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Variable Range Hopping Conductivity: Case of the non-constant density of states

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The variable range hopping theory has been widely used these last years to explain the electric conduction process in some biological systems as DNA. However, the experimental measurements on such systems reveal that the density of states varies strongly near Fermi level. This observation suggests that the theoretical concept of "constant density of states" near Fermi level is certainly insufficient to justify the observation of the $T^{-1/4}$ conductivity in such systems. To overcome this difficulty, we show in this work that this conductivity may be obtained for any odd number q when the density of states is expressed under the asymmetric power law form: $N(E) = N(E_F) + \text{const } E^q$. For this density of states, the thermoelectric power is also investigated.

1-The hopping conduction

1.1- History of the hopping conduction

Few years after the discovery of the transistor effect in the second half of the forties by Bardeen, Brattain and Shockley, it has been observed as early as 1950 a break in the behaviour of doped Germanium conductivity at low temperatures. Hung and Gliessman [1] attributed this behaviour to a distinct mechanism from usual conduction that governs doped semiconductors. Some years later in 1956, Conwell [2] and Mott [3] suggested a model for a "new" process of conduction in which charge carriers conduct the electric current by thermally activated tunnelling from an occupied site to an empty site. This process has been known as phonon assisted hopping and was the starting point of a number of transport theories as, the model of Miller and Abrahams [4] developed in 1960. This model became the most widely accepted theory of conduction between localized states for the sixties decade and was the inspiration source of the variable range hopping theory of Mott [5]. In the beginning of the seventies, some investigators [6,7] found some insufficiencies in the analysis of the conduction paths of Miller and Abrahams and to overcome such deficiencies, a more sophisticated treatment, based on the percolation theory was suggested. Such an approach is still considered today as the most reliable theory for the evaluation of the electric coefficients as conductivity and thermoelectric power of non-crystalline semiconductors. We discuss below in terms of percolation, the effect of the density of states shape on the $T^{-1/4}$ conductivity of Mott and we investigate the corresponding thermopower.

1.2- The random network of conductances

When states are localized in the Anderson sense [8] near Fermi level E_f , Miller and Abrahams [4] have shown that the conduction problem of disordered systems is equivalent to the conduction process of a random network of conductances σ_{ij} that link sites at energies E_i and E_j , separated in space by the distance R_{ij} . To conduct the electric current, σ_{ij} must be proportional to the hopping rate w_{ij} of the charge carrier from the i site to the j site. w_{ij} is in

fact the condition of the conductance existence and was expressed by Miller and Abrahams under the form:

$$w_{ij} = f(E_i)[1 - f(E_j)]\tau_{ij} \quad (1)$$

which means that the conductance σ_{ij} exists only if the i site is occupied, with the probability $f(E_i)$ and the j site is vacant with a probability $1 - f(E_j)$. In addition the charge transfer from i to j is possible only if there exist a transition rate τ_{ij} , depending on the wave functions overlapping and must be proportional to the phonons density distribution $\rho(\Delta)$. Before the evaluation of w_{ij} , let write these different expressions. We have:

$$f(E_i) = \frac{1}{1 + \exp\left\{\frac{E_i}{kT}\right\}}$$

and:

$$1 - f(E_j) = \frac{1}{1 + \exp\left\{-\frac{E_j}{kT}\right\}}$$

in these expressions k is the Boltzmann constant and T is the temperature of the system. All energies are measured from the Fermi level E_f , which is taken at the energies origin. The transition rates is written under the form:

$$\tau_{ij} = \text{const.} \exp\left\{-2\alpha R_{ij}\right\} \rho(\Delta) \quad (2)$$

in which α is the inverse localization length of the states and $\rho(\Delta)$ is the phonon density given by:

$$\rho(\Delta) = \frac{1}{\left| \exp\left\{\frac{\Delta}{kT}\right\} - 1 \right|}$$

this expression is in fact the Bose-Einstein distribution and represents the phonons density that will provide the energy $\Delta = E_i - E_j$, necessary to any hop from one site to another. By inserting equation (2) in (1) and by replacing the expressions of $f(E_i)$ and $f(E_j)$, we obtain:

$$w_{ij} = \text{const.} \exp\left\{-2\alpha R_{ij} - \frac{E_{ij}}{kT}\right\} \quad (3)$$

where E_{ij} is the hopping energy and will be discussed in details in the next sections. When w_{ij} takes a significant value, the i and j sites become connected via a conductance σ_{ij} proportional to w_{ij} . We can then write:

$$\sigma_{ij} = \exp\left\{-2\alpha R_{ij} - \frac{E_{ij}}{kT}\right\} \quad (4)$$

The most important parameters in this conductance expression are the random variables E_i , E_j and R_{ij} . The solution of the random network problem exists only when a continuous path of largest conductances cross the network from one side to the other. It is however not clear in this model when a conductance can be considered "large" and when it cannot. In other words it is unclear what are the physical conditions that must be satisfied for the existence of a continuous path of "large conductances" as the one shown in Figure-1.

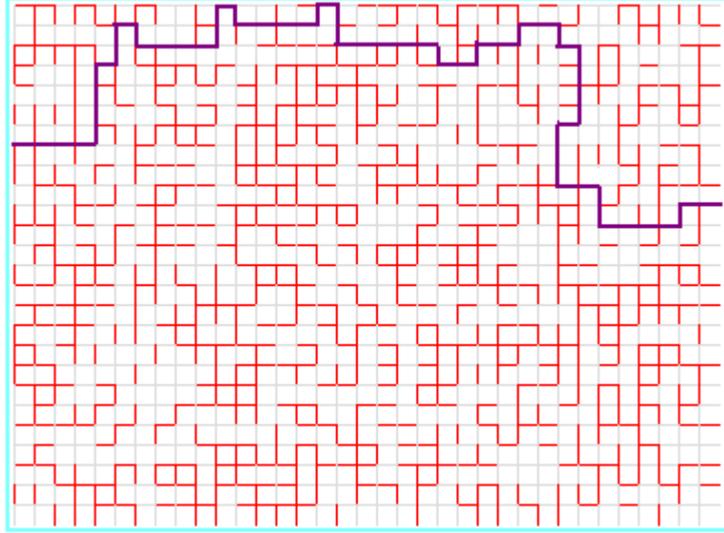


Figure-1: Simulation of a continuous path of "large conductances" in a random square network at the percolation threshold

In the beginning of the seventies, the authors of references [6] and [7] have shown that this problem is best handled if percolation theory is used. Based on the concept of "critical percolation threshold", such a theory is in fact perfectly adapted to the description of the problem of random conductances network. It is indeed possible to define a critical value σ_c and to consider only conductances larger than σ_c for the construction of the current continuous path. We have visualized such a situation in Figure-1 by representing only conductances with a value $\sigma > \sigma_c$.

2- Electric properties of the hopping conduction mechanism

2.1- Mott Conductivity

To some extent, the model of the hopping conduction was fruitful since it is the inspiration source of the variable range hopping theory of Mott [5]. According to this theory, when conduction between localized states near Fermi level E_F is by hopping, the temperature T dependence of the conductivity is given by:

$$\sigma = \sigma_0 \exp\left\{-\left(\frac{T_0}{T}\right)^{1/4}\right\} \quad (5)$$

To derive equation (5), Mott has minimized the argument of equation (4) with respect to the distance hop R_{ij} . To do this, he assumed that the density of states is constant over the energy range of hopping:

$$N(E) = N(E_F) \approx \frac{1}{E_{ij} R_{ij}^3} \quad (6)$$

In typical variable range hopping systems where Mott conductivity can be observed, the hopping energy ranges between 0.1 – 0.2 eV and it is difficult to believe that $N(E)$ remains constant over such an energy range. But what equations (5) and (6) become if the density of states is non-constant near E_F ?

Since Mott theory gives no answer to this question, it would be interesting to investigate this issue, particularly in the current microbiology/nanotechnology context for which it is believed that the DNA electric conductivity obeys [11,12] equation (5) with a strong density of states variation [13] near Fermi level.

2.2- The hopping thermo-electric power (or thermopower)

The thermo-electric power behaviour in the variable range hopping regime is also an acute problem. Indeed, all thermopower theories agree that the Peltier heat is zero for constant $N(E)$ and this means that the thermopower must be zero in this situation. But the experimental results show various metallic and non-metallic behaviours. To get around this difficulty Zvyagin first [9], then Overhof [10] tried to find a compromise between the constant character of the density of states for which Mott law is derived and the non-constant density of states nature, which yields a non-zero thermopower. They assumed that the density of states varies "linearly and slowly" near E_F so that the Mott conductivity can be observed simultaneously with a non zero thermo-electric power. They found the well known square root temperature dependence of the thermopower S :

$$S = \text{const. } T^{1/2} \quad (7)$$

It is then natural to ask also what equation (7) will become if the density of states $N(E)$ is not slowly varying?

3- Computation of the hopping conductivity for non-constant density of states.

3.1- The density of states

To compute the hopping conductivity when the density of states $N(E)$ is non-constant, we make use of the percolation theory. It is first necessary to make an assumption about the shape of $N(E)$. Intuition and observation must be the keys parameters on which any theoretical choice must be rested. As we do it previously [14], we consider first that $N(E_F)$ is the density of states at Fermi level, we suppose thereafter that the asymmetric part of $N(E)$ follows an odd power law form so that we can write:

$$\begin{aligned} N(E) &= N(E_F) + s_q E^q \\ &= N(E_F)[1 + v_q E^q] \end{aligned} \quad (8)$$

where $q = 1, 3, 5, \dots$ is an odd number and s_q is a constant (s_q is the slope for the linear case of $N(E)$).

3.2- Construction of a random network of conductances

According to the percolation theory, the current is conducted through a random network only if there exist a percolating channel that goes from one side of the system to the other. For this, two critical conditions must be satisfied: the first concerns the nature of each conductance σ_{ij} given equation (4), that must be at least equal to a critical conductance σ_c :

$$\sigma_{ij} \geq \sigma_c \quad (9)$$

and the second condition concerns the average number $\langle m(E_i) \rangle$ of conductances linked to each site located at energy E_i . Such a number must be equal at least to a critical concentration c of links per site:

$$c = \langle m(E_i) \rangle \quad (10)$$

When the conditions (9) and (10) are satisfied it appears in the random network a critical path of conductances (as shown in Fig-1) joining one side of the system to the other.

The problem of the random network is said solved only when σ_c is correctly identified and this happens when equation (10) is solved.

3.3- Resolution of the random network problem of conductances

With the help of equation (4), we can rewrite equation (9) under the form:

$$\exp\left\{-2\alpha R_{ij} - \frac{E_{ij}}{kT}\right\} \geq \exp\left\{-\frac{E_m}{kT}\right\} \quad (11)$$

The right side of this equation is proportional to σ_c and E_m is the energy that must be identified to solve our random network problem. To do this, we have first to evaluate the number $m(E_i)$ when the density of states is given by equation (8). To find $m(E_i)$ it is necessary to count all sites located at energies E_j accessible by the electron located at the site of energy E_i . Such E_j sites are randomly distributed within a sphere of radius R_{ij} that can be calculated from equation (11):

$$R_{ij} \leq \frac{1}{2\alpha kT}(E_m - E_{ij}) \quad (12)$$

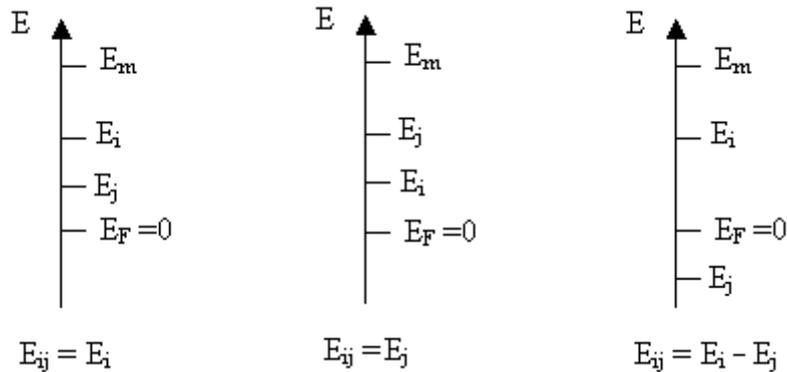
By writing:

$$m(E_i) = \frac{4\pi}{3} \int R_{ij}^3 N(E_j) dE_j \quad (13)$$

and by inserting equation (12) into equation (13) we obtain:

$$m(E_i) = \frac{4\pi}{3} \frac{1}{(2\alpha kT)^3} \int (E_m - E_{ij})^3 N(E_j) dE_j \quad (14)$$

The integration of this equation is made over all E_j , whether $E_j < E_i$ or $E_j > E_i$ and according to equations (1) and (2), the following configurations are expected for E_{ij} when $E_i > 0$:



By replacing these E_{ij} values and equation (8) in equation (14), we can write $m(E_i)$ as:

$$m(E_i) = \frac{4\pi}{3} \frac{N(E_F)}{(2\alpha kT)^3} \left[\int_0^{E_i} (E_m - E_i)^3 (1 + \nu_q E_j^q) dE_j + \int_{E_i}^{E_m} (E_m - E_j)^3 (1 + \nu_q E_j^q) dE_j + \int_{-E_m+E_i}^0 (E_m - E_i + E_j)^3 (1 + \nu_q E_j^q) dE_j \right] \quad (15)$$

To avoid an extremely tedious calculation in the next steps, it is more simple to write $m(E_i)$ under the form:

$$m(E_i) = m_0(E_i) + \mu(E_i, q) \quad (16)$$

where $m_0(E_i)$ represents the number of conductances resulting from the symmetrical part $N(E_F)$ of the density of states $N(E)$ and $\mu(E_i, q)$ is the number of conductances resulting from the asymmetrical part of $N(E)$. By comparing equations (15) and (16), we obtain for $E_i > 0$:

$$m_0(x) = \frac{2\pi}{3} \frac{N(E_F)}{(2\alpha kT)^3} E_m^4 (1+x)(1-x)^3 \quad (17)$$

and

$$\mu(x, q) = \frac{4\pi}{3} \frac{N(E_F)}{(2\alpha kT)^3} \frac{E_m^{q+4}}{E_0^q} \left\{ \frac{6q!}{(q+4)!} [1 - (1-x)^{q+4}] - \frac{3}{q+1} \left(\frac{x^{q+2}}{q+2} - 2 \frac{x^{q+3}}{q+3} + \frac{x^{q+4}}{q+4} \right) \right\} \quad (18)$$

and we obtain for $E_i < 0$:

$$m_0(x) = \frac{2\pi}{3} \frac{N(E_F)}{(2\alpha kT)^3} E_m^4 (1-x)(1+x)^3 \quad (19)$$

$$\mu(x, q) = \frac{4\pi}{3} \frac{N(E_F)}{(2\alpha kT)^3} \frac{E_m^{q+4}}{E_0^q} \left\{ \frac{6q!}{(q+4)!} [-1 + (1+x)^{q+4}] - \frac{3}{q+1} \left(\frac{x^{q+2}}{q+2} + 2 \frac{x^{q+3}}{q+3} + \frac{x^{q+4}}{q+4} \right) \right\} \quad (20)$$

where $x = E_i/E_m$ is a new dimensionless energy variable of integration and $-E_0$ is the energy solution of the equation $N(E) = 0$. Since $m(x)$ is a physical product of the density of states, it is not surprising to obtain $m_0(-x) = m_0(x)$ and $\mu(-x, q) = -\mu(x, q)$. We show in Figure-2

these parameters represented in unit of $\frac{2\pi}{3} \frac{N(E_F)}{(2\alpha kT)^3} E_m^4$ for the linear case $q=1$ of $N(E)$, when the temperature of the system is such $E_m \approx E_0$.

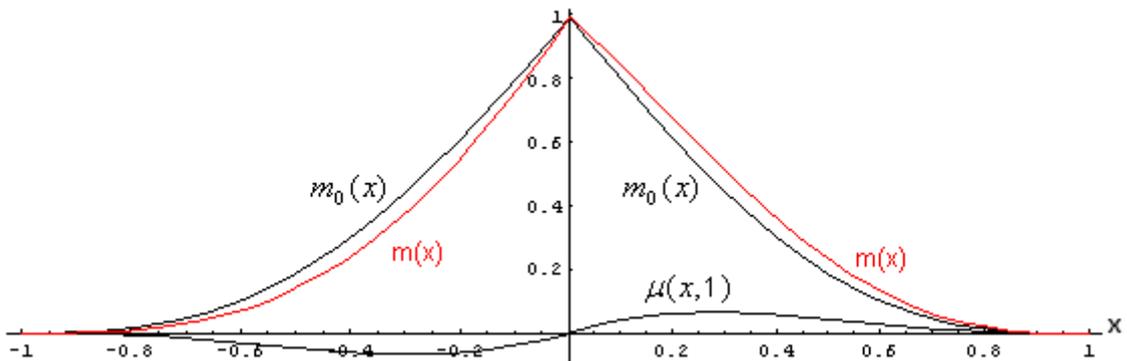


Figure-2: Plot of the $m(x)$ number of conductances attached to the site located at x for $q=1$.

The last step of the resolution of our percolation problem concerns the evaluation of the average number of conductances linked to the site located at energy E_i . The simplest way to obtain this number is to follow the procedure of Pollak [7] by weighting $m(E_i)$ with a probability factor that is proportional to $m(E_i)N(E_i)$, so that equation (10) becomes:

$$c = \frac{\int_{-E_m}^{E_m} m^2(E_i)N(E_i)dE_i}{\int_{-E_m}^{E_m} m(E_i)N(E_i)dE_i} = \frac{\int_{-1}^1 m^2(x)N(x)dx}{\int_{-1}^1 m(x)N(x)dx} \quad (21)$$

To reduce the tedious and important calculation volume for the evaluation of these integrals, it is more simple to expand their integrands under the form:

$$c = \frac{\int_{-1}^1 [m_0^2(x) + 2m_0(x)\mu(x,q)v_q(x) + \mu^2(x,q)]dx}{\int_{-1}^1 [m_0(x) + \mu(x,q)v_q(x)]dx} \quad (22)$$

In equation (22) we have omitted to write the asymmetrical functions since their integrations cancel over positive and negative energies. A detailed examination of the surfaces delimited by each term of the integrands (see Figure-2) shows that eq.(22) is quasi-similar [14] to that of ref.[7]:

$$c = \frac{\int_{-1}^1 m_0^2(x)dx}{\int_{-1}^1 m_0(x)dx} = \frac{2\pi}{3} \frac{115}{189} \frac{N(E_F)}{(2\alpha kT)^3} E_m^4 \quad (23)$$

derived for constant density of states $N(E) = N(E_F)$. By inserting equation (17) in eq(23) and by taking as in ref.[7], $c = 1.7$, we obtain:

$$\frac{E_m}{kT} = 1.8 \left[\frac{\alpha^3}{N(E_F)kT} \right]^{\frac{1}{4}} = \left(\frac{T_0}{T} \right)^{\frac{1}{4}}$$

We can then deduce that the hopping energy layer of equation(11): $E_m = kT.(T_0/T)^{1/4}$ and eq.(5) are valid for any odd q (and s_q) when $N(E)$ is given by eq.(8), as if $N(E) = N(E_F)$. These results are summarized in Figure-3.

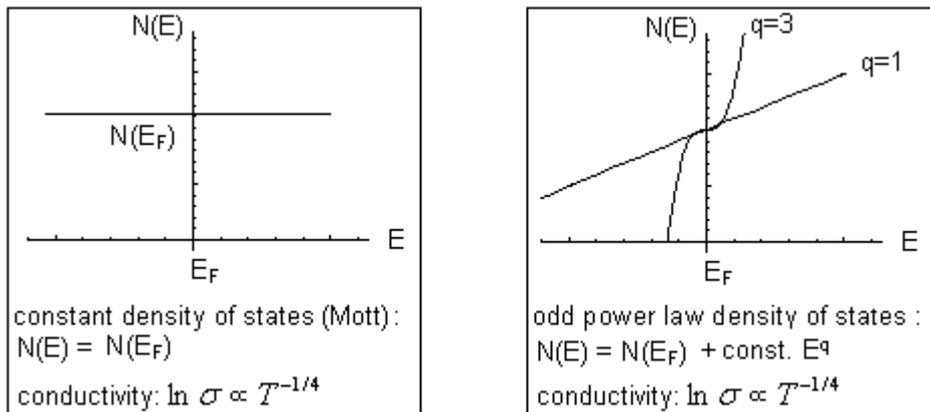


Figure-3: Some $N(E)$ shapes for which Mott conductivity is obtained

4- Thermo-electric power in the variable range hopping case

To compute the Seebeck coefficient S (or thermopower), we start from the formula:

$$S = \frac{k}{e} \frac{\Pi}{kT} \quad (24)$$

where e is the electronic charge and Π is an energy called the Peltier heat. Equation (24) is one of the classical Kelvin relations of thermo-electricity; for metals it gives [15]:

$$S = \frac{\pi^2}{3} \frac{k}{e} kT \left[\frac{\partial \ln \sigma(E)}{\partial E} \right]_{E=E_F} \quad (25)$$

In the variable range hopping regime, Π may be interpreted [14] as the mean energy of any site that belongs to the continuous critical path of conductances. We can then write:

$$\Pi = \frac{\int E.N(E).p(E)dE}{\int N(E).p(E)dE} \quad (26)$$

In this expression, we have weighted the energy E by a probability factor $p(E)$ that is assumed proportional to the number $m(E)$ of conductances attached to the site of energy E . By using equations (8) and (16), equation (26) becomes:

$$\Pi = \frac{\int [E.\mu(E, q) + m_0(E).\nu_q E^{q+1}] dE}{\int [m_0(E) + \nu_q E^q .\mu(E, q)] dE} \quad (27)$$

In this expression, we have again omitted to write the asymmetrical functions of E since their integrations cancel over positive and negative energies. After the evaluation of equation (27), equation (24) yields:

$$S = \frac{k}{e} \cdot \frac{E_m^{q+1}}{kT} \frac{d \ln N(E)}{dE^q} \cdot F(q) \cdot \left[1 + \frac{20}{3} \cdot G(q) \cdot \left(\frac{d \ln N(E)}{dE^q} E_m^q \right)_{E=E_f}^2 \right]^{-1} \quad (28)$$

In this thermoelectric power equation, the second term of the square brackets expression can be neglected for two reasons: firstly

$$G(q) = \frac{3}{(30 + 47q + 24q^2 + 4q^3)(q+1)^2} - \frac{6.\Gamma(q+1)^2}{\Gamma(2q+6)}$$

tends to zero with q as it is shown in the plot of Figure-4 (Γ is the Euler function).

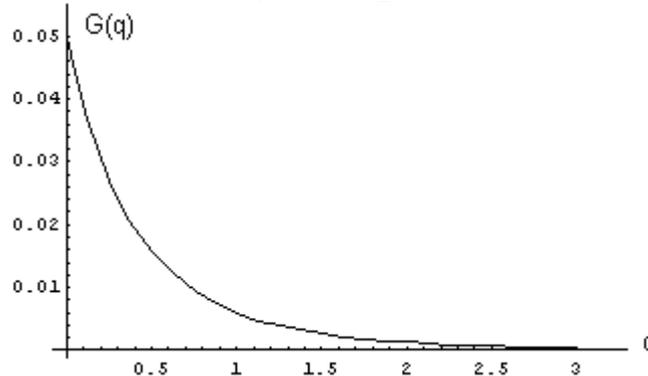


Figure 4: sketch of $G(q)$ in function of q

Secondly the term $((d \ln N(E)/dE^q)E_m^q)$ is always < 1 . We can then write:

$$S = F(q) \cdot \frac{k}{e} \cdot \frac{E_m^{q+1}}{kT} \left(\frac{d \ln N(E)}{dE^q} \right)_{E=E_F} \quad (29)$$

in which $F(q)$ is given by:

$$F(q) = \frac{60}{(q+2)(q+3)(q+5)(q+6)}$$

By replacing E_m by its value (see equation-23), we find [14] that the T dependence of the variable range hopping thermoelectric power is a class given by:

$$S = F(q) \frac{k}{e} k^q T_0^{\frac{q+1}{4}} T^{\frac{3q-1}{4}} \left(\frac{d \ln N(E)}{dE^q} \right)_{E=E_F} \quad (30)$$

For the linear asymmetry case ($q = 1$) of the density of states, the classical variable range hopping thermopower formula [9,10,16] is recovered:

$$S = F(1) \frac{k}{e} k(T_0 T)^{\frac{1}{2}} \left(\frac{d \ln N(E)}{dE} \right)_{E=E_F} \quad (31)$$

in which we have for the numerical constant: $F(1) = 5/42$.

5- Variable range hopping and DNA molecule conductivity

If we consider that DNA is a conductor substance of electric charges [12], and if in addition we admit that variable range hopping is the main process that governs the charges transport along the DNA molecule [12], then it would be difficult to conciliate the variable range hopping mechanism in its classic conception (constant density of states) and the strong $N(E)$ variation observed for this molecule [13, 17].

In this work, we have shown that the $T^{-1/4}$ conductivity of the variable range hopping mechanism can be valid even for non-constant density of states.

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