

Tunnelling process between a semiconductor or a metal and a polymer

T. Ouisse^aLaboratoire de Spectrométrie Physique, Université Joseph Fourier Grenoble 1^b, 140 rue de la physique, BP 87, 38042 Saint-Martin d'Hères Cedex, France

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Abstract. The tunnelling lifetime of an electron lying in a p -type orbital localised at a given distance from a semiconductor or a metal is calculated by using Bardeen's method. It is then shown that even in the absence of broad bands, the hole injection process from semiconductors and metals into polymers should follow a Fowler-Nordheim dependence, provided that the current is not bulk-limited. In the semiconductor case, the current can be expressed by a fully analytical formula, and by an approximate one in the case of a metal. It is demonstrated that the effective Fowler-Nordheim barrier is not the mere difference between the metal work function or the semiconductor electron affinity and the HOMO level of the polymer, but a simple function of both levels.

PACS. 82.35.Cd Conducting polymers

1 Introduction

Organic light-emitting diodes represent a growing research field [1]. This is due to a number of potential advantages, either in terms of mechanical properties or fabrication costs [1]. It is therefore important to clarify some of the physical mechanisms that govern the electrical behaviour of such devices. In particular, there are still some controversies concerning the injection mechanism which takes place between a metallic electrode and the polymer under investigation. At moderate field Schottky-type emission can describe well the current-voltage characteristics [1], and at higher fields some authors have found that their devices exhibit a Fowler-Nordheim (FN) tunnelling functional form (see, *e.g.*, [2–5]). However, it has been argued by others that FN tunnelling cannot describe contact injection into polymers, because these materials do not own broad energy bands, due to their short conjugation lengths [6]. Tunnelling from the highest occupied molecular orbital (HOMO) or into the lowest unoccupied molecular orbital (LUMO) should thus differ from what is expected in the case of broad band materials. There is indeed a fundamental difference between the conventional, one-dimensional Fowler-Nordheim model and the one exposed below: in our case the treatment must be three-dimensional, and tunnelling occurs between a localised state and a continuum, not between extended states. Here I would like to mention that a FN dependence is not specific to broad bands, and is for instance found in calcu-

lating the field-assisted, tunnelling escape of an electron from a delta potential [7,8]. Therefore, a first purpose of this letter is to calculate in the simplest way which electric field dependence can be expected in the case of the tunnelling from a localised orbital into a continuum formed by a neighbouring semiconductor or a metal. Then a second one is to show that even with localised p -type orbitals, one should still expect the injection current to be of the Fowler-Nordheim type. It is demonstrated in this article that a FN dependence is to be expected at high field, provided, of course, that the current is injection-limited, and not bulk-limited.

2 Theory

2.1 Tunnelling into a non-degenerate semiconductor

The system under consideration is an atom-like potential located at a distance x_0 of a semiconductor, the electron affinity of which is Φ . The binding energy of the p -state under consideration is $-E_0$. To simplify the calculations I use a constant effective mass m throughout and consider a p -type orbital the symmetry axis of which is directed along the z -axis. To calculate the tunnelling lifetime, I use a potential energy diagram as shown in Figure 1. Two wave functions are introduced, ψ_L and ψ_R , which characterise respectively an electron in the conduction band of the semiconductor and in the p -state. ψ_L and ψ_R are derived using the two different potential profiles V_L and V_R shown in Figure 1. The complete Hamiltonian of the problem is $H = H_L + H_R + \hbar^2/2m\nabla^2$. Close to the molecule atom,

^a e-mail: ouisse@enserg.fr^b CNRS UMR C5588

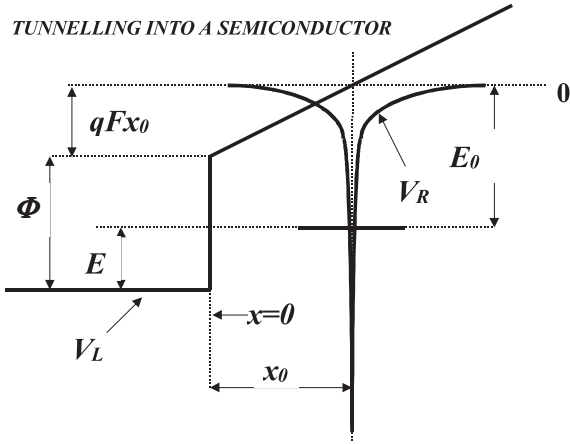


Fig. 1. Cross section of the energy diagram of the semiconductor/polymer system, perpendicular to the semiconductor plane.

the Hamiltonian H is close to $H_R = -\hbar/2m\nabla^2 + V_R$, and far from it, it is close to $H_L = -\hbar/2m\nabla^2 + V_L$. Bardeen has shown that the matrix element for the tunnel transition can then be written $T_{RL} = \langle \psi_R | H - E_L | \psi_L \rangle$, where E_L is an energy eigenvalue of H_L [9]. With our choice of potentials this reduces to $T_{RL} = \langle \psi_R | V_L | \psi_L \rangle$, and indeed corresponds to the method originally proposed by Oppenheimer [10]. Inside the semiconductor, the wave function ψ_L reduces to a plane wave. Outside of it, along the x -axis the potential is linear and equal to $qF(x - x_0)$ with our choice of origin, where F is the electric field. A standard solution of Schrödinger equation comes under the form of an Airy function [11,12]. The evanescent part of ψ_L is easily shown to be equal to

$$\psi_L = \frac{1}{L^{3/2}} \sqrt{\frac{2k_x^2}{k_x^2 Ai^2(c) + b^2 Ai'^2(c)}} \times Ai(bx + c) \exp(i(k_y y + k_z z)) \quad (1)$$

where $Ai(x)$ and $Ai'(x)$ are the standard Airy function and its derivative, respectively. L^3 is the volume of the semiconductor. b and c are given by

$$b = \left(\frac{2mqF}{\hbar^2} \right)^{1/3} \quad (2)$$

and

$$c = \left(\frac{2mqF}{\hbar^2} \right)^{-2/3} \left(\frac{2m\Phi}{\hbar^2} - k_x^2 \right). \quad (3)$$

k_x , k_y and k_z are linked through

$$\begin{aligned} \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) &= \Phi + qFx_0 - E_0 \\ &= E = \frac{\hbar^2 k^2}{2m}. \end{aligned} \quad (4)$$

The normalisation factor in (1) is found by equating the values of the wavefunction forms corresponding to neg-

ative and positive x values at $x = 0$, as well as their derivatives. I approximate the p -state by a Gaussian orbital of the form

$$\psi_R = \left(\frac{128a^5}{\pi^3} \right)^{1/4} z e^{-ar^2} \quad (5)$$

where $r = ((x - x_0)^2 + y^2 + z^2)^{1/2}$ is the distance from the atom, the coordinates of which are $x = x_0$, $y = 0$ and $z = 0$. This approximation presents two advantages. On the one hand, I can separate the integration variables when calculating the tunnel matrix element $T_{RL} = \langle \psi_R | V_L | \psi_L \rangle$. On the other hand, the result can then be used for many molecules or atoms, whose Gaussian orbital parameters are used and referenced in quantum chemistry. Although the case detailed here is restricted to a p -type orbital parallel to the semiconductor plane, a quite similar calculation could be achieved for a p -type orbital perpendicular to the semiconductor interface, using exactly the same calculation procedure. A more complete derivation will be given elsewhere as a function of the angle.

For $x > 0$, the contribution to the matrix element reduces to the simple form $\langle \psi_R | qF(x - x_0) | \psi_L \rangle_{x>0}$. Separating the variables, and apart from a simple proportionality factor, the integral with respect to x is equal to

$$I(F, x_0, k_x) = \int_0^\infty Ai(bx + c)(x - x_0) \times \exp(-a(x - x_0)^2) dx. \quad (6)$$

To calculate I , one can remark that the electron affinity of the semiconductor is larger than E_0 , so that the contribution to the overlap integral is mostly that of the $x > 0$ domain. Thus the total integral value is not appreciably changed by replacing the term in the sum for $x < 0$ by the same form as for $x > 0$. Then, the sum from minus infinity to plus infinity is calculated by making use of three properties of the Airy transforms. $\varphi_\alpha(y) = (1/\alpha) \int f(x) Ai((y - x)/\alpha) dx$ being the Airy transform of the function $f(x)$, one has [12]:

$$f(x + k) \rightarrow \varphi_\alpha(y + k) \quad (7)$$

$$f(kx) \rightarrow \varphi_{\alpha k}(ky) \quad (8)$$

$$xf(x) \rightarrow y\varphi_\alpha(y) - \alpha^3 \varphi_{\alpha''}(y) \quad (9)$$

and noting that the Airy transform of a Gaussian $\exp(-x^2)$ is [12]

$$\exp(-x^2) \rightarrow \frac{\sqrt{\pi}}{\alpha} \exp\left[\frac{1}{4\alpha^3} \left(y + \frac{1}{24\alpha^3} \right) \right] Ai\left(\frac{y}{\alpha} + \frac{1}{16\alpha^4} \right) \quad (10)$$

one eventually gets

$$\begin{aligned} I(F, x_0, k_x) &= \left[\frac{\sqrt{\pi} b^3}{8a^{5/2}} Ai\left(c + bx_0 + \frac{b^4}{16a^2} \right) \right. \\ &\quad \left. + \frac{\sqrt{\pi} b}{2a^{3/2}} Ai'\left(c + bx_0 + \frac{b^4}{16a^2} \right) \right] \\ &\quad \times \exp\left[\frac{b^2}{4a} (c + bx_0) + \frac{b^6}{96a^3} \right]. \end{aligned} \quad (11)$$

The integrations with respect to y and z are simple Gaussian integrals and do not lead to any difficulty. One finally obtains the following expression for T_{RL} :

$$T_{\text{RL}} = \frac{\pi^{5/4} 2^{9/4} q F k_z k_x}{a^{3/4} L^{3/2} \sqrt{k_x^2 A i^2(c) + b^2 A i'^2(c)}} \times \exp\left(\frac{k_{\parallel}^2}{4a}\right) I(F, x_0, k_x), \quad (12)$$

where $I(F, x_0, k_x)$ is given by (11) and $k_{\parallel}^2 = k_y^2 + k_z^2$. Owing to the magnitude of the various physical quantities involved in (11) and (12), it is somewhat tedious, but not difficult to show that equation (12) can be very closely approached by a simpler analytical formula. Considering the argument inside the Airy functions in (11) and (12), it can first be shown that $b^4/16a^2$ is negligible in front of c . Neglecting k_x^2 in front of $2m\Phi/\hbar^2$, the ratio between the latter and the former terms is equal to $mq^2/8\hbar^2\Phi a^2 F^2$. $a^{-1/2}$ is typically of the order of one angström, and Φ lies between 4 and 5 eV. Hence, even for electric fields in the range of a few MV/cm, the ratio $b^4/16a^2c$ remains in the range 10^{-5} . Then, remembering that the asymptotic expression of $Ai'(x)/Ai(x)$ is $x^{1/2}$, one can also show by quite similar considerations that in (11) and (12), one can keep only the derivatives of the Airy function and skip the Airy functions themselves. One then obtains

$$T_{\text{RL}} \cong \frac{\pi^{7/4} 2^{5/4} q F k_x k_z}{L^{3/2} a^{2+1/4}} \times \frac{Ai'\left(\frac{1}{b^2}\left(\frac{2mE_0}{\hbar^2} + k_{\parallel}^2\right)\right)}{Ai'\left(\frac{1}{b^2}\left(\frac{2m(E_0 - qFx_0)}{\hbar^2} + k_{\parallel}^2\right)\right)} \times \exp\left(\frac{mE_0}{2a\hbar^2}\right). \quad (13)$$

I note that this formula could also be applied in semiconductor device physics to study field-assisted de-trapping from an insulator into a metal or a semiconductor, in situations as those described in [13], or, *e.g.*, for calculating the escape from Si dots into a gate electrode [14]. For a constant $|T_{\text{RL}}|^2$ the Fermi golden rule gives a probability of transition

$$p = \frac{2\pi}{\hbar} |T_{\text{RL}}|^2 \frac{dN}{dE} \quad (14)$$

where $dN/dE = (L/2\pi)^3 4\pi mk/\hbar^2$ is the density of states of the semiconductor, taken at E . Now we have to weight and sum over the various combinations of k_x , k_y and k_z that lead to a given E value (*i.e.* on the sphere of radius k). This leads to the following integral, giving the transition

probability from the p -state to the continuum:

$$P(F, x_0) = \int_{k_{\parallel}=0}^k dk_{\parallel} \times \left(\int_{k_z=0}^{k_{\parallel}} \frac{2\pi}{\hbar} \frac{dN}{dE} |T_{\text{RL}}|^2 \frac{k_{\parallel}}{k\sqrt{k^2 - k_{\parallel}^2}} \frac{2}{\pi\sqrt{k_{\parallel}^2 - k_z^2}} dk_z \right) \quad (15)$$

which can be integrated with respect to k_z to give

$$P(F, x_0) = \frac{8\sqrt{2}\pi^{3/2}mq^2F^2}{\hbar^3a^{3/2}} \times \int_0^k \frac{k_{\parallel}^3 \sqrt{k^2 - k_{\parallel}^2} I^2(F, x_0, \sqrt{k^2 - k_{\parallel}^2})}{(k^2 - k_{\parallel}^2) Ai^2(c) + b^2 Ai'^2(c)} \exp\left(\frac{k_{\parallel}^2}{2a}\right) dk_{\parallel}, \quad (16)$$

c being a function of $k_x^2 = k^2 - k_{\parallel}^2$ through equation (3). (16) can be numerically integrated to give the tunnelling probability of the electron from the p -state into the semiconductor. A similar expression can also be derived in the same way to get the tunnelling probability from an s -state. It is worth noticing that one can make a further step by using the simpler but almost as accurate expression (13), instead of (12). After some easy calculation, one obtains

$$P(F, x_0) = \frac{2\sqrt{2}\pi^{5/2}mq^2F^2}{\hbar^3a^{9/2}} \exp\left(\frac{mE_0}{a\hbar^2}\right) \int_0^k k_{\parallel}^3 \sqrt{k^2 - k_{\parallel}^2} \times \frac{Ai'^2\left(\frac{1}{b^2}\left(\frac{2mE_0}{\hbar^2} + k_{\parallel}^2\right)\right)}{Ai'^2\left(\frac{1}{b^2}\left(\frac{2m(E_0 - qFx_0)}{\hbar^2} + k_{\parallel}^2\right)\right)} dk_{\parallel}. \quad (17)$$

Then, an interesting approximation of (17) can be obtained if we neglect the occurrence of k_{\parallel} inside the derivatives of the Airy functions, which is a justified procedure as long as the kinetic energy E of the electron released in the band is low in front of the electron affinity. As we shall see it below, this approximation is particularly suited and useful for calculating the overall current. In such a scheme the integral is easy to compute, and I obtain a fully analytical expression of the reciprocal tunnelling lifetime:

$$P(F, x_0) = \frac{2^5\pi^{5/2}m^{7/2}q^2F^2}{15\hbar^8a^{9/2}} (\Phi - E_0 + qFx_0)^{5/2} \times \frac{Ai'^2\left(\frac{2mE_0}{b^2\hbar^2}\right)}{Ai'^2\left(\frac{2m(E_0 - qFx_0)}{b^2\hbar^2}\right)} \exp\left(\frac{mE_0}{a\hbar^2}\right). \quad (18)$$

To calculate the tunnelling current I shall make the assumption that we have a uniform distribution of identical Gaussian orbitals inside the polymer. Of course, for

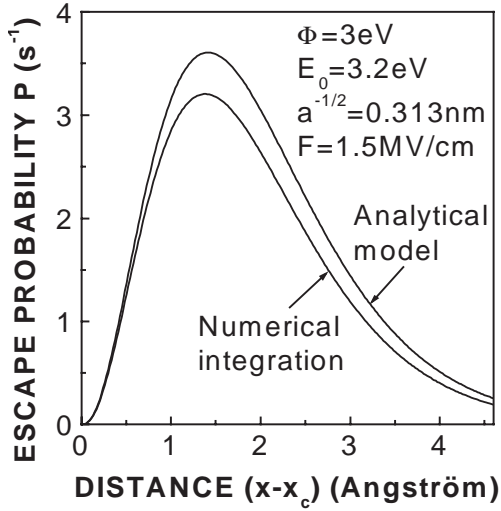


Fig. 2. Variation of the escape probability from an occupied p -type orbital as a function of the distance from the semiconductor interface. The physical parameters are indicated in the body of the figure.

a given polymer the summation should indeed be carried over orbitals with different a values and weighting factors, depending on the molecule under consideration. But there is no reason for which the results would then qualitatively differ from the simplified model of this paper. With a density D per unit volume of HOMO orbitals, the total current density J is immediately given by

$$J = qD \int_{x=x_C}^{+\infty} P(F, x) dx \quad (19)$$

where the lower integration bound x_C is equal to

$$x_C = \frac{E_0 - \Phi}{qF}. \quad (20)$$

In fact, it is easy to check that $P(F, x)$ is a sharply peaked function of x , the maximum of which always lies close to x_C (see Fig. 2 for a numerical example). By using expression (18), we can therefore obtain a very simple and accurate expression for J , through a rather straightforward calculation that I summarise as follows: First I use the usual asymptotic expansion of the derivative of the Airy function, and then develop the full expression to be integrated to the first order as a function of $(x - x_C)$, both in front of the exponential term and inside it. It then becomes apparent that the integral reduces to the sum of two Γ functions. The final result is therefore fully analytical, and J is given by

$$J = \frac{2^{-1/4} qD}{15\pi^2} \sqrt{\frac{E_0}{m}} \left(\frac{qF\pi\sqrt{m}}{\hbar a\sqrt{\Phi}} \right)^{9/2} \times \left(\Gamma(7/2) + \frac{qF\hbar}{4\sqrt{2m}\Phi^{3/2}} \Gamma(9/2) \right) \exp\left(\frac{mE_0}{a\hbar^2}\right) \times \exp\left(\frac{-4\sqrt{2m}(E_0^{3/2} - \Phi^{3/2})}{3\hbar qF}\right) \quad (21)$$

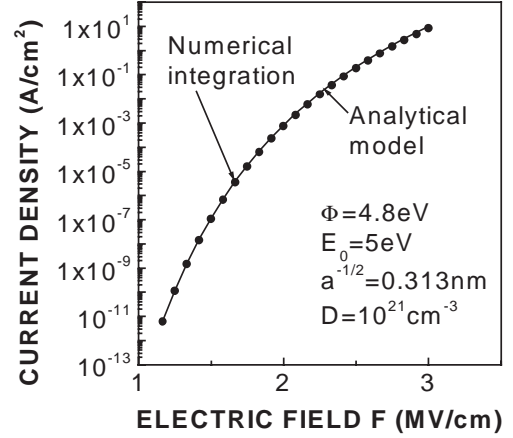


Fig. 3. Numerical example of the hole tunnelling current density *versus* electric field between a semiconductor and a polymer. The physical parameters are indicated in the figure body; points: numerical integration of equation (19) using equation (16) and full line: analytical formula (21).

which can safely be further simplified to

$$J = \frac{2^{-1/4} qD \Gamma(7/2)}{15\pi^2} \sqrt{\frac{E_0}{m}} \left(\frac{qF\pi\sqrt{m}}{\hbar a\sqrt{\Phi}} \right)^{9/2} \times \exp\left(\frac{mE_0}{a\hbar^2}\right) \exp\left(\frac{-4\sqrt{2m}(E_0^{3/2} - \Phi^{3/2})}{3\hbar qF}\right). \quad (22)$$

Equation (22) is the major result of this paper in the semiconductor case. It demonstrates that the hole tunnelling current from a semiconductor into a polymer should be of the Fowler-Nordheim type, provided that the current is contact-limited. The exponential term has an exact Fowler-Nordheim dependence, and the term in factor of it has a dependence close to $F^{9/2}$. It is thus somewhat different from the conventional F^2 dependence. But experimentally it should indeed be very difficult to make a difference between the two forms, due to the presence of the prevailing exponential term. In Figure 3, I give a numerical example and it is obvious from it that formula (22) is indeed a very accurate fit of a full numerical calculation, using equations (19, 16). A more realistic calculation would for instance be a sum of terms formally equivalent to (21), each one corresponding to the different molecular orbitals and associated weighting factors of the polymer segment under consideration. Besides, equation (21) demonstrates that the effective Fowler-Nordheim barrier Φ_{eff} is not the mere difference between the electron affinity of the semiconductor and the HOMO level. From (21) one immediately gets

$$\Phi_{\text{eff}} = \left(E_0^{3/2} - \Phi^{3/2} \right)^{2/3}. \quad (23)$$

A second feature can also be deduced from (22). The FN pre-factor is not equal to the conventional one, and indeed it highly depends on the density of p -type orbitals

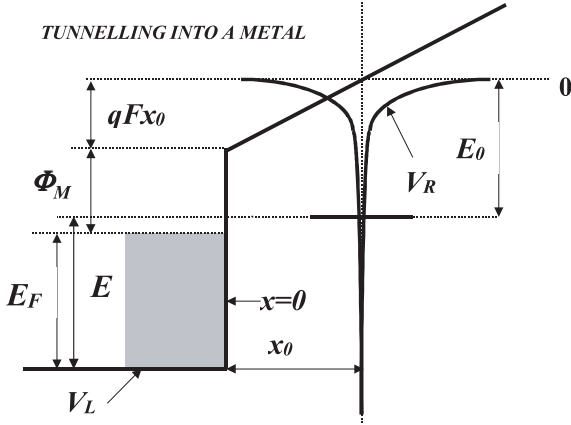


Fig. 4. Cross section of the energy diagram of the metal/polymer system, perpendicular to the metal plane.

of the polymer. It is therefore not abnormal to find pre-factors much lower than that expected in the case of broad bands. This depends not only on the packing density of the polymer, but also of the HOMO level and the characteristic spreading of the orbitals. It is worth noticing that a change in orientation (from parallel to perpendicular) can lead to an improvement of the current of several orders of magnitude. Serious attempts to fit experimental data would therefore require a complete knowledge of the polymer structure, especially close to the interface (molecule electron wave function and orientation as a function of depth). Here I would like to stress that I voluntarily chose the simplest potential form. I did not take into account image force effects or specific polarisation phenomena near the semiconductor/polymer interface, which are known to exist. However, I do not expect any of the qualitative conclusions of this section to be caught out once an overall potential shape more complex than a linear one is used for V_L out of the semiconductor. The physical factor which leads to a FN law is the presence of a potential term linear in the electric field and the distance, which will remain in more realistic models.

2.2 Tunnelling into a degenerate semiconductor or a metal

In the case of a metal, a more appropriate energy diagram is shown in Figure 4. Basically, we now have to take into account the Fermi energy E_F of the metal, which implies that the kinetic energy of the electrons released from the polymer be much higher. Equation (17) is still valid, but now it is no longer possible to neglect the presence of k_{\parallel} inside the derivatives of the Airy functions appearing inside the integral. Φ_M being the metal work function, in equation (17) k is now given by

$$k = \frac{1}{\hbar} \sqrt{2m(\Phi_M + E_F - E_0 + qFx_0)}. \quad (24)$$

The approximate formulae of Section 2.1 excepted, all equations and reasoning are still valid in the metal case,

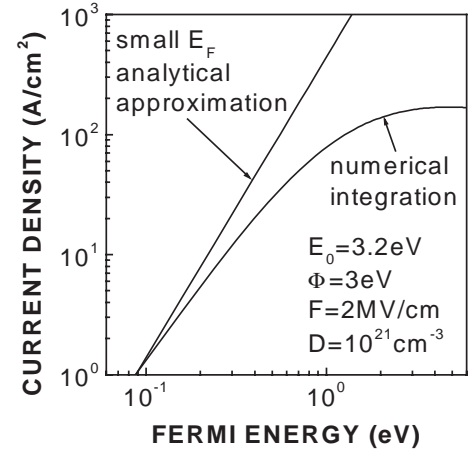


Fig. 5. Tunnelling hole current between a polymer and a metal, numerically integrated by using equation (19). The variable is the Fermi energy. The physical parameters are indicated inside the figure.

provided that one replaces Φ by $\Phi_M + E_F$ but in the expression of x_C , which is now given by $x_C = (E_0 - \Phi_M)/qF$. I did not find an analytical expression for large E_F values. But for small ones in front of E_0 and Φ_M , it is still possible to neglect the occurrence of k_{\parallel} inside the Airy functions and then calculations quite similar to that exposed in Section 2.1 give

$$J = \frac{2^4 \pi^{5/2} q^3 D m^3}{15 \hbar^7 a^{9/2} \sqrt{2}} F^2 \frac{E_F^{5/2}}{\Phi_M} \times \exp\left(\frac{mE_0}{a\hbar^2}\right) \exp\left(\frac{-4\sqrt{2m}(E_0^{3/2} - \Phi^{3/2})}{3\hbar q F}\right). \quad (25)$$

The Fermi energy of most metals used in practical situations will in general *not* be small in front of E_0 and Φ_M , but formula (25) might be used for degenerate semiconductors, as, *e.g.*, Indium Tin Oxide (ITO) or degenerate Si. It shows that the effective FN barrier still follows equation (23). For large E_F values, I have checked numerically by integrating equation (19) that formula (25) largely overestimates the current. This is illustrated by Figure 5. Through numerical calculations, I was led to the conclusion that it is a reasonable approximation as long as E_F remains below a few 0.1 eV, with E_0 and Φ_M being in the range of a few eV. In all my numerical investigations, I always obtained an effective FN barrier close to that given by (23), even for large E_F values. Besides, it is interesting to note that the larger is the Fermi energy, the larger is the FN pre-factor. Everything otherwise fixed, one can gain several orders of magnitude in comparison with the semiconductor case, once E_F reaches several eV. To illustrate this point, a numerical comparison is made in Figure 5, in which I take constant E_0 and Φ_M values and vary the Fermi energy. Although the parameters have been chosen in a somewhat arbitrary way, it is also worth

noticing that above a few eV, the tunnelling current saturates with E_F (in fact it reaches a maximum and then very slowly decreases). One can therefore conclude that with a constant work function, it is better to choose the metal with the highest Fermi energy, so as to maximise the tunnelling current.

3 Conclusion

In this article I have derived an analytical expression of the tunnelling transition between a p -type occupied orbital and a neighbouring semiconductor or a metal, as a function of the electric field applied to the considered molecule. Then I have obtained a fully analytical expression of the hole tunnelling current between a semiconductor and a model polymer. It is of the Fowler-Nordheim type. The model predicts that for hole tunnelling into a polymer the effective FN energy barrier is not the mere difference between the HOMO level and the electron affinity of the semiconductor or the metal work function, but a simple function of them. The formulae derived above result from a simplified model, but are nevertheless expected to be helpful in the interpretation of experimental data, especially in the case of organic electroluminescent diodes.

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