^{\infty} \exp(E_j/k_B T) \right]^{-1},$$

(10)

where $E_j/k_B T = -C/(j-1) - B(j-1)$ with $C = e^2/4\pi\epsilon\epsilon_0 k_B T r_0$ and $B = e\mathcal{E}r_0/k_B T$. A further simplification of Eq. (10) can be achieved if we replace the sum by an integral (Ref. [23], p. 307),

$$\sum_{j=1}^{\infty} \exp\left[-\frac{C}{j-1} - B(j-1) \right]$$

$$\approx \int_0^{\infty} \exp(-C/j' - Bj')dj' = \frac{2C}{\sqrt{CB}}K_1(2\sqrt{CB}), \quad (11)$$

where $K_1(x)$ is the modified Bessel function of the second kind, which has two asymptotic forms

$$K_1(2\sqrt{CB}) \approx \begin{cases} [\sqrt{\pi}/2(CB)^{1/4}]\exp(-2\sqrt{CB}) & \text{if } 2\sqrt{CB} \gg 1 \\ 1/2\sqrt{CB} & \text{if } 0 < 2\sqrt{CB} \ll 1, \end{cases} \quad (12)$$

corresponding to the high- and low-field limits, respectively. Combining Eqs. (10) and (11) with the high-field asymptotic form of Eq. (12) we obtain the field dependence of the exciton dissociation probability in the form

$$\eta_F(\mathcal{E}) \approx \left[1 + (\tau_0 a_0)^{-1} \left(\frac{\pi^2 C}{B^3}\right)^{1/4} \exp\left(\frac{-E_1 - \beta\sqrt{\mathcal{E}}}{k_B T}\right) \right]^{-1},$$

(13)

where β is the same as in Eq. (1). This result is identical to that of Frenkel [Eq. (1)], in spite of the fact that we consider the electron overcoming the Coulomb barrier in a diffusive manner instead of the single step as it was originally suggested by Frenkel [16]. The only difference between Eqs. (1) and (13) is the term $(\pi^2 C/B^3)^{1/4}$, which accounts for the diffusive character of the motion of the electron. This correction term is field- and temperature-dependent and proportional to $T^{1/2}\mathcal{E}^{-3/4}$. However, it only weakly affects the main field dependence of the dissociation probability, which is governed by the exponential term in Eq. (13).

At low fields, Eqs. (10)–(12) yield a linear dependence for the exciton dissociation probability on the magnitude of the applied electric field

$$\eta_F(\mathcal{E}) \approx a_0\tau_0(e\mathcal{E}r_0/k_B T) \exp(E_1/k_B T). \quad (14)$$

The crossover from the exponential to linear field dependence of the exciton dissociation probability—Eqs. (13) and (14), respectively—takes place at $2\sqrt{CB} \sim 1$, i.e., $\mathcal{E} \sim (k_B T/\beta)^2$. At room temperature for a material with the dielectric constant of 3.5, the corresponding electric field is of the order of 4 kV/cm. Experimentally, the linear dependence of the dissociation probability was reported for anthracene single crystals at fields of the order of 10 kV/cm [24].

Effect of disorder.—In molecular solids, the disorder shows up in fluctuations of the spatial positions and energy levels of transport states. These fluctuations result in a distribution of the transition rates between hopping sites, which are explicitly included in our model. As an example, we consider the field-assisted exciton dissociation at the interface between donor and acceptor phases, which are often used in solar cells in order to facilitate dissociation of photogenerated excitons. The structure of the interface and the relevant processes are illustrated in Fig. 2.

We assume the mobility of electrons in the acceptor phase to be much lager than the mobility of holes in the donor phase. Therefore, we consider the hole trapped at the interface, and the electron undergoing a random walk in the Coulomb potential modified by the external electric field. Disorder is modeled in the following way. The position of the jth localized state for the electron is given by $x_j = r_0 j + 2\delta r \xi$, where δr is the maximal deviation of the site position from its ordered value, and ξ is a random number with a uniform distribution in the range between -0.5 and 0.5. The origin of the spatial axis is set at the position of a hole, i.e., $x_0 = 0$. The spatial separation between the adjacent sites is given by $r_j = x_{j+1} - x_j$. Because electrons and holes are spatially separated, the recombination probability includes the tunneling term and has the form $\tau_0 = \tau_{\text{ex}} \exp(2r_0/\alpha)$, where τ_{ex} is the exciton radiative lifetime. The energies of the sites are determined by

$$E_j = E_j^0(\sigma) - \frac{e^2}{4\pi\epsilon\epsilon_0 x_j} - e\mathcal{E}x_j, \quad (15)$$

which includes the intrinsic energetic disorder. Here, $E_j^0(\sigma)$ is a random number chosen from a Gaussian distribution with zero mean value and standard deviation σ, which determines the scale of the energetic disorder. Transition rates between sites are determined by the Miller-Abrahams hopping rates [Eq. (3)]. Once the hopping rates and energies are known, the dissociation probability is readily calculated using Eq. (8). In the case of disorder, the dissociation probability is averaged over 10^4 realizations. The dissociation is considered as occurred, when the separation between carriers exceeds the Onsager radius, i.e., when the Coulomb binding energy of the electron-hole pair is less than the temperature.

The field dependence of the dissociation probability at the interface between donor and acceptor phases is shown in Fig. 3 for different cases (with and without disorder) assuming typical values of the material parameters in organic semiconductors [19]. Note that the range of fields shown in Fig. 3 corresponds to much higher values than those corresponding to the applicability of Eq. (14). In the absence of disorder, the field dependence of the dissociation probability coincides with the simple Frenkel result. Apparently, the disorder makes the dissociation probability
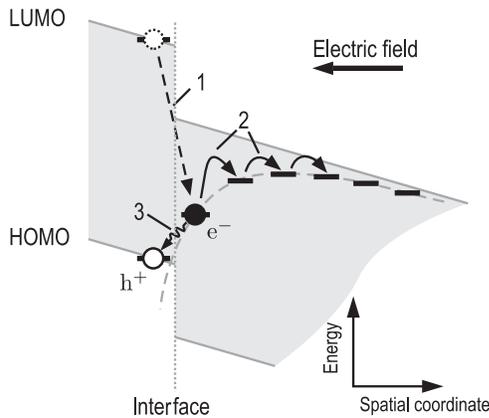
FIG. 2.   Energy level diagram illustrating the exciton breaking at the interface between the donor and acceptor phases (1) and subsequent field-assisted dissociation (2) of the electron-hole pair in the Coulomb potential modified by the external electric field. The dissociation competes with recombination via tunneling (3).

less sensitive to the value of the electric field. This result is really remarkable. Thus far the dissociation problem has been studied in straightforward computer simulations for disordered systems and the following result has been obtained [21]. Computer simulations provide an essentially smoother field dependence of the dissociation probability as compared to the analytical theories for ordered systems with initial parameters equal to those taken in the simulations. In order to fit the results of the simulations with analytical theories, which do not contain disorder, one needed to insert into these analytical theories initial parameters essentially different from those really used in the simulations [21]. Our exact calculations on the basis of Eq. (8) shown in Fig. 3 demonstrate that in the case of disorder the field dependence is smoother as compared to the ordered system, which resolves the puzzle with the

necessity to insert wrong initial parameters into the analytical theories for ordered systems in order to get agreement with simulation results in the case of disorder.

In conclusion, we proposed a general analytical solution for the field-assisted dissociation of a geminate electron-hole pair on a chain of hopping sites. For ordered chains, the limiting cases yield the famous results of Frenkel and Onsager. The energetic disorder, as well as its combination with the positional disorder, promotes dissociation at low electric fields and suppresses it at high fields.

FIG. 3.   Exciton dissociation probability as a function of external electric field calculated including positional ($\delta r \neq 0$) and energetic ($\sigma \neq 0$) disorder. "Approximate" refers to Eq. (13) with $E_1/k_B T = -(C + B)$.

*Oleg.Rubel@Physik.Uni-Marburg.de

[1] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Clarendon, Oxford, 1999).
[2] *Semiconducting Polymers*, edited by G. Hadziioannou and P. van Hutten (Wiley, New York, 2000).
[3] *Organic Photovoltaics: Concepts and Realization*, edited by C. Brabec, V. Dyakonov, J. Parisi, and N. Sariciftci (Springer, Berlin, 2003).
[4] V. I. Arkhipov and H. Bässler, in *Physics of Organic Semiconductors*, edited by W. Brütting (Wiley-VCH, Berlin, 2006), pp. 183–233.
[5] Y. A. Berlin, J. Bullot, P. Cordier, and M. Gauthier, Radiat. Phys. Chem. **15**, 297 (1980).
[6] U. Seiferheld, B. Ries, and H. Bässler, J. Phys. C **16**, 5189 (1983).
[7] C. L. Braun, J. Chem. Phys. **80**, 4157 (1984).
[8] Z. D. Popovic, Chem. Phys. **86**, 311 (1984).
[9] R. Kersting *et al.*, Phys. Rev. Lett. **73**, 1440 (1994).
[10] Y. N. Gartstein and E. M. Conwell, Chem. Phys. Lett. **255**, 93 (1996).
[11] H. Bässler, Polym. Adv. Technol. **9**, 402 (1998).
[12] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bässler, J. Appl. Phys. **84**, 848 (1998).
[13] U. Wolf, V. I. Arkhipov, and H. Bässler, Phys. Rev. B **59**, 7507 (1999).
[14] M. A. Baldo and S. R. Forrest, Phys. Rev. B **64**, 085201 (2001).
[15] L. Onsager, J. Chem. Phys. **2**, 599 (1934).
[16] J. Frenkel, Phys. Rev. **54**, 647 (1938).
[17] M. D. Tabak and P. J. Warter, Phys. Rev. **173**, 899 (1968).
[18] K. M. Hong and J. Noolandi, Surf. Sci. **75**, 561 (1978).
[19] H. Bässler, Phys. Status Solidi B **107**, 9 (1981).
[20] S. Baranovski and O. Rubel, in *Charge Transport in Disordered Solids With Applications in Electronics*, edited by S. Baranovski (John Wiley & Sons, Chichester, England, 2006), pp. 221–266.
[21] U. Albrecht and H. Bässler, Chem. Phys. Lett. **235**, 389 (1995).
[22] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).
[23] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980).
[24] R. R. Chance and C. L. Braun, J. Chem. Phys. **59**, 2269 (1973).