A very general rate expression for charge hopping in semiconducting polymers

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Abstract

We propose an expression of the hopping rate between localized states in semiconducting disordered polymers that contains the most used rates in the literature as special cases. We stress that these rates cannot be obtained directly from electron transfer rate theories as it is not possible to define diabatic localized states if the localization is caused by disorder, as in most polymers, rather than nuclear polarization effects. After defining the separate classes of accepting and inducing nuclear modes in the system, we obtain a general expression of the hopping rate. We show that, under the appropriate limits, this expression reduces to (i) single-phonon rate expression or (ii) the Miller-Abrahams rate or (iii) a multi-phonon expression. The description of these limits from a more general expression is useful to interpolate between them, to validate the assumptions of each limiting case, and to define the simplest rate expression that still captures the main features of the charge transport. When the rate expression is fed with a range of realistic parameters the deviation from the Miller-Abrahams rate is large or extremely large, especially for hopping toward lower energy states, due to the energy gap law.

1. Introduction

Charge transport in semiconducting polymers is thought to take place by a sequence of charge hopping events between localized states.[1] Given the great technological importance of these materials,[2-4] a large number of theoretical works have been devoted to the study of various aspects of the charge transport mechanism. A good fraction of these works focuses on the phenomenological description of the transport,[5,6] i.e. they are based on hypotheses on the nature of the states relevant for transport, their energy distribution and the hopping rates between them, and attempt to describe the relationship between a limited number of material properties (density of states, localization of the charge) and the observable charge mobility. This class of methods is rooted in the study of charge transport in disordered inorganic materials and is the topic of several reviews and monographs.[1,7] More recently, it became possible to build atomistic models of realistic polymers and sometimes even to evaluate their electronic structure.[8-14] These more detailed models aim at elucidating the relationship between the chemical structure and the mobility of the materials. There is an increasing number of examples of materials where modest chemical differences cause enormous changes in charge mobility[15,16] and one of the challenges for theoreticians is to develop models that describe correctly the chemical details but also the charge transport at macroscopic levels. A multi-scale approach is deemed necessary to tackle this problem and few excellent attempts have been proposed recently.[17,18]

Crucial for all types of models (phenomenological, atomistic or multi-scale) is the expression used to compute the hopping rate between two different electronic states. In the literature, different rate expressions, usually derived from different branches of physics, are adopted, and their validity is discussed on the basis of the comparison between computed and experimental results. In this paper, we derive a more general expression for the hopping rate that includes the most commonly used hopping rates as limiting cases. The first advantage of having such a general expression is that it makes it easy to understand the relationships between the different rate expressions and the assumptions needed to make each of them valid. Furthermore, such a general expression allows one to interpolate between limiting cases, i.e. study how the assumptions of a particular limiting expression influence the final results. If one is interested in a more "universal" behaviour of semiconducting polymers, it would be desirable to start from a general rate expression that contains the minimum number of assumptions. Finally, a more general expression is typically best suited to incorporate the details of atomistic calculations and can therefore be used to create the link between detailed electronic structure calculations and larger scale models.

When looked at individually, the hopping rate expressions that have been recently used seem to be in contradiction with each other and with other theories. The most used rate expression to study charge transport in polymers is the Miller-Abrahams rate k_{12} for the hopping between two electronic states (say 1 and 2):[19]

$$k_{12} = \begin{cases} k^0 & for\ \Delta E_{12} < 0 \\ k^0 \exp\left(-\Delta E_{12}/k_{\mathrm{B}}T\right) & for\ \Delta E_{12} > 0 \end{cases} \qquad (1)$$

k^0 is a function that depends on the distance and localization of the states (not relevant for this discussion), ΔE_{12} is the energy of the final state minus the energy of the initial state and $k_{\mathrm{B}}T$ is the thermal energy. According to this expression, the downhill rate is independent of ΔE_{12}. This contradicts what is known in photophysics as the energy gap law,[20,21] i.e. an exponential decrease of the non-radiative transition rate between two states with the increase of the energy gap between them. The rate expressions based on Marcus theory[22] or alternative formulations with a similar dependence on the energy gap[23] seem to err in the opposite direction, making $k_{12} \propto \exp\left(-(\Delta E_{12}+\lambda)^2/4\lambda k_{\mathrm{B}}T\right)$, i.e. the rate decreases too rapidly (as a Gaussian) for very negative ΔE_{12}. In a series of recent works, Vukmirovic et al.[8,24-26] have used an alternative expression where the hopping between states is promoted via electron-phonon coupling by a phonon matching the energy difference between them. The results depend strongly on the phonon spectrum, unlike the other two models mentioned above. The main objective of this paper is to reconcile the various models proposed and describe the relation between them in a simple fashion.

Aspects that will not be discussed here include the effect of the distance between the states, their relative localization, and the possibility that stronger or weaker coupling between them can result from the details of the electronic structure. These are also extremely important effects. It was shown for example that the distance dependence normally included in the Miller-Abrahams rate is too approximate.[25] This was later found also in ref. [23] where the importance of variable localization of states was highlighted. The rest of this paper, however, will consider only the hopping between two states, with arbitrary localization and distance between them.

2. Theory

2.1 Two electronically coupled manifolds of vibronic states

To define more clearly the notation and compare with well-known results from the literature, we start by reconsidering the classical problem of non-adiabatic electron transfer between two manifolds of vibronic states. We will explain in the next section why this framework is *not* appropriate for the problem of charge hopping in polymeric systems but, as we will see, there is a component of this theory that can be transferred to the case of charge hopping in polymeric systems and there are relevant similarities between the results under certain conditions. We indicate with $\{|1,w\rangle\}$ and $\{|2,w'\rangle\}$ two sets of vibronic states localized on two different sites (see Figure 1). The indexes 1 and 2 label the two electronic states and the indexes w and w' are the vibrational quantum numbers (we treat them as scalar but, in the presence of many nuclear modes, they can represent the vectors of the quantum numbers). We assume that the vibrational degrees of freedom are described by quantum harmonic oscillators. The sets of harmonic oscillators in states 1 and 2 have the same frequencies but they can be displaced with respect to each other, i.e. the equilibrium position along certain modes is different in electronic states 1 and 2.

A very general Hamiltonian can be written as:

$$H = \sum_{w} \varepsilon_{1,w} |1,w\rangle\langle 1,w| + \sum_{w'} \varepsilon_{2,w'} |2,w'\rangle\langle 2,w'| + \sum_{w,w'} H_{12,ww'} |1,w\rangle\langle 2,w'| + h.c. \tag{2}$$

$\varepsilon_{1,w}$ (or $\varepsilon_{2,w'}$) is the energy of the unperturbed vibronic state. According to the Condon approximation, one can separate the matrix element $H_{12,ww'}$ into an electronic component V_{12} and the Franck-Condon overlap $S_{ww'}$ between the vibrational states w and w' in electronic states 1 and 2, respectively:

$$H_{12,ww'} = \langle 1,w|H|2,w'\rangle = \langle 1|H^{el}|2\rangle\langle w|w'\rangle = V_{12}S_{ww'} \tag{3}$$

The hopping rate k_{12} from any state in the manifold $\{|1,w\rangle\}$ to any state in the manifold $\{|2,w'\rangle\}$ can be given by the Fermi Golden Rule, if the coupling is sufficiently weak:

$$\begin{aligned} k_{12} &= \frac{2\pi}{\hbar} \sum_{w,w'} P_T(w) \left|H_{12,ww'}\right|^2 \delta(\varepsilon_{2,w'} - \varepsilon_{1,w}) \\ &= \frac{2\pi}{\hbar} \left|V_{12}\right|^2 \sum_{w,w'} P_T(w) \left|S_{ww'}\right|^2 \delta(\varepsilon_{2,w'} - \varepsilon_{1,w}) \\ &= \frac{2\pi}{\hbar} \left|V_{12}\right|^2 \rho_{\mathrm{FCWT}}\left(\Delta E_{12}\right) \end{aligned} \tag{4}$$

where $P_T(w)$ is the probability that vibronic state *w* on electronic state 1 is occupied at temperature T and δ is the Dirac delta function. The summation in the second equality is written more

compactly as $\rho_{\mathrm{FCWT}}\left(\Delta E_{12}\right)$, a density of states weighted by the Franck-Condon factor and temperature, where $\Delta E_{12} = \varepsilon_{2,0} - \varepsilon_{1,0}$ is the energy difference between the lowest vibronic states of each manifold.

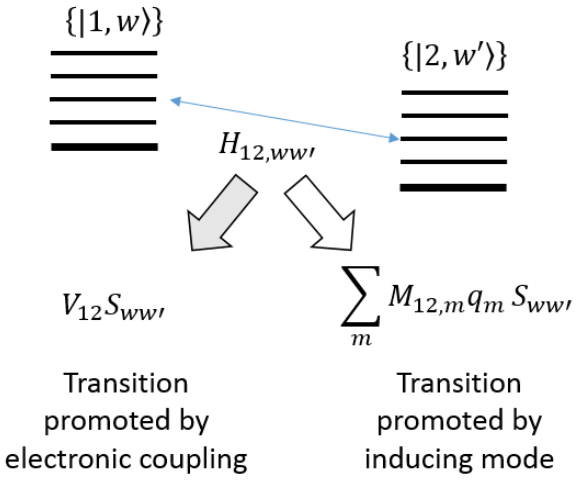

Figure 1. Schematics of the interacting manifold of vibronic states. If the two sets are coupled by a common electronic coupling term V_{12} we obtain the general structure of most non-adiabatic electron transfer theories. This work discusses a general rate in the case where the electronic coupling between the two manifolds is promoted by nuclear modes $\{q_m\}$ and would be otherwise zero in the absence of this mode.

The function $\rho_{\mathrm{FCWT}}\left(\Delta E_{12}\right)$ depends on the Franck-Condon factors, which are in turn determined by the relative displacement from the equilibrium position in going from state 1 to state 2. An analytical expression for $S_{ww'}$ is available if one assumes that the vibrational modes are harmonic. Two limiting cases are particularly useful. If one assumes that the all nuclear modes can be treated classically, the function ρ_{FCWT} can be written as[27]

$$\rho_{FCWT}^{Marcus}\left(\Delta E\right) = \sqrt{\frac{1}{4\pi\lambda_c k_{\mathrm{B}} T}} \exp\left[-\frac{(\Delta E + \lambda_c)^2}{4\lambda_c k_{\mathrm{B}} T}\right] \tag{5}$$

where the effect of the different equilibrium geometry between states 1 and 2 is parameterized by the classical reorganization energy λ_c. The combination of eq. (4) and (5) gives the same charge hopping rate derived by Marcus.[22]

If one assumes that a single vibrational mode should be treated quantum mechanically and all the others classically, the function ρ_{FCWT} can be written as

$$\rho_{FCWT}^{MLJ}\left(\Delta E\right)=\sqrt{\frac{1}{4\pi\lambda_c k_{\mathrm{B}}T}}\sum_{w}P(w)\sum_{w'}\left|S_{ww'}\right|^2\exp\left[-\frac{(\Delta E+\lambda_c+(w'-w)\hbar\omega^A)^2}{4\lambda_c k_{\mathrm{B}}T}\right], \qquad (6)$$

where the Franck-Condon integrals $S_{ww'}$ are calculated as:[28]

$$S_{ww'}=\exp\left(-\frac{G}{2}\right)\sum_{u=0}^{w}\sum_{u'=0}^{w'}\frac{(-1)^{u'}\left(\sqrt{G}\right)^{u+u'}}{u!u'!}\sqrt{\frac{w!w'!}{(w-u)!(w'-u')!}}\delta_{w-u,w'-u'}\ . \qquad (7)$$

G is the Huang-Rhys factor, which describes the relative displacement along the quantum normal mode with energy $\hbar\omega^A$ and is related to the quantum component of the reorganization energy as $\lambda_q=G\hbar\omega^A$. The rate given by the combination of eq. (4) and eq. (6) is very similar to that known as Marcus-Levich-Jortner rate,[29] which is more commonly evaluated with the further simplification $P(w=0)=1$ and $P(w>0)=0$ valid when $\hbar\omega^A\gg k_{\mathrm{B}}T$. We have used above the notation more common in chemical physics. However, expressions equivalent to eq. (5) and eq. (6) respectively have been derived in the context of small polaron hopping in solid state physics by Holstein[30] and Emin.[31]

2.2 Hopping promoted by inducing vibrational modes

The theoretical framework described in the previous section cannot be used to describe hopping between states localized by disorder in polymeric semiconductors. States 1 and 2 are obtained by diagonalizing the electronic Hamiltonian and, by construction, the matrix element V_{12} is null. It is not easy to decompose the states of polymeric semiconductors into weakly interacting pairs (diabatic states) as many of them overlap considerably in space.[11,23] The natural generalization of the theory is to consider that the electronic coupling between states is modulated by vibrational modes that induce the transition. The electronic coupling between state 1 and 2 is therefore zero *on average* but the displacement of certain nuclear modes may induce a coupling proportional to the displacement.[32] This linear non-local coupling is known in other areas of chemical physics as the Herzberg-Teller coupling (responsible for the intensity of optically forbidden electronic transitions),[33] non-adiabatic coupling (responsible for (photo)chemical dynamics involving multiple potential energy surfaces)[34] or non-local electron-phonon coupling (used in the solid state physics of molecular crystals).[35] In the original paper by Miller and Abrahams,[19] it was assumed that acoustic modes were responsible for this coupling, while here we have not made any assumption on their nature. To describe this situation the Hamiltonian in eq. (2) needs to be modified as follows:

$$H=\sum_{w}\varepsilon_{1,w}\left|1,w\right\rangle\left\langle 1,w\right|+\sum_{w'}\varepsilon_{2,w'}\left|2,w'\right\rangle\left\langle 2,w'\right|$$

$$+\sum_m M_{12,m} q_m \sum_{w.w'} S_{ww'} \left|1,w\right\rangle\left\langle 2,w'\right| + \sum_m \hbar\omega_m^I \left(-\frac{1}{2}\frac{\partial^2}{\partial q_m^2} + \frac{1}{2} q_m^2 \right) + h.c \qquad (8)$$

With respect to the Hamiltonian in eq. (2) we have substituted the matrix element V_{12} with the electron-phonon coupling term $M_{12,m} q_m$. q_m is the (adimensional) displacement along mode m that modulates the coupling between states 1 and 2. As these modes induce the transition we denote them as *inducing* modes, each with energy $\hbar\omega_m^I$. An approximation implicit in the Hamiltonian above is that the accepting modes (those associated with the quantum numbers w or w') and the inducing modes are separate. The accepting modes have different equilibrium geometries in states 1 and 2 but do not affect the coupling between 1 and 2, whereas the inducing modes influence the coupling between states 1 and 2 but their equilibrium position is not affected by the electronic states of the system. This separation is rigorous in systems with symmetry elements where the accepting modes are always totally symmetric and the inducing modes are non-totally symmetric.[36] In general, it is a (very reasonable) approximation as only a small fraction of all modes are important accepting or inducing modes and it is unlikely that they coincide. Understanding the different role played by the two classes of nuclear modes is essential to compare and discuss the different rate expressions given in the literature. Many authors discuss the role of the electron-phonon coupling but refer to just one of the classes of electron-phonon couplings, which can be confusing when we wish to compare different results, as in this case. Accepting modes are often discussed in the context of small polaron theories and are determined by local electron-phonon coupling, i.e. stabilization of the on-site energy along a nuclear mode. Inducing modes are those responsible for the breakdown of the Born-Oppenheimer approximation (non-adiabatic effects) and are associated with the non-local electron-phonon coupling.

If we indicate with $\left|v_m\right\rangle$ the eigenstates of $\hbar\omega_m^I \left(-\frac{1}{2}\frac{\partial^2}{\partial q_m^2} + \frac{1}{2} q_m^2 \right)$, where v_m is the quantum number of the oscillator m, we have $\left\langle v_m' \middle| v_m \right\rangle = \delta_{v_m', v_m}$, and we can write the unperturbed wavefunction of the Hamiltonian in eq. (8) as $\left|1,w\right\rangle\left|v_1\right\rangle ... \left|v_m\right\rangle ...$ and $\left|2,w'\right\rangle\left|v_1'\right\rangle ... \left|v_m'\right\rangle ....$

The matrix element $M_{12,m} q_m$ promotes the transition between the manifold $\left|1,w\right\rangle$ and the manifold $\left|2,w'\right\rangle$ where all the vibrational quantum numbers of the inducing modes except v_m remain unchanged. To simplify the notation for a few steps we can evaluate the transition between electronic states 1 and 2 as

$$k_{12} = \sum_m k_{12}^m , \qquad (9)$$

where k_{12}^m is the rate resulting only from the coupling $M_{12,m} q_m \sum_{w.w'} S_{ww'} \left|1,w\right\rangle\left\langle 2,w'\right|$, i.e. considering only one inducing mode m. The rate can be expressed as a sum over all the initial and final vibronic states with thermal averaging of the population of the initial states:

$$k_{12}^{m} = \sum_{v_m, v'_m} P_T(v_m) \sum_{w,w'} P_T(w) k^{m}_{12, w v_m \to w' v'_m} \ , \tag{10}$$

where $P_T(v_m)$ is the probability that the state with quantum number v_m is occupied at a given temperature, and $k^{m}_{12, w v_m \to w' v'_m}$ is the rate for the transition between state $|1, w\rangle |v_m\rangle$ and state $|2, w'\rangle |v'_m\rangle$. The latter can be expressed by a Golden Rule expression (note the energy conservation relation in the delta function):

$$k^{m}_{12, w v_m \to w' v'_m} = \frac{2\pi}{\hbar} \left| \langle v_m | \langle 1, w | H | 2, w' \rangle | v'_m \rangle \right|^2 \delta\left(\varepsilon_{2,w'} - \varepsilon_{1,w} + \hbar \omega_m^I (v'_m - v_m) \right). \tag{11}$$

From our Hamiltonian (eq. (8)), we have $\left| \langle v_m | \langle 1, w | H | 2, w' \rangle | v'_m \rangle \right|^2 = \left| M_{12,m} \right|^2 \left| \langle v_m | q_m | v'_m \rangle \right|^2 \left| S_{ww'} \right|^2$ and we can use the harmonic oscillator relation

$$\left| \langle v_m | q_m | v'_m \rangle \right|^2 = \tfrac{1}{2} \left(v_m \ \delta_{v_m, v'_m - 1} + (v_m + 1) \delta_{v_m, v'_m + 1} \right) \tag{12}$$

to express

$$\begin{aligned} k_{12}^{m} = \frac{\pi}{\hbar} \left| M_{12,m} \right|^2 & \sum_{v_m} P_T(v_m) v_m \sum_{w,w'} P_T(w) \left| S_{ww'} \right|^2 \delta\left(\varepsilon_{2,w'} - \varepsilon_{1,w} - \hbar \omega_m^I \right) \\ & + \sum_{v_m} P_T(v_m)(v_m + 1) \sum_{w,w'} P_T(w) \left| S_{ww'} \right|^2 \delta\left(\varepsilon_{2,w'} - \varepsilon_{1,w} + \hbar \omega_m^I \right). \end{aligned} \tag{13}$$

The terms in the last summation are identical to those defining the function ρ_{FCWT} (eq. (4))

$$k_{12}^{m} = \frac{\pi}{\hbar} \left| M_{12,m} \right|^2 \sum_{v_m} P_T(v_m) v_m \ \rho_{\mathrm{FCWT}}\left(\Delta E_{12} - \hbar \omega_m^I \right) + \sum_{v_m} P_T(v_m)(v_m + 1) \rho_{\mathrm{FCWT}}\left(\Delta E_{12} + \hbar \omega_m^I \right) \tag{14}$$

Moreover, $\sum_{v_m} P_T(v_m) v_m$ is just the phonon occupation number $N(\omega_m) = \left(\exp(\hbar \omega_m^I / k_B T) - 1 \right)^{-1}$. The resulting rate for a single inducing mode *m* is therefore:

$$k_{12}^{m} = \frac{\pi}{\hbar} \left| M_{12,m} \right|^2 \left[N(\omega_m^I) \rho_{\mathrm{FCWT}}\left(\Delta E_{12} - \hbar \omega_m^I \right) + \left(N(\omega_m^I) + 1 \right) \rho_{\mathrm{FCWT}}\left(\Delta E_{12} + \hbar \omega_m^I \right) \right] \tag{15}$$

Our final and main result is obtained by summing over the inducing modes *m* (eq. (9)):

$$k_{12} = \frac{\pi}{\hbar} \sum_m \left| M_{12,m} \right|^2 \left[N(\omega_m^I) \rho_{\mathrm{FCWT}}\left(\Delta E_{12} - \hbar \omega_m^I \right) + \left(N(\omega_m^I) + 1 \right) \rho_{\mathrm{FCWT}}\left(\Delta E_{12} + \hbar \omega_m^I \right) \right] \tag{16}$$

The expression above is essentially a generalization of several existing models and the best way to explore its meaning is to take few limits to show that it can be reduced to any of the expressions that have been proposed so far to discuss charge transport in semiconducting polymers.

2.3 Limiting cases

Absence of active accepting modes. In this limit, there are no vibrations with different equilibrium position in electronic states 1 and 2. Thus, only transitions where $w = w'$ can take place and the function $\rho_{\mathrm{FCWT}}\left(\Delta E_{12}\right)$ simply becomes the Dirac delta function $\delta\left(\Delta E_{12}\right)$. One can obtain the same expression also by taking the limit $\lambda \to 0$ of eq. (5), which highlights the nature of accepting modes as "broadening" of the electron donor and acceptor levels, as noticed for example by Gerisher's formulation of Marcus theory.[37]

The hopping rate in this limit becomes simply

$$k_{12} = \frac{\pi}{\hbar}\sum_{m}\left|M_{12,m}\right|^2\left[N(\omega_m^I)\delta\left(\Delta E_{12}-\hbar\omega_m^I\right)+\left(N(\omega_m^I)+1\right)\delta\left(\Delta E_{12}+\hbar\omega_m^I\right)\right]. \qquad (17)$$

This is the rate that has been extensively used by Vukmirovic et al.[18] in their exploration of the charge transport in polymeric systems from atomistic calculations.[38] This derivation highlights that eq. (17) is valid in the limit of vanishing reorganization energy (or local electron-phonon coupling). Good polymers supporting very delocalized states have indeed very low reorganization energy (the latter is inversely proportional to the delocalization of the orbital)[39] and it is therefore expected that eq. (17) should be a good approximation if the important transitions do not involve very localized trap states. Obviously, in this limit there is a vanishing rate between states whose energy difference is larger than any inducing vibration present in the system. This can be a problem if the transitions to and from deep traps in the polymer are important, a situation possibly encountered at low temperature and charge density.[40]

An alternative way to interpret eq. (17) is to assume that there is a set of electronic states weakly coupled with a thermal bath (the inducing phonons). The eq. (17) can be also derived using the language of quantum dynamics of open systems, where the electronic states of interest are considered the "system" and the inducing phonons represent the "bath". The weak nature of the interaction only allows single phonon transitions to take place. Such derivation is presented *in the supporting information*.

The Miller-Abrahams limit. The Miller-Abrahams limit is obtained in the same limit of eq. (17) with further (and fairly stringent) conditions. In the original Miller-Abrahams paper,[19] the inducing modes were assumed to be acoustic modes (below the Debye cut-off) and no accepting modes were included. To recover the Miller-Abrahams limit we rewrite eq. (17) with an integral instead of a summation as we wish to describe the continuum of acoustic modes:

$$J(\omega) = \sum_{m}\left|M_{ij,m}\right|^2\delta\left(\omega-\omega_m^{\mathrm{I}}\right) \qquad (18)$$

$$k_{12} = \frac{\pi}{\hbar}\int_0^{\infty} J(\omega)\left[N(\omega)\delta\left(\Delta E_{12}-\hbar\omega\right)+\left(N(\omega)+1\right)\delta\left(\Delta E_{12}+\hbar\omega\right)\right]d\omega \qquad (19)$$

$J(\omega)$ is a spectral density, measuring how strongly the inducing modes promote the electronic transition a given frequency. Using the properties of the delta function we have

$$k_{12} = \begin{cases} \dfrac{\pi}{\hbar} J(-\Delta E_{12}/\hbar)\left(N(-\Delta E_{12}/\hbar)+1\right) & \text{for } \Delta E_{12} < 0 \\ \dfrac{\pi}{\hbar} J(\Delta E_{12}/\hbar) N(\Delta E_{12}/\hbar) & \text{for } \Delta E_{12} > 0 \end{cases} \tag{20}$$

or, more explicitly,

$$k_{12} = \begin{cases} \dfrac{\pi}{\hbar} J(-\Delta E_{12}/\hbar) \dfrac{\exp\left(-\Delta E_{12}/k_{\mathrm{B}}T\right)}{\exp\left(-\Delta E_{12}/k_{\mathrm{B}}T\right)-1} & \text{for } \Delta E_{12} < 0 \\ \dfrac{\pi}{\hbar} J(\Delta E_{12}/\hbar) \dfrac{1}{\exp\left(\Delta E_{12}/k_{\mathrm{B}}T\right)-1} & \text{for } \Delta E_{12} > 0 \end{cases} \tag{21}$$

The equations above have the form of the Miller-Abrahams expression (eq. (1)) as a limit for $\Delta E_{12} >> k_{\mathrm{B}}T$ and $J(\omega) \sim$ constant. It was already noted[31] that the Miller-Abrahams rate is a (very) low temperature limit. The fact that J becomes a constant for sufficiently large frequencies is acceptable in the original formulation of the theory, where localized impurities are coupled by acoustic modes. If the wavelength of the acoustic phonon is shorter than the distance between interacting sites (which happens at large ΔE), the relative displacement between the two sites is little dependent on the wavelength. Also, in the opposite limit of $\omega \to 0$ the electron-phonon coupling should vanish for acoustic phonons because the inter-site distance is not changed by the phonon displacements. In summary, for acoustic phonon coupling and localized impurities the rate expression becomes *similar* to the Miller-Abrahams rate. The equation becomes *exactly* the Miller-Abrahams (eq. (1)) if the following spectral density is used

$$J(\omega) = A \frac{\exp\left(\hbar\omega/k_{\mathrm{B}}T\right)-1}{\exp(\hbar\omega/k_{\mathrm{B}}T)} \tag{22}$$

The conditions required for the Miller-Abrahams rate to be valid are very difficult to justify in the context of charge hopping in polymeric materials. Computations have revealed the importance of optical modes and, very often, the hopping takes place between sites that are very close in space, while the original theory is developed for well separated (diluted) impurities.[19] On the other hand, only by comparing the rate computed under more lenient conditions with the Miller-Abrahams rate it is possible to establish whether the differences are important for the description of the material's properties.

Classical inducing modes. We consider now the case were accepting modes play a role and we consider the limit where inducing modes can be assumed to be classical, i.e. $\hbar\omega_m^I \ll k_B T$. In this limit we have $N(\omega_m^I) = k_B T / \hbar\omega_m^I \gg 1$ and eq. (16) becomes

$$k_{12}^{\{\omega_m\}\to 0} = \frac{2\pi}{\hbar} \sum_m \left|M_{12,m}\right|^2 \frac{k_{\mathrm{B}}T}{\hbar\omega_m} \rho_{FCWT}\left(\Delta E_{12}\right) \tag{23}$$

In the classical limit, $\frac{k_B T}{\hbar\omega_m}$ is the average squared displacement $\left\langle q_m^2 \right\rangle$ of an oscillator with potential energy $\frac{1}{2}\hbar\omega_m q_m^2$. The rate can be rewritten as

$$k_{12}^{\{\omega_m\}\to 0} = \frac{2\pi}{\hbar}\rho_{FCWT}\left(\Delta E_{12}\right)\sum_m \left|M_{12,m}\right|^2 \left\langle q_m^2 \right\rangle \ . \tag{24}$$

The quantity in the summation has a very intuitive meaning in the classical limit: this is the thermal fluctuation of the electronic coupling between electronic states 1 and 2 and can be written as $\left\langle |V_{12}|^2 \right\rangle$. The final rate in this limit takes a particularly simple form:

$$k_{12}^{\{\omega_m\}\to 0} = \frac{2\pi}{\hbar}\left\langle |V_{12}|^2 \right\rangle \rho_{FCWT}\left(\Delta E_{12}\right). \tag{25}$$

This is just like the electron-transfer rate where the electronic coupling is replaced by its average value (see eq. (4)). In this way it is particularly easy to "visualize" the role of inducing modes in the hopping process: thermal fluctuations mix initial and final states and the hopping rate is related to the magnitude of this mixing. Eq. (25) was used for the study of charge transport in polymers in refs.[23,41] and different derivations that can be reduced to eq. (25) have been also proposed.[42,43] The same result has often been used in the context of electron transfer in donor-bridge-acceptor systems or in biological systems.[44-46] When comparing eq. (25) with the more general eq. (16) it becomes easier to understand the general process of charge hopping in polymeric systems. The static disorder in the polymer generates localized states with a given ΔE_{12}. The accepting modes generate an effective Gaussian "broadening" of these states, allowing transition also when initial and final energy are far off-resonance. The coupling between states is zero by construction but there are fluctuations around the equilibrium position that promote the transition between the states.

3. Discussion

The main advantage of our formulation of the hopping rate is that it is possible to build a model that continuously interpolates between the various limiting cases. This is useful to appreciate under what conditions a particular limit is invalid or, equivalently, what is the minimal model with the desired qualitative features. The drawback of a general formulation is that the parameter space is extremely large. In fact, it is essentially impossible to start with something as general as eq. (16) to build a phenomenological model because the model would depend on too many choices that one has to make. To use eq. (16) for interpreting realistic data, it is essential to feed the equation with detailed computational results on the electron-phonon coupling terms so that the adjustable parameters are kept to a minimum.

In this work, we wish to study the main qualitative differences of the general rate expression (eq. (16)) with respect to the other expressions used in the literature. A rather surprising property of the Miller-Abrahams rate is that this rate does not decrease as ΔE_{12} becomes more negative. Such behaviour would be expected for non-radiative transitions involving molecular levels and it is well

documented in the photophysics literature.[21] We therefore express the hopping rate as a function of ΔE_{12} for various choices of the system parameters at a constant temperature of 300 K.

We consider a system with four inducing modes and all matrix elements $M_{12,m}$ = 10^{-3} eV set to give plausible rates. We consider a Model 1 where the inducing modes are low energy (i.e. comparable to k_BT) and fixed at 0.01, 0.02, 0.03 and 0.04 eV. Then we consider a Model 2 where two of the modes are at low energies, 0.01 and 0.03 eV, and two at intermediate/high energies (0.10 and 0.18 eV). We further consider a Model 3 where the inducing modes are at high energy (0.16, 0.17, 0.18, 0.19 eV). Model 1 is in line with the assumption of ref.[23] that low frequency modes, mostly hindered torsions, are the main inducing modes. Model 2 samples more uniformly across the vibrational spectrum of a typical material. Model 3 is more unrealistic but useful to see the effect of quantum inducing modes, otherwise hidden in the other models.

For ρ_{FCWT} we consider a case with a single quantum oscillator (eq. (6)), whose energy is set to 0.186 eV, the energy of the C=C bond stretching as a representative quantum mode in conjugated molecules. The function ρ_{FCWT} can be fully determined by the total reorganization energy, $\lambda = \lambda_q + \lambda_c$, and the fraction f determining the partition of the reorganization between the classical and quantum component ($\lambda_q = f\lambda$ and $\lambda_c = (1-f)\lambda$). We consider the cases of $\lambda =$ 0.06, 0.2, 0.6 eV, corresponding to small, intermediate and extremely large reorganization energies using electronic structure calculations as a reference,[47] and f = 0.15 (close to the Marcus limit of fully classical reorganization energy), f = 0.50 (closer to the what emerges from electronic structure calculations[48]) and f = 0.85 (a more extreme case where the quantum mode is dominating).

The results are provided in Figure 2, where each panel reports the rate as a function of ΔE_{12} for three different ratios of classical versus quantum reorganization energies. In the panels, we have added the Miller-Abrahams dependence for comparison purposes. The curves are reported in a broader energy range, to better see the trends, however it is unlikely that hopping between states whose energy difference is larger than 0.3 eV would be relevant in realistic polymers. The results for Model 1 are very simple to interpret, because they are qualitatively similar to the behaviour of standard non-adiabatic rate theory given the relation we have shown in (eq. (23)) for low energy inducing modes. The maximum rate is observed for $\Delta E_{12} = -\lambda$. The rate decreases more steeply than the Miller-Abrahams limit and the difference between the two rates is particularly remarkable for negative ΔE_{12}. It is coincidental that the curve that most resembles the Miller-Abrahams limit is that for high reorganization energy and strong quantum component of the reorganization energy. Large values of reorganization energy are in fact found in the opposite limit with respect to the Miller-Abrahams limit and the weak energy dependence for negative ΔE_{12} is due to multi-phonon transitions involving the quantum mode (also absent in the Miller-Abrahams theory).

When inducing modes at higher frequency are introduced in going from Model 1 to Model 2, the differences are qualitatively modest. For this reason one may argue that, to define an appropriate charge transport model with a limited number of parameters, it may not be necessary to have a very detailed set of electron-phonon couplings $M_{12,m}$. A similar conclusion was achieved with different arguments in ref. [25]. Moreover, if quantum inducing modes are not too important, one can neglect them altogether using the equation valid in the classical limit of inducing modes (eq.

(25)) where there is only one parameter incorporating the effect of all inducing modes, which is the approach adopted in ref. [23]. However it can be instructive to consider also the situation of only high energy inducing modes, i.e. our Model 3. At low reorganization energy, the hopping rate is reduced at $\Delta E_{12} = 0$, because the ρ_{FCWT} functions are very narrowly peaked at the origin and the closest maxima in the rates are found near $\Delta E_{12} \sim \pm\hbar\omega_m^I$. The anomaly of k_{12} increasing as ΔE_{12} increases disappears when the reorganization energy becomes comparable with the inducing mode energy.

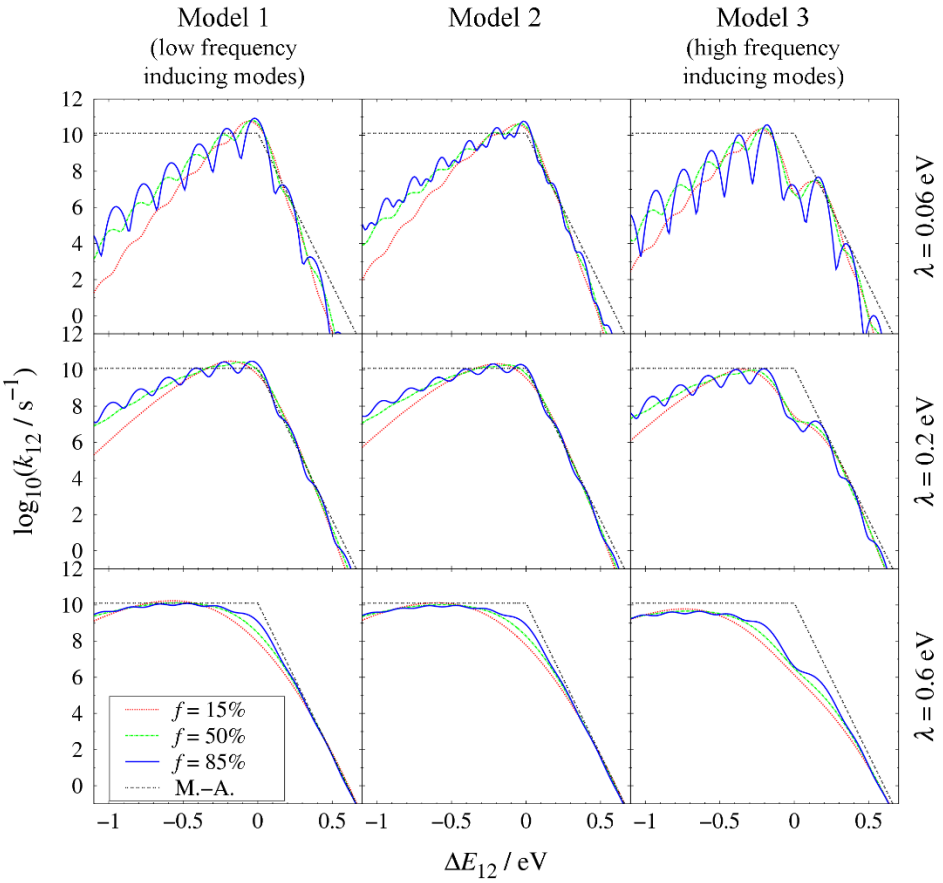

Figure 2. Charge hopping rates as a function of ΔE_{12} for different parameter sets. Moving from top to bottom row the total reorganization energy is increased from 0.06 to 0.6 eV. Moving from left to right column the importance of quantum (high frequency) inducing modes is increased (see text for the definition of Model 1, 2, 3). The curves in each panel correspond to the rate with the same total reorganization energy but a different fraction (15% red, 50% green, 85% blue) of the quantum high frequency mode contributing to the reorganization energy. The grey line (for reference) is the Miller-Abrahams rate.

It seems not possible to approach the Miller-Abrahams limit using a reasonable choice of parameters. Nevertheless, for the development of a phenomenological theory, in the limit of small reorganization energy (the same where the Miller-Abrahams rate was developed), it seems possible to substitute the expression in eq. (1), with the following empirical variant:

$$k_{12} = \begin{cases} k^0 \exp\left((\alpha - 1)\Delta E_{12}/k_B T\right) & for\ \Delta E_{12} < 0 \\ k^0 \exp\left(-\alpha \Delta E_{12}/k_B T\right) & for\ \Delta E_{12} > 0 \end{cases} \quad (26)$$

which would reproduce the behaviour of the realistic rates at the cost of only one additional parameter $\alpha > 1$ that re-establishes the energy gap law.

Finally, and very importantly, this work was concerned with the evaluation of the correct rate expression and did not explore the effect on the coupling matrix elements of the distance between sites. It has been noted that k^0 is not a simple function of the distance between states 1 and 2 and this may have a dramatic effect on the global theory. Thereby, if one is interested in exploring the effect of different rate expressions on the charge carrier mobilities of polymers, it is essential to consider a rate expression that not only includes the correct dependence on the energy difference (energy gap law) but also the correct distance dependence. As the latter depends on a number of further assumptions, it will not be explored here.

Several assumptions implicit in the use of the Fermi Golden rule to obtain rates (coupling should be weak, hopping rate should be slower than thermal relaxation rate, i.e. the process is always incoherent) have not been described in detail as they are common to all other models discussed here. However, it is important to stress that the Hamiltonian we started with is based on the assumption that initial and final states are obtained by diagonalizing the electronic Hamiltonian of the system and they are localized by the disorder in such Hamiltonian. If the polaronic effects are stronger than the disorder effect, i.e. if the charge is localized more by polarization than by disorder, this treatment is invalid. There is some consensus that charge carriers in most polymers are localized by disorder[3,6] but it should be mentioned that some more recent experimental and theoretical works suggested that, in the best available polymers, the disorder is not very effective in localizing the carriers and the polarization effect can effectively compete with the disorder effects.[41,49] This could be the effect in action in the recently reported Hall effects in polymeric semiconductors.[50]

In summary, this paper establishes a relation between various hopping rate expressions proposed in the literature to study charge hopping in semiconducting polymers by building a more general rate expression from a Hamiltonian that should capture the main physics of charge hopping in various situations. We have stressed the different roles played by vibrations associated with polarization effects (accepting modes) and vibrations that promote the electron transfer via non-adiabatic coupling (inducing modes). The final rate expression can incorporate the effect of any number of modes with any frequency and it is therefore suitable to be used in conjunction with atomistic models that provide the appropriate parameters for the simulation of realistic polymers. Like in many physical problems, it is very difficult to establish the best level of simplification for any given model so that only the details that are essential are kept in the description. The formulation of the hopping rate proposed in this work will allow a more systematic study of the level of detail that needs to be included to understand charge transport in semiconducting polymers.

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