Comment on “Charge transport in disordered semiconducting polymers driven by nuclear tunneling”

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In [Phys. Rev. B **93**, 140206\(R\) \(2016\)](#), electron transport governed by nuclear tunneling was claimed to be a more realistic transport mechanism in semiconducting polymers as compared to Marcus and Miller-Abrahams transport mechanisms. The conclusion was based on the analysis of the field-dependent charge carrier mobility. We point out the unjustified simplification in the theoretical description of the electron transport governed by nuclear tunneling which caused such a conclusion.

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In a recent paper [1] the charge carrier mobility μ was studied experimentally in semiconducting polymers MEH-PPV and calculated for three different electron transport mechanisms. The results of the calculations depicted in Fig. 1 in Ref. [1] show that μ decreases with rising electric field F at large fields for the Marcus and Miller-Abrahams electron transfer mechanisms, whereas $\mu(F)$ supposedly increases with F in the whole range of considered fields for the nuclear tunneling mechanism. Nuclear tunneling theory was argued to predict “a power law at high fields” for $\mu(F)$ [1]. The latter mechanism was concluded to describe charge transport consistently “unlike other semiclassical models,” i.e., the Miller-Abrahams and Marcus approaches.

In this comment, we argue that the above-mentioned conclusions in Ref. [1] were caused by an unjustified simplification of the theory for the electron transfer mechanism based on nuclear tunneling. The transfer rate for this mechanism was previously calculated by Asadi *et al.* [2] in the form

$$k = \frac{H_{ij}^2}{\hbar^2 \omega_c} \left(\frac{\hbar \omega_c}{2\pi k_B T} \right)^{1-2\alpha'} \left| \Gamma \left(\alpha' + i \frac{\varepsilon_{ij}}{2\pi k_B T} \right) \right|^2 \times \Gamma(2\alpha')^{-1} \exp \left(\frac{\varepsilon_{ij}}{2k_B T} \right) \exp \left(-\frac{|\varepsilon_{ij}|}{\hbar \omega_c} \right). \quad (1)$$

The parameters in this equation are described in Ref. [2]. For our comment, it is sufficient to note that ω_c is the characteristic frequency of the bath, and ε_{ij} is the energy difference between the initial and final states in the electron transfer between sites i and j . In Ref. [1] the last factor $\exp[-|\varepsilon_{ij}|/(\hbar \omega_c)]$ in Eq. (1) has been omitted. This omission is the reason for the unjustified conclusions in Ref. [1].

The energy difference ε_{ij} contains the term $eF \Delta x_{ij}$, where e is the carrier charge and Δx_{ij} is the distance between the states along the field direction. Therefore, the omitted factor $\exp[-|\varepsilon_{ij}|/(\hbar \omega_c)]$ is an exponentially decreasing function of F at large F . As shown in Ref. [1], Eq. (1) without the last factor leads to a power-law increase of $\mu(F)$ at high fields. However, a power-law function cannot compete with an exponential dependence at large F . Therefore, Eq. (1), as derived by Asadi *et al.* [2], leads, in fact, to a *decrease* of $\mu(F)$ at high fields. Consequently, the dependence $\mu(F)$ for the nuclear tunneling mechanism looks qualitatively similar to that for Marcus transfer rates, i.e., an exponential decrease at high fields. In Ref. [1] the Miller-Abrahams and Marcus mechanism were rejected because they both predict a decreasing $\mu(F)$ at high F , whereas experiments display a continuously increasing $\mu(F)$.

In conclusion, we argue that the electron transfer based on nuclear tunneling was favored in Ref. [1] because this mechanism allegedly causes a continuously increasing $\mu(F)$ for the experimentally accessible range of fields, in contrast to the Miller-Abrahams and Marcus mechanisms. However, as we explained in this comment, the nuclear tunneling mechanism may also lead to a decreasing $\mu(F)$ at high fields F .

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