Invited Paper

HOPPING TRANSPORT IN AN ISOENERGETIC SPATIALLY-RANDOM ARRAY OF SITES - THE EFFECT OF JUMPS INTO DISTANT SITES

J. M. Marshall[*], V. Arkhipov[a]

Professor Emeritus, School of Engineering, University of Wales Swansea, U.K.
[a]IMEC, Kapeldreef 75, B-3001 Heverlee-Leuven, Belgium

Semiconductors and insulators in which quantum mechanical tunnelling ("hopping") between localised sites is the dominant charge transport process are often characterised by appreciable disorder in the spatial positions of the sites, and usually by similar disorder in their energies. In this paper, we confine ourselves to the case of iso-energetic sites, and employ a Monte Carlo simulation technique to explore various aspects of the hopping process. In particular, we examine in detail the consequences of confining allowed transitions to a restricted number of nearby sites. It is shown that the assumptions and averaging procedures employed in various prior analytical approaches to the problem can have a much more profound effect than has been anticipated. The present study thus suggests that a re-consideration of such factors would be merited.

1. Introduction

The presence of positional and energetic disorder into semiconductors and insulators causes the generation of appreciable numbers of localised defect states in the energy gap of the otherwise perfectly ordered material [1]. Where the concentrations of such states are sufficiently high, carrier transport by quantum mechanical tunnelling ("hopping") directly between these sites can replace transport in extended states as the dominant mechanism [1].

Most prior examinations of this situation have utilised analytical techniques, involving various significant assumptions. In particular, it has often been assumed that, except for highly concentrated conditions (very closely separated sites), transport will be dominated by transitions to the 1st-nearest neighbour sites. Moreover, with or without such an assumption, the analytical models have proceeded by calculating some form of averaged transition probability, which can then legitimately be applied to the ensemble of sites.

One way of examining the validity and implications of the above approaches is adopt a much more fundamental approach, using a sufficiently large computer-generated random array of sites, and then to study hopping transport within this array using (e.g.) very simple Monte Carlo procedures involving relatively few assumptions or simplifications. The advantage of such an approach is that the underlying assumptions of the analytical models can be removed, and/or subjected to detailed scrutiny. One disadvantage is that it requires considerable computer storage space (for the random array, and then for the recording the locations of, and transition time constants to, the specified number of allowed nearest neighbours of each site). A second disadvantage is that computation of actual carrier drift and diffusion characteristics is time consuming - data for a large number of carriers need to be generated individually, and then combined together to give (e.g.) the diffusion or drift characteristics of an overall carrier ensemble.

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[*] Corresponding author: joe.marshall@killay9.freeserve.co.uk

When one of the authors (JMM) first adopted this approach, in the late 1970s and early 1980s [2-4], these considerations seriously limited the realisable array size and the features which could be examined using it. However, significant improvements in storage size and computing speed now make it viable to perform much more extensive studies on realistic timescales. We are presently undertaking such an examination. Below, we present some of the initial insights arising from it, related to the importance of the role of various orders (1st nearest, 2nd nearest, etc.) of neighbouring sites to which hopping transitions are considered (i.e. permitted).

2. The Monte Carlo simulation procedure

In the general case, the rate of carrier jumps from a site of energy E to another of energy E', over a distance r, is normally described in terms of the Miller-Abrahams [5] expression:

$$\nu_j\left(r,E,E'\right)=\nu_0\exp\left(-r/r_0\right)\begin{cases}\exp\left[-\left(E-E'\right)/kT\right], & \left(E>E'\right), \\ 1, & \left(E<E'\right).\end{cases} \tag{1}$$

where ν_0 is the "attempt to hop" frequency, r_0 is an effective localisation distance for the sites, and T the temperature. For iso-energetic sites, as considered here, $E-E'$ will be zero in the absence of an applied electric field. At finite fields, it will be determined by the field-induced potential difference between the two sites. However, in the present paper, we do not consider the effects of applying such a field. Thus, $\nu_j(r,E,E')$ is replaced by $\nu_j(r)$ below.

The site array generated for these studies comprised 12 slices, each of dimensions x = 8, y = z = 100. Within each slice, 80,000 sites were generated, giving an average site density of unity. Each such slice was then examined in conjunction with the neighbouring ones (one for the edge slices, and two for the bulk ones - except as explained below), to determine the identities of the 8 nearest neighbours (i.e. those with the 8 highest values of $\nu_j(r)$). The full simulation array thus comprised 960,000 sites, randomly distributed in a volume of 96 x 100 x 100 units (total computer storage space for the array data = 374 Mb). For (e.g.) studies of diffusion over an extended time period, the first and last x-position slices could be looped back together, to produce an *apparently* infinite allowed diffusion distance (subject to the vital requirement that the original array must be sufficiently large to fully be representative of the bulk material, in terms of significant local variations in environment).

The Monte Carlo studies of hopping within this array featured the following steps:

- A random number was used to select the initial site upon which a carrier was located. This depended upon the situation being examined - e.g. it could be a site close to the left hand side of the array for studies of drift under an applied field, etc., or anywhere within the "looped back" array for studies of diffusion at zero applied field.

- To simulate a single hopping event, a second random number was used to select between the (up to eight, as chosen in the particular case under study) adjacent sites, according to their relative values of $\nu_j(r)$.

- A third random number was then used to calculate the individual dwell time of the carrier on the initial site before hopping, with such values being properly distributed about the calculated overall time constant for hopping to the total collection of allowed nearest neighbours.

- This procedure was repeated for the new site etc., with the change in position and other characteristics of the drifting carrier being recorded as functions of elapsed time since initial generation.

- Data were combined for a large number of carriers (initially randomly generated on different sites, as above), to compile the overall characteristics of a diffusing/drifting charge packet.

3. Carrier diffusion at zero applied field

The above procedure was used, in the study reported here, to examine carrier diffusion at zero applied electric field, for the cases of allowed transitions to between $n = 1$ and $n = 8$ nearest neighbours. Here, v_0 was set at 10^{12} Hz, and r_0 at 0.3 (relative to the mean site density of unity). The latter parameter is quite large, giving significant probabilities for hope to neighbours well beyond the nearest one. However, using $r_0 = 0.1$ gave similar general conclusions to those presented below. Note, in this context, that at zero applied electric field, although the value of r_0 determines the relative probabilities of transitions to neighbouring sites, *it does not change the identities of the sites comprising the nearest neighbours of various orders.*

For this element of the study, charge carriers were initially positioned upon sites selected at random throughout the (looped back) array. Their initial positions were recorded, so that their subsequent diffusive motions (Δx) away from these positions could be combined, to give an overall diffusion profile.

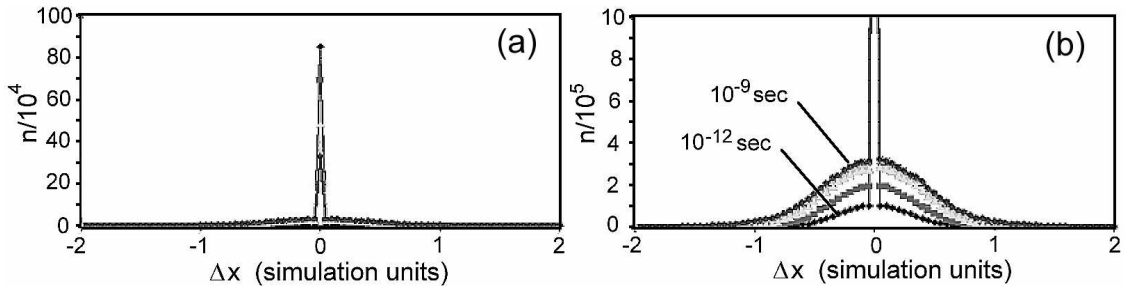### 3.1 Diffusion to 1st-nearest neighbours only

Fig. 1. Diffusive carrier displacement profiles for the case when only hopping to 1st-nearest neighbours is allowed. In the right hand figure, the vertical scale is expanded by a factor of ten. The curves span timescales from 10^{-12} to 10^{-9} s. At still longer times, there are essentially no further changes in the packet shape.
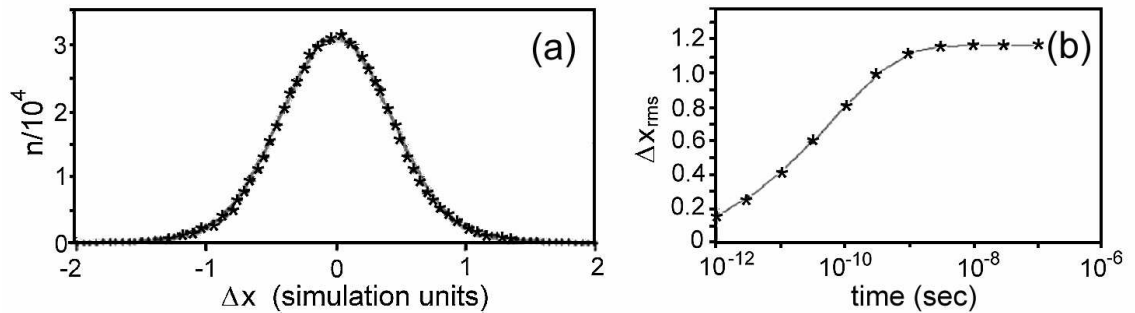

Fig. 2. (a): Gaussian fit to the long-time carrier diffusion profile (without the central spike).
(a): Root mean square displacement of the diffusing carrier packet, as a function of time.

Fig. 1 shows how a carrier packet spreads out by diffusion (relative to the original x positions of each carrier), for the case in which only transitions to the 1st-nearest neighbours are permitted. It can immediately be seen that there is a very sharp spike of carriers which remain either at or very close to their initial positions. This comprises about 35% of the total population. The remaining carriers diffuse further, giving a profile well described by a Gaussian function (Fig. 2a). However, it is also clear that the diffusion process slows down rapidly at about 10^{-9} s, and essentially ceases after about 10^{-8} s. This is illustrated dramatically by the computed r.m.s. diffusion distances, Δx_{rms}, as displayed in fig. 2b.

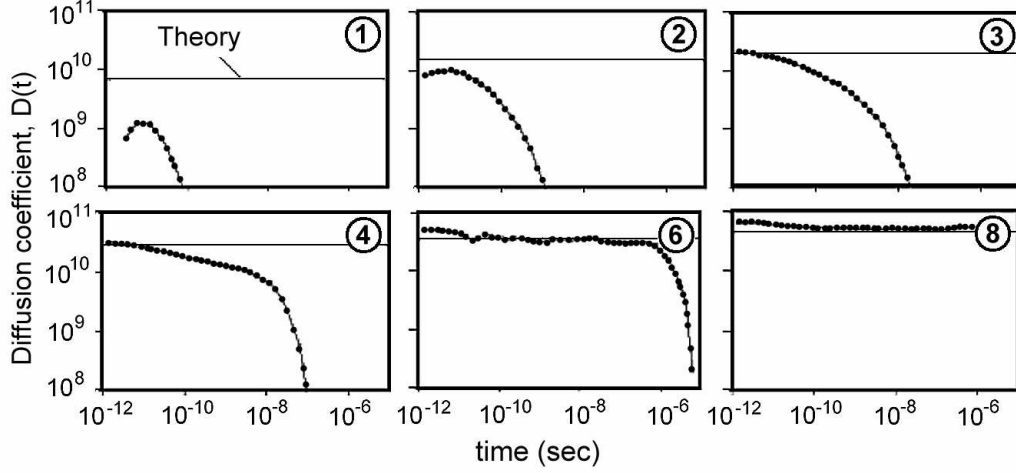### 3.2 Diffusion including higher-order nearest neighbours

Fig. 3. Calculated differential diffusion coefficient as a function of time, for simulations in which transitions to various numbers of nearest neighbours (as indicated) are allowed. The horizontal lines are the values calculated from the analytical expressions derived by Arkhipov *et al.* [7].

If transitions to both 1st- and 2nd-nearest neighbours are permitted, the situation is qualitatively similar to that above. However, there are differences of detail in that the residual central spike is smaller, the long-time value of Δx_{rms} is slightly higher, and the final carrier profile is less Gaussian in shape.

We will demonstrate below that similar situations exist, to a progressively less dramatic degree, for higher orders of allowed nearest neighbours. However, before doing so, it is necessary to address a more fundamental problem. This is that if the values of Δx_{rms}, as calculated above, were used in the conventional way to compute a diffusion coefficient, D (i.e. from $D = \Delta x_{rms}^2/6t$), then this would be a time-dependent quantity. Moreover, it would not be suitable for comparison with the time-dependent drift mobility (e.g. as obtained from a transient photoconductivity experiment [6]). This is because the mobility, $\mu(t)$, calculated from the transient photocurrent, $I(t) = e.F.\mu(t).n$, where F is the applied field and n is the number of excess carriers, represents the *instantaneous* mobility, whereas the diffusion coefficient calculated as above reflects the overall net diffusion since zero time.

Fortunately, although we are not aware that this problem has been addressed previously, we have found - and have confirmed using various assumed functional forms of $I(t)$ - that it can be resolved quite easily and logically. The solution is simply to define and use a *differential* form of the diffusion coefficient, to define its instantaneous time dependent value:

$$D(t) = (1/6)\, d\left(\Delta x_{rms}^2\right)/dt \,. \tag{2}$$

The results, for different numbers of nearest neighbours to which transitions are permitted, are as shown in fig. 3. The horizontal lines are the theoretical values of the diffusion coefficient for the various cases, i.e.:

$$D = \sum_n (v_0/6) \int_0^\infty r^2 \; w(r,n) \; \exp(-r/r_0) \; dr \tag{3}$$

where the probabilities $w(r,n)$ are as derived by Arkhipov *et al.* [7] for an arbitrarily large number of nearest neighbours to which transitions are included.

When only 1st-nearest neighbour transitions are permitted, the Monte Carlo simulated values of $D(t)$ never reach the expected values. If transitions to higher numbers of nearest

neighbours are allowed, the agreement at short times becomes progressively better. However, at longer times, $D(t)$ still falls away dramatically. When transitions to all eight nearest neighbours are included, this effect is not detectable within the time range accessible to the present simulation. However, as we shall argue below, we consider that it should still take place at longer times.

One final thing to note is that for the cases of 6 and 8 nearest neighbours, the simulated diffusion coefficients actually slightly exceed the predicted values. We tentatively ascribe this to the finite lateral dimensions of the simulation array. Even though the array is large, there will still be initial sites close to its y and z boundaries. Carriers generated in these will be obliged to jump to neighbouring sites which are slightly further away than those in the bulk.

4. Origins of the behaviour observed in the Monte Carlo simulations

It is clear that strictly confining allowed transitions to a specified number of nearest neighbours has a much more pronounced effect than might have been anticipated. We will now outline two separate factors that contribute to this. We term these "Site Wetting" and "Irreversible Capture". Although the two phenomena are related in some respects, there are important differences between them, in terms of their effects upon the time dependence of both $D(t)$ and other related transport phenomena.

4.1 Site Wetting

Suppose that we: (i) Take a single array slice (of dimensions 8x100x100 units), and "wet" (i.e. occupy) all sites in a thin ($0 < x < 0.1$) region on its left hand side. (ii) Now connect each of these to all other sites within the array which are its I^{st} to n^{th} (as specified) nearest neighbours. These sites are then also regarded as having become "wet". (iii) Repeat this process until no further sites become wet on further repetition. In the spirit of percolation theory, it could then be argued that if connected paths are established between the left and right hand sides of a (sufficiently long) site array, then these paths will control the d.c. electrical conductivity and other macroscopic transport properties.
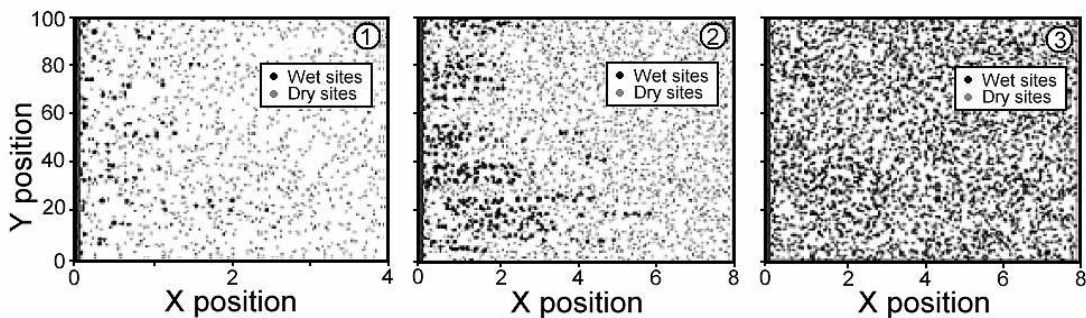

Fig. 4. "Site wetting", as described in the text, for the cases $n = 1$ to 3.

Fig. 4 shows the results of such a procedure for the cases $n = 1$ to 3. Here, for ease of display, only those sites with z positions (into the plane of display) between 0 and 5 are shown. It is important to note that at first sight, this gives the impression "wetting" misses out significant numbers of sites which are closer than those which do actually become "wet". However, this is not the case - such sites are further away in the z direction, and so in three dimensional space.

For the case $n = 1$, only about 1400 of the 80,000 sites in the slice finally become "wet", in addition to those initially specified as being so. For $n = 2$, "wetting" progresses further, but still ceases after a relatively small penetration distance. For $n = 3$, "wetting" continues throughout the slice, implying that connected paths have been established and thus permitting (e.g.) d.c. electrical conduction. Further increases in n simply reduce the residual number of "dry" sites.

It is important, here, to stress again that these conclusions are *not dependent upon the relative dilution (i.e. the value of r_0) of the system* - they only consider the specified numbers of allowed neighbours, and not the actual transition rates.

This exercise indicates that the value of *n* is important (i.e. that confining transitions solely to 1st- or 1st plus 2nd-nearest neighbours will not yield d.c. conduction). It also *appears* to indicate that including the 3rd and higher-order neighbours removes this restriction. This, in itself, is important, given that many analytical treatments have ignored anything other than 1st-nearest neighbour transition probabilities. However, as we shall show below, and as indicated in fig. 3, this is not the only important consideration.

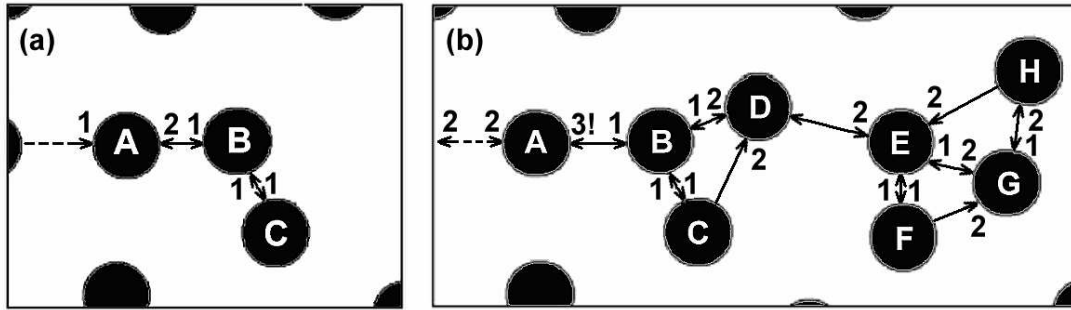### 4.2 Irreversible capture (black holes)

Fig. 5. Examples of irreversible capture ("black hole") clusters. The numbers adjacent to the respective arrows represent the nearest neighbour rank, *n*, of the site to which a transition may occur.

Consider first the case where only transitions to 1st-nearest neighbours are permitted. Fig. 5a illustrates a situation that can and will then arise. A carrier which enters site A is allowed to hop to site B, since this is its 1st-nearest neighbour. From there, it can hop backwards and forwards between sites B and C, since these are mutual nearest neighbours. However, it can never return to site A or out of the B-C site pair. It is thus permanently trapped in a "black hole". Inspection of the simulation array shows that about 34% of all sites exist in such mutual nearest neighbour pairs.

This immediately means that carriers initially generated in such a pair can only hop backwards and forwards within it, giving the sharp central spike in fig. 1. It also means that carriers which are not initially generated in such a pair will fairly rapidly find themselves entering one, and then being unable to escape. This, then, explains the subsequent decline to zero of the diffusion coefficient.

For the case *n* = 2, it is obviously possible (although statistically less likely) that a carrier will be created in, or will subsequently enter, a group of three sites which are all either each other's 1st- or 2nd-nearest neighbours. However, various more complex "black holes" now also become possible, An example (detected by inspection within the present simulation array) is given in fig. 5b. Here, a carrier entering through site A is allowed to hop repeatedly within the cluster of sites B-H. However, it can never return to site A, since this is the 3rd-nearest neighbour of site B. Thus, it is again permanently trapped in a "black hole".

For higher orders of *n*, the likelihood of initial generation within a "black hole" will obviously decrease. However, *such ensembles still have a finite probability of existence*. Therefore, it can be argued that *eventually*, a drifting or diffusing carrier will encounter one, and that macroscopic diffusion beyond the ensemble will then cease. The only question would whether this is likely to happen to a significant extent before (e.g.) a carrier completed its transit of a specimen of realistic finite size.

5. Caveats and further comments

Of course, the above considerations do not bear a one-to-one correspondence to reality. In practice, there is no mechanism restricting a carrier to a particular value of n. In a sufficiently dilute system, a carrier would tend to diffuse back and forth within such a cluster until it finally (albeit with a very low probability) chanced to make a transition beyond it. This low probability of such escape transitions would (as in conventional percolation theory) then determine (e.g.) the overall time for the carrier to drift across a specimen.

None the less, since many of the present analytical models of hopping transport totally ignore these issues, or lose them within the averaging procedures which they employ, we consider that the dangers of doing so have been illustrated dramatically above. In reality, positional randomness always creates energetic disorder, which somewhat reduces the relative density of black holes but does not fully eliminate them [8].

An important prior example of the pitfalls that can occur by use of inappropriate averaging procedures is the Scher-Montroll analysis [9] of hopping in an iso-energetic spatially random site array. Here, the authors computed an average distribution function for the probability of release from a localised state. They then applied this distribution function to hopping within a *regular three-dimensional array* of sites. In doing so [10] (see also [2-4]), the relationship between the probability of escaping from a relatively isolated site or cluster was not weighted in proportion to the probability of entering it in the first place. Thus, the resulting distribution was badly skewed in favour of such events.

We believe that similar considerations may apply in respect of the issues raised in the present paper. Thus, they should be taken into account by those formulating analytical models of the hopping process.

In this respect, and others, we believe that despite the demands upon computer storage space and computation time, computer simulations such as the present Monte Carlo based study have the potential to continue to provide valuable insights into the validity or otherwise of the underlying assumptions upon which simplified analytical models (including our own, some of which are contained in this volume) are being, and necessarily will continue to be, based.

6. Conclusions

- The effect of formally restricting the allowed hopping transitions to a specified number of nearest neighbour sites has been examined, by means of Monte Carlo and other associated techniques.

- It has been demonstrated that the imposition of such limitations, along with their various implications, if taken literally, can have unexpected and serious consequences.

- Such assumptions (and others, involving (e.g.) procedures for utilising averaged hopping probabilities) are frequently (maybe unavoidably) made in the formulation of analytical and more simplified simulation procedures.

- Therefore, although relatively demanding in terms of computer storage space and calculation time (and maybe not so elegant in other respects), the use of Monte Carlo type modelling can provide valuable insights into the validity, or otherwise, of the approaches being adopted in analytical models.

- The data presented here are part of a larger study, which will employ the same formalism to study various other aspects of hopping transport in disordered semiconductors (for example, the rigidity of the conventionally-assumed relationship between the carrier mobility and diffusion coefficient, and the details of low-temperature (variable-range) hopping). The results of these studies will be published in due course.

- The study will also be extended to examine situations in which localised sites are distributed not just randomly in space, but also appropriately in energy.

Acknowledgement

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