

Resonance Energy Transfer in Activationless Hopping Conductivity

A. A. Berezin

Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(Received 1 March 1983)

Activationless hopping conductivity in a strong electric field is caused by downward jumps of localized carriers along the electric field. Here, the specific mechanism of energy release is considered, which involves an energy-transfer process when energy gained by a downward jump of one electron is radiationlessly transferred to another electron, allowing it to make an upward energy jump. An estimate shows that such processes may provide a noticeable contribution to the total hopping conductivity.

PACS numbers: 72.20.Ht, 71.55.-i

Activationless hopping conductivity (HC) in a strong electric field (SEF) was observed in a number of heavily doped, compensated semiconductors,^{1,2} and in amorphous semiconductors,³ as well as in β -rhombohedral crystalline boron.⁴⁻⁶ In the last case, the existence of activationless HC is probably an intrinsic property caused by a self-compensation effect in the very complex unit cell of β -boron's lattice.

An imposition of a SEF tilts the Fermi level along the direction of the field. As a result, localized carriers can tunnel on vacant trapping levels in the vicinity of the Fermi level which lie downward in energy (process *a* in Fig. 1). This type of non-Ohmic HC induced by a SEF does not require temperature activation and gives nonzero conductivity σ even if $T \rightarrow 0$, namely

$$\sigma = \sigma_0 \exp[-(F_0/F)^{1/4}]. \quad (1)$$

Here, F is the intensity of the SEF and σ_0 and F_0 are (temperature-independent) experimentally

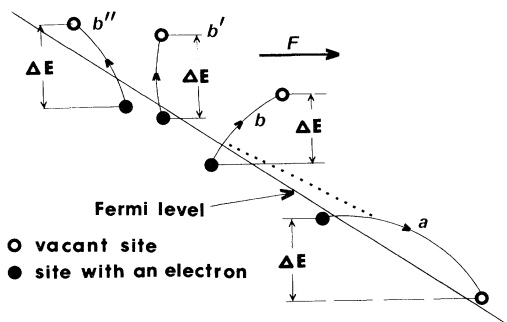


FIG. 1. Resonance energy transfer processes in activationless hopping conductivity in a strong electric field. Dotted line shows energy transfer from an electron of the site pair *a* to an electron of the site pair *b*. Site pairs *b*, *b'*, and *b''* symbolically represent various spatial orientations of energy-accepting site pairs in respect to the direction of electric field \vec{F} .

determined fitting parameters. The excess energy ΔE released during each hopping act is determined by the difference of energy levels for the participating pair of filled and vacant sites and can be emitted in a form of either phonon(s) or long-wavelength photon(s). The last subtype of the variable-range activationless SEF HC was considered earlier by the present author⁷⁻⁹ and called SEF HC by means of radiative tunnel transitions (RTT). In some favorable situations, SEF HC by RTT can become comparable with the HC accompanied by the phonon emission.

In the present paper, I would like to pay attention to the possibility of an alternative energy release mechanism in activationless SEF HC, namely the transfer of excess energy to another localized carrier (electron or hole). In this process, the energy ΔE gained by a downward (along the field) jump of one electron (hole) is radiationlessly transferred to another electron (hole), allowing it to make an upward energy jump which would be otherwise energetically impossible. Some of these possible upward jumps are denoted in Fig. 1 as *b*, *b'*, or *b''* processes. Such jumps can occur for any pair of filled and empty sites for which the difference of energy levels is in resonance with the originally released energy ΔE within the limits specified by the energy indeterminacy of final levels in the theory of resonance energy transfer (RET) (see, e.g., Dexter, Forster, and Knox,¹⁰ Trifonov,¹¹ and Kenkre and Knox¹²).

While energetically energy-accepting site pairs (e.g., *b*, *b'*, or *b''*) should be in a (quasi) resonance with energy-donating pair *a*, they should not necessarily be spatially oriented downward along the field. An empty (vacant) site can be positioned in any direction relative to the filled site; and also, spatially, the energy-accepting site pair itself can be located in any direction from the site pair *a*. Thus, the act of RET from

the jumping electron of the site pair a to that of site pair b (this process is shown in Fig. 1 by a dotted line) can be visualized as a specific process of correlated two-electron, four-site hopping, which, along with RTT's may contribute to the total SEF HC. Its only difference from "usual" processes of RET between impurity centers is that in our case, both "excited" and "ground" states of both energy donor (site pair a) and energy acceptor (site pair b) are formed by two spatially separated lattice sites.

Note here that the possibility of enhancement of hopping conductivity due to the direct electron-electron interaction for the Ohmic case (weak fields) was considered earlier by Butcher and Swierkowski.¹³ It was shown that in favorable cases the hopping rate involving electron-electron interaction can even exceed that involving electron-phonon coupling.

The probability of the interelectron RET can be calculated by the Fermi "golden-rule" formula (in atomic units):

$$\tau_{\text{tr}}^{-1} = 2\pi |\langle \psi_i | \hat{V} | \psi_f \rangle|^2 (1/W). \quad (2)$$

Here, τ_{tr} is the energy transfer rate, ψ_i and ψ_f are the wave functions of the initial and final states, respectively, \hat{V} is an interaction responsible for the RET, and W is the characteristic energy indeterminacy of the final electronic state due to the electron-vibrational interaction.

Let us take the wave functions ψ_i and ψ_f in the form

$$\begin{aligned} \psi_i(\vec{r}_1, \vec{r}_2) &= \varphi_{a1}(\vec{r}_1) \varphi_{b1}(\vec{r}_2), \\ \psi_f(\vec{r}_1, \vec{r}_2) &= \varphi_{a2}(\vec{r}_1) \varphi_{b2}(\vec{r}_2); \\ \varphi(\vec{r}) &= (\gamma/2\pi)^{1/2} (e^{-\gamma r}/r). \end{aligned} \quad (3)$$

Here, \vec{r}_1 is the radius vector of the "independently" jumping electron (a electron), which donates energy ΔE to the b electron while undergoing spontaneous tunnel transition from its "excited" state at site $a1$ to its "ground" state at site $a2$. Similarly, \vec{r}_2 is the radius vector of the b electron subjected to a "forced" tunnel transition with an energy increase ΔE from its "ground" state at site $b1$ to its "excited" state at site $b2$. For individual localized states, we took here the wave functions φ in the form of delta-well-like orbitals, where $a^* = \gamma^{-1}$ is the localization parameter. The geometrical configuration of this four-site system is shown in Fig. 2. Note that Fig. 1 is a mixed spatial-energy diagram, whereas the diagram in Fig. 2 is a purely spatial one. Note also that vectors \vec{a} , \vec{b} , and \vec{n} need not nec-

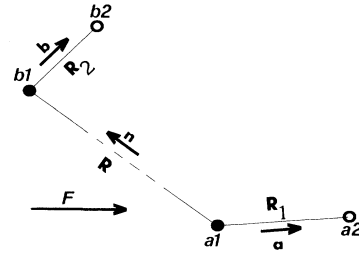


FIG. 2. Typical geometry of a four-site two-electron resonance energy transfer. \vec{a} , \vec{b} , and \vec{n} are unit directional vectors. Note that this diagram is purely spatial, i.e., it does not show explicitly the relative energy positions of site levels $a1$, $a2$, $b1$, and $b2$.

essarily lie in the same plane.

Let us take an energy transfer operator \hat{V} in a form of a dipole-dipole interaction between two dumbbell-like subsystems a and b :

$$\hat{V} = \kappa^{-1} R^{-3} [\vec{r}_1 \cdot \vec{r}_2 - 3(\vec{r}_1 \cdot \vec{n})(\vec{r}_2 \cdot \vec{n})]. \quad (4)$$

In Eq. (4), the radius vectors \vec{r}_1 and \vec{r}_2 are counted from the sites $a1$ and $b1$, respectively, i.e., from the initial positions of the jumping electrons; $R = |\vec{R}_{a1} - \vec{R}_{b1}|$, κ is the dielectric constant, and $\vec{n} = (\vec{R}_{b1} - \vec{R}_{a1})/R$ is the directional unit vector. Let us also denote as $R_1 \equiv |\vec{R}_{a2} - \vec{R}_{a1}|$ and $R_2 \equiv |\vec{R}_{b2} - \vec{R}_{b1}|$ the shoulders of both participating tunnel jumps; their corresponding unit vectors are \vec{a} and \vec{b} , respectively. The validity of Eq. (4) requires that $R \gg R_1$ and $R \gg R_2$; however, in view of our semiquantitative consideration, these inequalities need not really be very strong.

Substituting Eqs. (3) and (4) into Eq. (2), we obtain

$$\frac{1}{\tau_{\text{tr}}} = 2\pi \left(\frac{D_1 D_2}{\kappa R^3} \right)^2 \frac{1}{W} \{ \vec{a} \cdot \vec{b} - 3(\vec{a} \cdot \vec{n})(\vec{b} \cdot \vec{n}) \}^2, \quad (5)$$

where D_1 and D_2 are the absolute values of dipole matrix elements of both one-electron jumps, respectively:

$$\begin{aligned} D_1 &= |\langle \varphi_{a1}(\vec{r}_1) | \vec{r}_1 | \varphi_{a2}(\vec{r}_1) \rangle| = \frac{1}{2} R_1 \exp(-\gamma R_1); \\ D_2 &= |\langle \varphi_{b1}(\vec{r}_2) | \vec{r}_2 | \varphi_{b2}(\vec{r}_2) \rangle| = \frac{1}{2} R_2 \exp(-\gamma R_2). \end{aligned} \quad (6)$$

An RET rate can be compared with the rate of a spontaneous single-electron RTT for the site pair a :

$$\tau_{\text{RTT}}^{-1} = \frac{4}{3} \alpha^3 (\Delta E)^3 |\langle \varphi_{a1}(\vec{r}_1) | \vec{r}_1 | \varphi_{a2}(\vec{r}_1) \rangle|^2, \quad (7)$$

where $\Delta E \approx q_0 F R_1$ (the direction of \vec{a} is close to or the same as the direction of the electric field \vec{F}) and $\alpha = q_0^2 / \hbar c = \frac{1}{137}$ is the fine-structure constant.

It is instructive to contrast the field dependence of RET and RTT processes. For a *fixed pair* of sites the probability of RTT [Eq. (7)] has an explicit dependence on F ($\sim F^3$) through ΔE (see Fig. 1). RTT, however, is a *nonresonance* transition (the excess of energy is emitted as a photon). Equation (5), on the contrary, imminently implies the resonance situation (both participating jumps have the same transition energy within the limits of uncertainty W). Here the presence of the electric field is implicit: Because of the random lengths and orientations of shoulders of both jumps a *given* quadruplet of sites will form a resonance system only at the specific value of F (within the limits $\Delta F \sim W/q_0 R_{\text{typ}}$; R_{typ} is the typical jump length). The change of F puts this quadruplet out of the resonance while some other quadruplets are brought into a resonance situation. As a result, the spatial pattern of resonance quadruplets will be entirely different for each "new" value of F (within the limits ΔF specified above). Qualitatively, it seems likely that the increase of F favors the formation of more and more compact resonance quadruplets (with correspondingly smaller τ_{tr}) and therefore enhances the total role of two-electron RET processes.

As an example, I calculate the distance $R = R_0$ for which both rates are the same, i.e., $\tau_{\text{tr}} = \tau_{\text{RTT}}$. Let us take, for simplicity, the geometric factor in Eq. (5) equal to unity (e.g., $\vec{a} \perp \vec{n}$ and $\vec{a} \parallel \vec{b}$) and $R_1 = R_2$. In Table I, the values of $\tau_{\text{tr}} = \tau_{\text{RTT}}$ and R_0 are calculated for typical values⁹ $a^* = 2, 5$, and 10 \AA ; $R_1 = R_2 = 5a^*$; $F = 100 \text{ kV/cm}$; $\kappa = 10$; and $W = 1 \text{ meV}$. Usually, the accepted values of energy-level widths W are of the order of the Debye energy¹¹; since, however, $R_0 \sim W^{-1/6}$, the calculated R_0 's are not very sensitive to the particular choice of W .

The results given in Table I indicate that the probability of the tunneling accompanied by RET (two-electron process) is comparable with the probability of single-electron RTT's even for rather large distances between participating pairs of sites. Moreover, for smaller values of R , the two-electron RET processes can be even predominant. Since the typical spread of site energies is of the order of $\epsilon \sim 0.1 \text{ eV}$, the typical energy uncertainties W are only 2 orders of magnitude smaller, i.e., $\sim 1\%$ of ϵ . In view of the enormous number of possible four-site combinations (any hopping carrier can play a double role of energy donor and energy acceptor; similarly, any vacant site is available as a

TABLE I Representative resonance energy transfer rates for a four-site, two-electron hopping process for $F = 100 \text{ kV/cm}$, $\kappa = 10$, $W = 0.001 \text{ eV}$.

$a^* = \gamma^{-1}$ (\AA)	$R_1 = R_2$ (\AA)	ΔE (eV)	$\tau_{\text{tr}} = \tau_{\text{RTT}}$ (sec)	R_0^a (\AA)
2	10	0.010	232	425
5	25	0.025	2.38	365
10	50	0.050	7.43×10^{-2}	325

^a $R = R_0$ corresponds to the condition $\tau_{\text{tr}} = \tau_{\text{RTT}}$.

destination point for many various jumps), this rather large ratio ($\sim 1\%$) furnishes the availability of a resonance site pair well within the sphere of radius R_0 from a given site pair a . Therefore, the results of the present paper give a reasonable basis to regard four-site RET (at least in some favorable situations) as a noticeable elementary process in activationless SEF HC.

In conclusion, let me mention that there may exist similar, more complex, multielectron energy exchange processes which also assist in the promotion of hopping carriers along the electric field. For example, it is possible to point out a three-electron process in which the energy ΔE released by a downward jump of one electron is shared between two other simultaneously jumping-up electrons, or, vice versa, two electrons simultaneously jumping downward can cumulate their energy gains ΔE 's on a third single electron, etc. These and similar processes can provide further contributing components to the total non-Ohmic hopping conductivity in a strong electric field.

¹A. G. Zabrodskii, A. I. Ionov, and I. S. Shlimak, *Fiz. Tekh. Poluprovodn.* **8**, 503 (1974) [*Sov. Phys. Semicond.* **8**, 322 (1974)].

²D. S. Volzhenskii, V. G. Savitskii, and B. K. Kotlyarchuk, *Fiz. Tverd. Tela (Leningrad)* **19**, 2552 (1977) [*Sov. Phys. Solid State* **19**, 1495 (1977)].

³A. Yoshida, S. Nakashima, and M. Ieda, *J. Non-Cryst. Solids* **35/36**, 421 (1980).

⁴A. A. Berezin, O. A. Golikova, M. M. Kazanin, E. N. Tkalenko, and V. K. Zaitsev, *Phys. Status Solidi (a)* **20**, 447 (1973).

⁵O. A. Golikova, A. A. Berezin, V. K. Zaitsev, M. M. Kazanin, V. M. Orlov, L. S. Stil'bans, and E. N. Tkalenko, *J. Less Common Metals* **47**, 129 (1976).

⁶O. A. Golikova, M. M. Kazanin, Z. Mirzazhonov,

V. M. Orlov, E. N. Tkalenko, and T. Khomidov, *Fiz. Tekh. Poluprovodn.* 14, 88 (1980) [*Sov. Phys. Semicond.* 14, 49 (1980)].

⁷A. A. Berezin, *J. Phys. C* 13, L947 (1980).

⁸A. A. Berezin, *Phys. Lett.* 86A, 480 (1981).

⁹A. A. Berezin, *J. Less Common Metals* 82, 143 (1981).

¹⁰D. L. Dexter, Th. Forster, and R. S. Knox, *Phys.*

Status Solidi 34, K159 (1969).

¹¹E. D. Trifonov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 35, 1330 (1971) [*Bull. Acad. Sci. USSR Phys. Ser.* 35, 1216 (1971)].

¹²V. M. Kenkre and R. S. Knox, *Phys. Rev. Lett.* 33, 803 (1974).

¹³P. N. Butcher and L. Swierkowski, *Solid State Commun.* 33, 1151 (1980).