

Theory of Geminate Recombination as a Molecular Process

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(Received 9 November 1983)

A molecular model of field-dependent photogeneration is presented. The model, diffusion on a lattice in a combined Coulomb and external dc field, is solved exactly. The solution for the quantum efficiency η has a larger range of applicability than the continuum theory to which it can be compared in the infinite-sink case. It is shown that η can vary greatly with small variation of key molecular parameters and that the high-field limit of η is controlled by the same molecular properties which determine its field dependence.

PACS numbers: 72.20.Jv

Geminate recombination of a localized charge-carrier pair is the primary process responsible for limiting the efficiency of charge photogeneration in a wide class of condensed phases. In solids it has been studied experimentally in amorphous semiconductors,¹ molecularly doped polymers,² and molecular crystals.³ In many materials the variation of η , the photogeneration quantum efficiency, with E (electric field), can be successfully fitted by a theory originally proposed by Onsager.⁴

The parameters used in the fitting are φ_0 and r_0 , the initial yield and separation of thermalized ion pairs, respectively. The main insight one derives from this procedure is that the final rate-determining step in photogeneration, for separated pairs, is the overcoming of a field-modulated Coulomb barrier with the aid of thermal fluctuations. This procedure leaves open a number of questions: How valid is the continuum model of carrier diffusion in solids,⁵ e.g., those studied in Refs. 1–3? Are the parameters φ_0 and r_0 convenient phenomenological parameters or can they be interpreted literally? Is the separation of charge carriers into two groups, those reflecting “ $1 - \varphi_0$ ” events and those associated with “ r_0 ” events, field independent? How are these parameters related to clearly identifiable molecular properties of the system?

In order to deal with these issues, and to obtain a more microscopic understanding of geminate recombination, we have developed a comprehensive molecular theory of this process. The main feature of this theory is its focus on the competition between all the intermolecular and intramolecular transition rates operating in the

system, and the effect on this competition of a few controllable parameters, e.g., E , T (temperature), and c (the molecular concentration in doped systems). The solution we obtain has a larger range of applicability than the Onsager theory,⁵ is more versatile in terms of initial conditions⁶ and the modeling of transient phenomena, and shows a diversity of behavior of $\eta(E, T, c)$ dependent on the relative magnitudes of the intermolecular and intramolecular rates.

We consider an electron executing a nearest-neighbor random walk on a lattice under the joint influence of an applied electric field and a Coulomb field due to a hole fixed at the origin. The use of a lattice enables us to incorporate all the important site properties which determine the transition rates. The sites of the lattice are divided into two types: a set L of sites, for which the transition rate to leave the site is affected by both the external field E and the Coulomb field, and the complementary set, for which the transition rate is dependent only on E . The site at the origin has two states, S_0 (the ground state) and S_1 (the lowest excited level). If the electron occupies S_0 , recombination has occurred and the walk is at an end. This can only occur through transitions from S_1 , from which the electron can either occupy S_0 or transfer to a nearest-neighbor site. Associated with these two types of sites are different sets of probability densities for a displacement from site \vec{l}' to site \vec{l} in an interval t : $\hat{\psi}(\vec{l} - \vec{l}'; t)$ if $\vec{l}' \notin L$, $\hat{\psi}(\vec{l} - \vec{l}'; \vec{l}'; t)$ if $\vec{l}' \in L$, and $\hat{\psi}_{12}(t)$ for $S_1 \rightarrow S_0$ transitions at the origin.

Let $\hat{R}(\vec{l}, t)$ be the probability/(unit time) that the electron has just arrived at site \vec{l} at time t , having started at \vec{l}_0 at $t=0$. The Laplace transform

(LT) of the equation for $\hat{R}(\vec{I}, t)$ can be written⁶

$$R(\vec{I}, u) = \sum_{\vec{I}' \in L} \psi(\vec{I} - \vec{I}', u) R(\vec{I}', u) + \sum_{\lambda} \psi(\vec{I} - \vec{\lambda}; \vec{\lambda}; u) R(\vec{\lambda}, u) + \delta_{\vec{I}, \vec{I}_0}, \quad (1)$$

$$R_1(0, u) = \psi_{12}(u) R(0, u), \quad (2)$$

where $R_1(0, u)$ is the R function for state S_0 at the origin, $R(0, u)$ that for S_1 , and λ denotes the sites in L . These equations can be easily generalized to include transitions directly from nearest neighbors to S_0 . The formal solution⁶ of Eq. (1) is

$$R(\vec{I}) = G(\vec{I} - \vec{I}_0) - \sum_{\lambda} [G(\vec{I} - \vec{\lambda}) - \delta_{\vec{I}, \vec{\lambda}} - f(\vec{I}; \vec{\lambda})] R(\vec{\lambda}), \quad (3)$$

where, for brevity, we have dropped the Laplace variable. Here $G(\vec{I}, u)$ is the Green's function for the perfect lattice, including the external field, but excluding the Coulomb field, and

$$f(\vec{I}; \vec{\lambda}) = \sum_{\vec{I}'} G(\vec{I} - \vec{I}') \psi(\vec{I}' - \vec{\lambda}; \vec{\lambda}). \quad (4)$$

Equation (3) gives a closed set of linear equations for the function $R(\vec{\lambda})$ for sites in the set L :

$$G(\vec{\lambda} - \vec{I}_0) = \sum_{\lambda'} M_{\vec{\lambda}\vec{\lambda}'} R(\vec{\lambda}'), \quad (5)$$

where $M_{\vec{\lambda}\vec{\lambda}'} \equiv G(\vec{\lambda} - \vec{\lambda}') - f(\vec{\lambda}; \vec{\lambda}')$.

As there are no transitions out of S_0 , one can easily show that the probability of finding the electron in S_0 at $t \rightarrow \infty$ is

$$\hat{P}_1(0, \infty) = \psi_{12}(0) R(0, 0). \quad (6)$$

The recombination probability is determined directly (no LT inversion) by one R function evaluated at $u = 0$. $R(0, u)$ is one solution of Eq. (5) and is equal to the ratio of two determinants with elements $M_{\vec{\lambda}\vec{\lambda}'}$ and $G(-\vec{I}_0)$.

It remains to sketch briefly the evaluation of the Green's function and transition probabilities. Analytic expressions for some of the lattice Green's functions have been obtained on a number of lattices.⁷ However, there has been little work

for the fcc lattice we have chosen (as being the most isotropic) and none for E -dependent Green's functions. We have discovered⁶ an important symmetry relation, which has greatly simplified the evaluation:

$$G(m, n, l) = e^{\gamma} F(m, n, l), \quad (7)$$

where $F(m, n, l)$ is invariant under interchange of the lattice indices, $\gamma \equiv eEa/2kT$, $a/\sqrt{2}$ is the nearest-neighbor distance, and E is in the z direction. With this relation, the F functions for the indices we needed can be derived from recurrence relations and straightforward integrals over elliptic integrals.⁶ Now using as the transition rate between sites

$$W_{\lambda \rightarrow i} = W_0 \exp[-\beta(E_i - E_{\lambda})], \quad (8)$$

we obtain

$$\psi(\vec{I}; \vec{\lambda}) = \Omega(\vec{\lambda} + \vec{I}', \vec{\lambda}) [\sum_i \Omega(\vec{\lambda} + \vec{I}', \vec{\lambda}) + \delta_{\vec{\lambda}, \vec{I}_0} R]^{-1}, \quad (9)$$

where E_i is the energy of the electron at site i , W_0 is proportional to the molecular overlap factor, $\Omega(\vec{\lambda}, \vec{\lambda}') = \exp(-\beta[E_{\lambda'} - E_{\lambda}])$, $\beta = (kT)^{-1}$, and the energy difference is given by

$$E_{\lambda'} - E_{\lambda} = -e(\vec{r}_{\lambda'} - \vec{r}_{\lambda})E - (1 - \delta_{\lambda, 0})(1 - \delta_{\lambda', 0})(e^2/\epsilon)(r_{\lambda'}^{-1} - r_{\lambda}^{-1}) + (\delta_{\lambda, 0} - \delta_{\lambda', 0})E_{ex}. \quad (10)$$

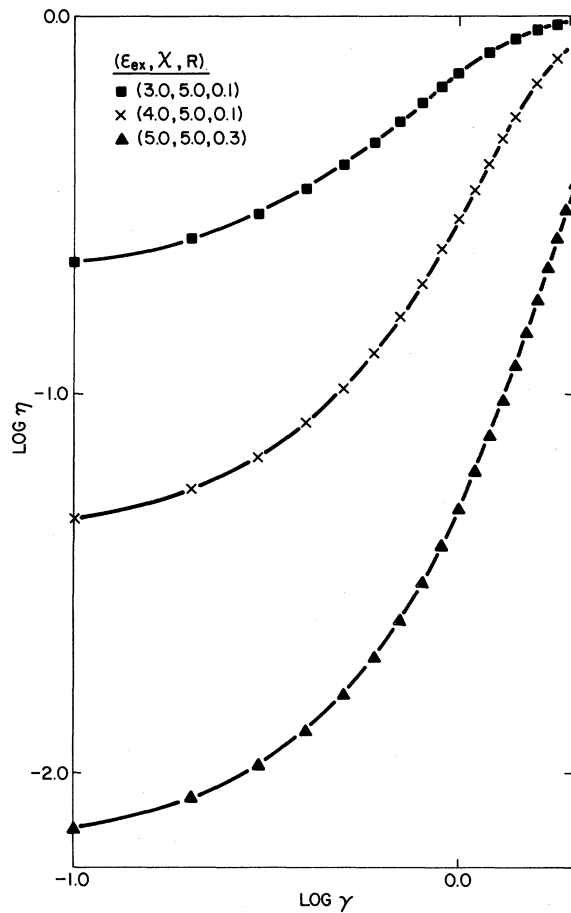
The first term is the energy difference between sites due to the E field, the second term arises from the Coulomb field, and the last term is proportional to E_{ex} , the energy difference between the state with S occupied and that with a hole at the origin and the electron on a nearest-neighbor site, in the absence of E ; ϵ is the dielectric constant.

Equations (9) and (10) define the geminate recombination problem in terms of four dimensionless variables. The factor R is the ratio of the $S_1 \rightarrow S_0$ transition rate to W_0 , γ is a dimensionless E field, $\epsilon_{ex} \equiv E_{ex}/kT$, and $\chi = 2e^2/\epsilon akT$ is a measure of the strength of the Coulomb field.

In what follows, we restrict L , the set of sites

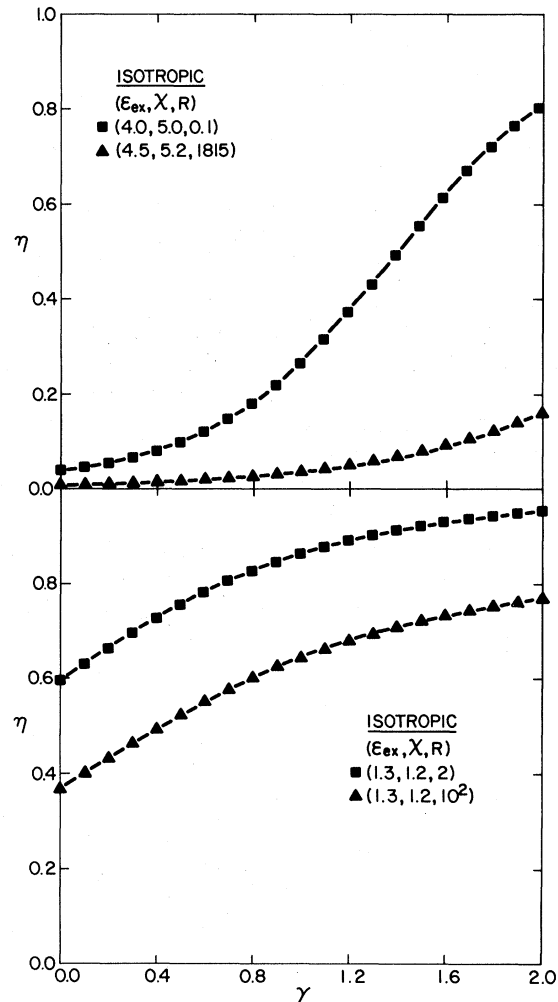
affected by the Coulomb field, to the site at the origin and its nearest neighbors. This is equivalent to the statement that transitions from second-nearest neighbors to more distant sites are unaffected by the Coulomb field; it can be shown⁶ to impose the condition $\chi \leq 5.44$. Extension to longer-range Coulomb interaction is straightforward but will not change the essential features of our results.

Figure 1 shows three curves obtained by numerical evaluation of Eq. (6), giving $\eta(\gamma)$ for different (ϵ_{ex}, χ, R) values. [$\eta \equiv 1 - P_1(0, \infty)$.] In the plot shown χ and R are essentially fixed, and ϵ_{ex} is allowed to vary. Two points in particular are

FIG. 1. $\eta(\gamma)$ as a function of ϵ_{ex} , low- R limit.

evident from Fig. 1. First, the qualitative resemblance between results calculated by the lattice approach and experimental results^{2,3} is quite striking. Second, we note that *it is possible to obtain order-of-magnitude variation in $\eta(\gamma)$ by varying molecular parameters*, with no change in initial distribution. One can change ϵ_{ex} , with fixed χ , by changing the intrinsic energy levels of the molecule at the origin or of the anion at a nearest-neighbor site. This change can be associated with the use of different molecules or local energy fluctuations, i.e., diagonal disorder. Note that in Fig. 1 the changes in η were caused by variation in the energy difference in steps of kT . In the Onsager theory this change in η can only occur by varying of r_0 . Thus, in this case r_0 would be parametrizing a variation in molecular energy levels!

The results of Fig. 1 illustrate another strength of the lattice theory: the ability to treat an arbitrary initial distribution of electrons about the

FIG. 2. $\eta(\gamma)$, comparison of low- and high- R regimes.

hole. The results of Fig. 1 are for an initial distribution in which the electron is on a nearest-neighbor site of the hole, with angular distribution weighted by the applied field (Boltzmann average). This type of distribution has not previously been considered. The effect of various initial distributions (including a Frenkel exciton at the origin) will be considered in more extended work.⁶

In Fig. 2 we turn to some results in the high- R regime. (In the limit of high R the molecule at the origin tends to an infinite sink.) This regime is of interest because, when R is large, we expect the loss mechanism which limits the high-field value of η to be significant. Indeed, it is clear that, in contrast to the curves of Fig. 1, those in Fig. 2 with large R are saturating at values of $\eta(\infty) < 1.0$. Also note this comparison in the lower part of the figure. These two curves,

for weak Coulomb interaction, differ only in R value. In the upper part of Fig. 2 it is demonstrated that the high-field behavior of η is controlled by the same molecular parameters and rate processes that determine the field dependence of η , and that it is not necessary to invoke a phenomenological quantum efficiency φ_0 to understand the physics of geminate recombination. The same parameter (R) that shifts $\eta(\infty)$ changes the field dependence!

Details of the model—temperature dependence, low-field behavior, dependence on molecular parameters, etc.—as well as a comparison with the continuum approximation, and systematic answers to all the questions raised above, will be explored in forthcoming publications. It is expected that this approach will provide a useful laboratory in which these and other factors, such as site-energy disorder, dimensionality, and electron-phonon interactions, can be studied to advantage.

One of us (S.R.) would like to thank Professor R. S. Knox and Professor H. M. Van Horn for their kindness and support during much of this work.

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