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# Simulation of Hopping Transport Based on Charge Carrier Localization Times Derived for a Two-Level System<sup>†</sup>

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Incoherent hopping models are commonly used to describe charge transport in many classes of electrically conducting materials. An important parameter in these models is the charge carrier hopping rate or its inverse, the charge carrier lifetime at a localization site. Among the most common approaches to calculating the charge hopping rate are those based on the hydrogen molecular ion ( $H_2^+$ ) theory and on the Marcus theory of electron transfer reactions. The former is typically used when describing doped inorganic crystalline semiconductors, while the latter is commonly employed for organic systems. In the present paper the limitations of these approaches are examined and a generalized expression for the charge carrier lifetime at a localization site is proposed, which includes the expressions found from  $H_2^+$  theory and Marcus theory as limiting cases. Charge transport simulations based on all three expressions are compared.

## 1. Introduction

Incoherent hopping is a charge transport mechanism that has steadily attracted considerable attention of researchers over the past few decades, as it is encountered in a very wide variety of electrically conducting materials.<sup>1</sup> Among systems to which hopping conductivity models have been applied are doped inorganic crystalline and amorphous semiconductors (dominant charge transfer mechanism at low temperatures),<sup>2–6</sup> disordered liquid crystalline materials,<sup>7–11</sup>  $\pi$ -conjugated molecular wires,<sup>12–14</sup> DNA,<sup>15–18</sup> and even the Earth's mantle.<sup>19,20</sup>

Hopping transport is characterized by the loss of the charge carrier wave function coherence (phase information) after each hopping event, due to interaction with molecular or crystal lattice vibrations. The charge transport process can in this case be described classically as a random walk of a localized charge carrier over a lattice of localization sites.<sup>1,13</sup> If the charge carrier hopping rate  $\Gamma_h$  (or its lifetime  $\tau_h = 1/\Gamma_h$  on a localization site) is known, then its mean squared displacement as a function of time can be expressed as<sup>21</sup>

$$\langle r^2(t) \rangle = l_h^2 \Gamma_h t = l_h^2 t / \tau_h \quad (1)$$

where  $l_h$  is the length of a single hop. If the values of  $l_h$  or  $\Gamma_h$  are different for different pairs of localization sites, as in the case of variable-range hopping,<sup>22,23</sup> the mean squared displacement of the charge carrier can easily be found from numerical simulations.

The mean squared displacement  $\langle r^2(t) \rangle$  can be directly related to the charge carrier mobility in a material using the Kubo formula<sup>24</sup>

$$\mu_{ac}(\omega) = -\frac{e\omega^2}{2\alpha k_B T} \int_0^\infty \langle r^2(t) \rangle \exp(i\omega t) dt \quad (2)$$

where  $e$  is the elementary charge,  $\omega$  is the (angular) frequency of the probing electric field,  $\alpha$  is the sample dimensionality,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. For normal Gaussian diffusion, which occurs if the sample extends infinitely in all dimensions, eq 2 can be reduced to the Nernst–Einstein relation (for DC mobility)<sup>24</sup>

$$\mu_{dc} = \frac{e}{k_B T} D \quad (3)$$

where the diffusion coefficient  $D$  is related to the mean squared displacement of the charge carrier by  $\langle r^2(t) \rangle = 2\alpha D t$ .<sup>25,26</sup>

Determining the charge carrier hopping rate  $\Gamma_h$  for real materials is an important task when studying their conductive properties. The two most common approaches to estimating  $\Gamma_h$  are based on the hydrogen molecular ion ( $H_2^+$ ) theory,<sup>27</sup> typically used for doped inorganic crystalline semiconductors,<sup>6,28</sup> and on the Marcus theory of electron transfer reactions,<sup>29,30</sup> typically used for organic systems.<sup>13,31</sup> Unlike the widely used Miller–Abrahams model,<sup>1,23,32</sup> in which a hopping attempt frequency is usually assumed, these two theories do not employ any fitting parameters. However, they predict a substantially different dependence of the hopping rate  $\Gamma_h$  between two localization sites on the orbital coupling  $J$  between sites (also called charge transfer integral), and on the charge localization energy difference  $\Delta E$  between the initial and the final site.

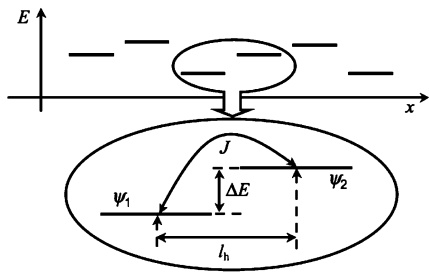
The discrepancy in the hopping rates  $\Gamma_h$  predicted by the Marcus and  $H_2^+$  theories is a consequence of the different applicability ranges of these theories. Fundamentally, they describe different limits of the incoherent hopping regime of charge transport, which itself is the classical limit of fully quantum mechanical band-like transport that arises due to the

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**Figure 1.** One-dimensional chain of charge carrier localization sites.

interaction of the charge carrier with vibrational modes (phonons). The transition from band-like to hopping transport via various hopping regimes has been studied for both exciton and electron transfer in some detail, using the stochastic Liouville equation and similar approaches.<sup>33–36</sup> This provided the general framework for describing charge transport in an arbitrary system. However, such a description is relatively complex and more particular theories for specific charge transport regimes, such as Marcus theory or  $H_2^+$  theory, continue to be widely used.<sup>31</sup>

Parameters of a material that are important for charge transport are often estimated from comparison of calculations based on Marcus theory or  $H_2^+$  theory to experimental data. However, uncertainties in the calculated electronic structures and thermodynamic and kinetic properties of molecules or crystals introduce substantial complications into this analysis. It is known that, due to the differences in approximations made in calculations with various quantum chemical or molecular dynamics methods, variations between the obtained results can be quite significant.<sup>13,37,38</sup> Furthermore, experimental uncertainties of charge carrier mobility measurements with contactless methods, such as pulse radiolysis–time-resolved microwave conductivity (PR–TRMC),<sup>39,40</sup> may exceed several tens of percent. Mobility measurements on single molecules between electrodes, as well as measurements on materials in devices (such as FETs) present the additional problem of accounting for contact effects.

In view of the above, it becomes evident that using an adequate model of charge transport is critical, if the charge transport parameters estimated from comparison of the calculations based on that model with experimental results are to have any predictive value. One must always remember that both Marcus theory and  $H_2^+$  theory are approximate and have a limited applicability range. This is particularly important because many molecular systems of practical interest, for which Marcus theory is commonly used,<sup>13,41–43</sup> may actually be outside of its applicability limits.

In this paper a generalized expression for the charge carrier lifetime,  $\tau_h$ , at a localization site is derived from a simple two-state model. This expression yields lifetimes obtained within the framework of Marcus theory or  $H_2^+$  theory as limiting cases. It is demonstrated how direct numerical simulations of charge transport based on the general expression for the charge carrier lifetime can help circumvent the restrictions placed upon the applicability of Marcus theory and  $H_2^+$  theory by the approximations used in their derivation.

## 2. Derivation of Marcus Rate of Charge Transport

Consider charge transport along a one-dimensional chain of localization sites (Figure 1). If the charge carriers are assumed sufficiently localized, which is the same as saying that the interaction between localization sites is assumed to be weak,

then events of charge transfer (“hops”) between each pair of localization sites can be considered as independent. Each “hop” is an event of fast coherent motion from the initial to the final localization site. On the other hand, between hops the coherence of the charge carrier wave function is lost, as the charge carrier lifetime,  $\tau_h$ , at a localization site is much larger than the charge transfer time. The loss of wave function coherence is due to interaction with some vibrational modes.<sup>36</sup> However, the microscopic details of this process are neglected, and it is simply assumed that the loss of the charge carrier wave function coherence after each hop is complete.

The time scale of a single tunneling event can be found by solving the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (4)$$

for a system of two interacting charge carrier localization sites with energies  $E$  and  $E + \Delta E$ , and a charge transfer integral  $J$  between the two sites (see Figure 1).

Within the tight-binding approximation, the Hamiltonian of a charge in this system can be written in the form<sup>31</sup>

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (5)$$

where  $\hat{H}_0 = E\hat{a}_1^\dagger\hat{a}_1 + (E + \Delta E)\hat{a}_2^\dagger\hat{a}_2$  is the Hamiltonian of two noninteracting localization sites and  $\hat{H}'$  is the interaction Hamiltonian  $\hat{H}' = J(\hat{a}_1^\dagger\hat{a}_2 + \hat{a}_2^\dagger\hat{a}_1)$ , with  $\hat{a}_i^\dagger$  and  $\hat{a}_i$  being the creation and annihilation operators of a charge on the  $i$ th site.

The wave function of the charge can be represented as a linear combination of wave functions localized on each of the two sites with time-dependent coefficients

$$\Psi(t) = C_1(t) \exp\left(-i\frac{E}{\hbar}t\right)\psi_1 + C_2(t) \exp\left(-i\frac{E + \Delta E}{\hbar}t\right)\psi_2 \quad (6)$$

where  $\psi_1$  and  $\psi_2$  are the solutions of the time-independent Schrödinger equations for two noninteracting localization sites

$$\hat{H}_0\psi_1 = E\psi_1, \quad \hat{H}_0\psi_2 = (E + \Delta E)\psi_2 \quad (7)$$

Introducing eqs 5 and 6 into eq 4, and taking into account eqs 7, it can be found that

$$C_1 \exp\left(-i\frac{E}{\hbar}t\right)\hat{H}'\psi_1 + C_2 \exp\left(-i\frac{E + \Delta E}{\hbar}t\right)\hat{H}'\psi_2 = i\hbar \frac{dC_1}{dt} \exp\left(-i\frac{E}{\hbar}t\right)\psi_1 + i\hbar \frac{dC_2}{dt} \exp\left(-i\frac{E + \Delta E}{\hbar}t\right)\psi_2$$

Multiplying the left and right parts of this equation by  $\psi_1^* \exp[i(E/\hbar)t]$  or by  $\psi_2^* \exp[i(E + \Delta E)/\hbar)t]$  and integrating over all space produces a system of two first-order linear differential equations with respect to the coefficients  $C_1$  and  $C_2$

$$\begin{cases} i\hbar \frac{dC_1}{dt} = C_2 \langle \psi_1 | \hat{H}' | \psi_2 \rangle \exp\left(-i\frac{\Delta E}{\hbar}t\right) \\ i\hbar \frac{dC_2}{dt} = C_1 \langle \psi_2 | \hat{H}' | \psi_1 \rangle \exp\left(i\frac{\Delta E}{\hbar}t\right) \end{cases} \quad (8)$$

where, according to eq 5,  $\langle \psi_1 | \hat{H}' | \psi_2 \rangle = \langle \psi_2 | \hat{H}' | \psi_1 \rangle = J$ .

Equations 8 can be solved exactly, however, an approximate solution using perturbation theory will be considered first.

Assume that the charge carrier is initially localized on the site with energy  $E$ , such that  $|C_1|_{t=0}^2 = 1$ ,  $|C_2|_{t=0}^2 = 0$ . If there is no coupling between the orbitals on the two charge carrier localization sites, then charge transfer between these sites will never occur:  $[dC_i^{(0)}/dt] = 0$ . This situation can be taken as the unperturbed state (zeroth approximation of perturbation theory); the interaction part of the Hamiltonian,  $\hat{\mathbf{H}}' = J(\hat{\mathbf{a}}_1^\dagger \hat{\mathbf{a}}_2 + \hat{\mathbf{a}}_2^\dagger \hat{\mathbf{a}}_1)$ , is then a perturbation. The  $(p + 1)$ st approximation of the perturbation expansion for the second of eqs 8 can now be expressed as<sup>44</sup>

$$i\hbar \frac{dC_2^{(p+1)}}{dt} = C_1^{(p)} \langle \psi_2 | \hat{\mathbf{H}}' | \psi_1 \rangle \exp\left(i \frac{\Delta E}{\hbar} t\right)$$

If the charge transfer integral  $J$  is small, the solution may be restricted to first-order perturbation theory

$$C_2(t) \approx C_2^{(1)}(t) = C_1^{(0)} \frac{J}{i\hbar} \int_0^t \exp\left(i \frac{\Delta E}{\hbar} t'\right) dt' = C_1^{(0)} \frac{J}{\Delta E} \left[1 - \exp\left(i \frac{\Delta E}{\hbar} t\right)\right] = -2iC_1^{(0)} \frac{J}{\Delta E} \exp\left(i \frac{\Delta E}{2\hbar} t\right) \sin\left(\frac{\Delta E}{2\hbar} t\right)$$

The probability to find the charge carrier on the site with charge carrier localization energy  $E + \Delta E$  is then

$$|C_2|^2 \approx \frac{4J^2}{\Delta E^2} \sin^2\left(\frac{\Delta E}{2\hbar} t\right) |C_1^{(0)}|^2 = \frac{4J^2}{\Delta E^2} \sin^2\left(\frac{\Delta E}{2\hbar} t\right) \quad (9)$$

since  $|C_1^{(0)}(t)|^2 \equiv 1$ .

The rate of charge transfer from the site with localization energy  $E$  to the site with localization energy  $E + \Delta E$  can be defined as

$$\Gamma_h = \int_{-\infty}^{+\infty} \frac{|C_2(\Delta E, t)|^2}{t} \rho(\Delta E) d(\Delta E) \quad (10)$$

where  $\rho(\Delta E)$  is the density of states for the site to which the charge is transferred, and the integration is over all possible energies of the final state.

Since the expression given by eq 9 shows a sharp peak at  $\Delta E = 0$  and quickly vanishes as  $\Delta E$  increases, it is assumed in the derivation of the Marcus rate that the value of the integral in eq 10 is mostly determined by the energy range close to  $\Delta E = 0$ . It is further assumed that the variations of the density of states and of the charge transfer integral within this energy interval are relatively small, and thus  $\rho = \rho(\Delta E = 0)$  and  $J = J(\Delta E = 0)$  can be taken out of the integration. Using these assumptions and taking into account eq 9, it becomes possible to rewrite eq 10 as

$$\Gamma_h = 4J^2 \rho \int_{-\infty}^{+\infty} \frac{\sin^2\left(\frac{\Delta E}{2\hbar} t\right)}{\Delta E^2 t} d(\Delta E) = \frac{2J^2}{\hbar} \rho \int_{-\infty}^{+\infty} \frac{\sin^2 x}{x^2} dx = \frac{2\pi J^2}{\hbar} \rho \quad (11)$$

which can be recognized as Fermi's golden rule.

It was implicitly assumed in the derivation of eq 11 that the energies of a charge carrier at localization sites,  $E$  and  $E + \Delta E$  are constant. In real systems, variations in these energies due to thermal fluctuations, as well as due to polarization induced by the charge carrier, are always present. However, for materials of practical interest, which have relatively high charge carrier mobility values, the characteristic time scales of fluctuations in  $E$  and  $E + \Delta E$  are much slower than the charge carrier localization time. Thus, eq 11 is still correct to a very good approximation.

Since instantaneous charge carrier localization site energies can deviate from the equilibrium energy values, the probability density of the initial and final site energies coinciding ( $\Delta E = 0$ ) can be written as<sup>30</sup>

$$\rho(E_a) = \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{(\lambda + \Delta G_0)^2}{4\lambda k_B T}\right] \quad (12)$$

with  $E_a = (\lambda + \Delta G_0)^2/(4\lambda k_B T)$  being the activation energy of charge transport calculated in the harmonic approximation,<sup>30</sup>  $\lambda$  being the site reorganization energy, and  $\Delta G_0$  being the difference between the *equilibrium* Gibbs energies of the initial and the final sites. Note that  $\Delta G_0$  is not equivalent to the *instantaneous* difference in the energies of the initial and the final sites,  $\Delta E$ . Introducing eq 12 into eq 11 produces the Marcus rate.

### 3. Derivation of the Charge Transfer Rate from Hydrogen Molecular Ion Theory

When describing small polaron hopping in ionic crystals, Holstein introduced the concept of a "coincidence event" for polaron potential wells.<sup>29</sup> He assumed that charge transfer only occurs when energies of the initial (occupied) and final (unoccupied) states coincide ( $\Delta E = 0$ ). The tunneling time for a charge carrier between two equivalent sites can be found by solving the time-dependent Schrödinger equation (eq 4) with the Hamiltonian given by eq 5 and charge carrier wave function given by eq 6, assuming  $\Delta E = 0$ . In this particular case eqs 8 reduce to

$$\begin{cases} i\hbar \frac{dC_1}{dt} = C_2 J \\ i\hbar \frac{dC_2}{dt} = C_1 J \end{cases} \quad (13)$$

Solving eqs 13 with the same initial conditions as were used in the derivation of the Marcus rate,  $|C_1|_{t=0}^2 = 1$  and  $|C_2|_{t=0}^2 = 0$ , results in following the probabilities of finding the charge carrier on each of the two sites:

$$|C_1(t)|^2 = 1 - |C_2(t)|^2 = \cos^2(Jt/\hbar) \quad (14)$$

It is obvious from eq 14 that at the start of each period of cosine squared,  $Jt_1/\hbar = \pi n$ ,  $n \in \mathbb{Z}$ , the charge carrier is definitely localized on the initial site. Half a period later,  $Jt_2/\hbar = \pi(n + 0.5)$ ,  $n \in \mathbb{Z}$ , the charge carrier is fully localized on the final site. This means that charge transfer occurs within a period of time

$$\tau_h^{H_2^+}(\varepsilon) = t_2 - t_1 = \frac{\pi\hbar}{2J(\varepsilon)} \quad (15)$$

where  $\varepsilon$  is the value of the energy level of both the initial and final localization site. This expression is equivalent to the expression obtained for the charge carrier tunneling time from hydrogen molecular ion theory:<sup>27,45</sup>  $\tau_h^{H_2^+}(\varepsilon) = \pi\hbar/\delta E_\tau(\varepsilon)$ , since the energy level splitting of two interacting sites is  $\delta E_\tau(\varepsilon) = 2J(\varepsilon)$ .<sup>13</sup>

Charge transfer from the initial to the final charge carrier localization site is assumed to occur continuously as long as the energies of the two sites coincide.<sup>6,28</sup> Let  $t_c(\varepsilon)$  be the total time of energy level coincidence at energy  $\varepsilon$  within the time interval  $t$ . The conditional probability of exactly  $j$  transitions of the charge carrier between two localization sites occurring within the time interval  $t$  can then be approximated by the Poisson distribution<sup>6,46,47</sup>

$$P\{j|\varepsilon\} = \frac{[t_c(\varepsilon)/\tau_h^{H_2^+}(\varepsilon)]^j}{j!} \exp\left[-\frac{t_c(\varepsilon)}{\tau_h^{H_2^+}(\varepsilon)}\right]$$

where  $t_c(\varepsilon)/\tau_h^{H_2^+}(\varepsilon) = \sum_{j=0}^{\infty} jP\{j|\varepsilon\}$  is the average number of charge carrier transitions between two localization sites at energy  $\varepsilon$ . The average frequency of hops can then be written as

$$\Gamma_h^{H_2^+}(\varepsilon) = t^{-1} \sum_{j=0}^{\infty} jP\{j|\varepsilon\} = t_c(\varepsilon)t^{-1}[\tau_h^{H_2^+}(\varepsilon)]^{-1} \quad (16)$$

From the theory of Markov chains<sup>46,47</sup> it follows that, if charge carrier transitions between two localization sites are observed over a sufficiently long time interval,  $t \gg \tau_h^{H_2^+}(\varepsilon)$ , then the fraction of time, simultaneously spent by the two localization sites at a given energy  $\varepsilon$ , is approximately equal to the stationary probability  $dW(\varepsilon)$  of finding both sites at that energy<sup>6</sup>

$$t_c(\varepsilon)t^{-1} = dW(\varepsilon) \quad (17)$$

Assuming a continuous energy distribution  $dW(\varepsilon) = w(\varepsilon)d\varepsilon$ , with  $w(\varepsilon)$  being the probability density of finding both sites at energy  $\varepsilon$ , eq 16 can be rewritten as

$$\Gamma_h^{H_2^+}(\varepsilon) = [\tau_h^{H_2^+}(\varepsilon)]^{-1} w(\varepsilon) d\varepsilon \quad (18)$$

The total charge carrier hopping frequency (average number of charge carrier transitions between localization sites per unit time) is obtained by integrating eq 18 over all possible energy values

$$\Gamma_h^{H_2^+} = \int_{-\infty}^{+\infty} [\tau_h^{H_2^+}(\varepsilon)]^{-1} w(\varepsilon) d\varepsilon \quad (19)$$

An analytical expression for the hopping rate  $\Gamma_h^{H_2^+}$  has been obtained from eq 19, assuming a normal distribution for the localization site energies and Fermi–Dirac energy level occupation probabilities. The calculations of charge carrier mobilities for various moderately doped inorganic semiconductors at low temperatures based on this rate are in good agreement with experimental mobility values.<sup>6,48</sup>

#### 4. Charge Carrier Lifetime at a Localization Site for Nonequivalent Sites

The charge transfer rates derived within the framework of Marcus theory or that of hydrogen molecular ion theory can both be calculated analytically, and thus offer an easy way of estimating the charge carrier mobility in a material. Mobility estimates based on Marcus rate are frequently made for organic materials ( $\pi$ -conjugated or  $\pi$ -stacked systems).<sup>31</sup> The rate based on  $H_2^+$  theory is used for moderately doped inorganic semiconductors at low temperature, where hopping is known to be the dominant charge transport mechanism.<sup>6,28</sup> These mobility estimates are in many cases reasonably accurate (within an order of magnitude of the experimental mobility values). However, as it has been shown above, assumptions about the relative magnitudes of the charge transfer integral  $J$  and the energy difference between the initial and final charge carrier localization sites  $\Delta E$  have to be made in the derivation of both rate expressions, limiting their applicability range.

Today, when the computing power available to researches demonstrates a fast and steady increase, it becomes possible to set more ambitious goals than just reproducing the correct order of magnitude of the charge carrier mobility in materials. Particularly, the finer effects of various intra- and intermolecular interactions on charge transport in organic materials can be studied.<sup>13</sup> However, it is still not possible to obtain a more or less accurate numerical solution of the time-dependent Schrödinger equation for larger systems.

In this section, an expression for the charge carrier lifetime at a localization site is derived that can be used directly in charge transport simulations, even though it does not yield an analytical expression for the hopping rate. Such simulations require fewer assumptions than the traditional calculations based on Marcus theory or  $H_2^+$  theory and can be performed for systems that fall outside the applicability range of these theories. The simulations do not require solving the Schrödinger equation for the complete molecular or supramolecular system under consideration. All parameters needed are local parameters that can be computed for relatively small fragments of the system studied. Highly accurate quantum chemical correlated methods (higher-order perturbation theory, coupled-cluster methods) can be used for these calculations.<sup>49</sup>

The fundamental assumption that has to be made in the following derivation is the same as in the previous two sections: a charge carrier should be sufficiently localized to describe hops between localization sites as independent. If this condition is not satisfied, a band-like model of charge transport has to be used.<sup>13,31</sup> If, however, the assumption is valid, one can proceed to derive eqs 8 as described in section 2. An approximate solution of these equations using first-order perturbation theory, as well as an exact solution for the specific case  $\Delta E = 0$  (eqs 13) have been presented in sections 2 and 3, respectively. Solving eqs 8 exactly with the same initial conditions as above,  $|C_1|_{t=0}^2 = 1$  and  $|C_2|_{t=0}^2 = 0$ , yields the following probabilities of finding the charge carrier on the localization sites with energies  $E$  and  $E + \Delta E$ :

$$\begin{cases} |C_1|^2 = \cos^2\left(\frac{\sqrt{\Delta E^2 + 4J^2}}{2\hbar}t\right) + \frac{\Delta E^2}{\Delta E^2 + 4J^2} \sin^2\left(\frac{\sqrt{\Delta E^2 + 4J^2}}{2\hbar}t\right) \\ |C_2|^2 = \frac{4J^2}{\Delta E^2 + 4J^2} \sin^2\left(\frac{\sqrt{\Delta E^2 + 4J^2}}{2\hbar}t\right) \end{cases} \quad (20)$$

respectively; the total probability of finding the charge carrier in the system is  $|C_1(t)|^2 + |C_2(t)|^2 \equiv 1$ . Note that solutions given



by eq 20 do not violate the law of energy conservation, as there is a coupling  $J$  between the orbitals on the initial and final sites, and thus in the steady state there is a finite probability of finding the charge carrier on either site. From comparison of the approximate solution found from first-order perturbation theory, eq 9, with the second part of eq 20, it is obvious that the approximate solution is valid when  $|2J| \ll |\Delta E|$ .

In section 3, it has been shown how the transition rate between two equivalent localization sites can be found from eq 14. Similar reasoning can be used to obtain the rate in the general case of nonequivalent sites,  $\Delta E \neq 0$ , from eqs 20. However, in this case the charge carrier wave function never transfers completely from the initial to the final localization site, as in the second of eqs 20 the prefactor  $4J^2/(\Delta E^2 + 4J^2) < 1$ . Thus, there is a finite probability  $\Delta E^2/(\Delta E^2 + 4J^2)$  of the charge carrier remaining localized on the initial site after a half-period of cosine squared. The total probability of exactly one charge transfer between sites occurring within  $n$  half-periods of cosine squared is thus

$$P = \frac{4J^2}{\Delta E^2 + 4J^2} \left( \frac{\Delta E^2}{\Delta E^2 + 4J^2} \right)^{n-1} \quad (21)$$

Taking into account eq 21, the average lifetime of a charge at the initial localization site can then be written in the form

$$\begin{aligned} \tau_h(\Delta E) &= \sum_{n=1}^{\infty} \frac{n\pi\hbar}{\sqrt{\Delta E^2 + 4J^2}} \frac{4J^2}{\Delta E^2 + 4J^2} \left( \frac{\Delta E^2}{\Delta E^2 + 4J^2} \right)^{n-1} \\ &= \frac{4\pi\hbar J^2}{(\Delta E^2 + 4J^2)^{3/2}} \frac{d}{dn} \sum_{n=1}^{\infty} \left( \frac{\Delta E^2}{\Delta E^2 + 4J^2} \right)^n = \frac{\pi\hbar \sqrt{\Delta E^2 + 4J^2}}{4J^2} \end{aligned} \quad (22)$$

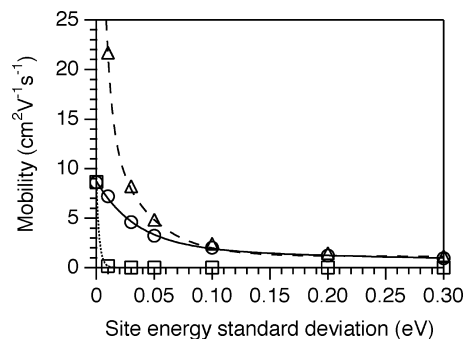
Although very large values of  $n$  are unlikely to contribute to charge transport due to decoherence, the occurrence probability of such values decays quickly with increasing  $n$ , so summation over the full series in eq 22 is a good approximation. Note, that the time  $\tau_h(\Delta E)$  is characteristic of a charge carrier hop between two sites with a localization energy difference  $\Delta E$ . This means that the charge transfer integral  $J$  can be energy dependent. If more than one final state is available to the charge, then the total hopping time can be found as  $\tau_h^{\text{tot}} = [\sum_n \tau_h^{-1}(\Delta E_n) P(\Delta E_n)]^{-1}$ , where  $P(\Delta E_n)$  is the probability of finding an energy difference of  $\Delta E$  between the initial and final sites. This can be rewritten as  $\tau_h^{\text{tot}} = [\int \tau_h^{-1}(\epsilon) \rho(\epsilon) d\epsilon]^{-1}$  in the case of a continuous density of states  $\rho(\epsilon)$ .

If  $\Delta E = 0$ , then eq 22 reduces to eq 15, as expected. If  $|2J| \ll |\Delta E|$ , then eq 22 can be approximated as

$$\tau_h(\Delta E) \approx \frac{\pi\hbar|\Delta E|}{4J^2} \quad (23)$$

The same result can be obtained directly from the intermediate result in the derivation of Marcus rate, eq 9, using the same procedure as for the derivation of eq 22 and the charge carrier wave function normalization condition  $|C_1(t)|^2 + |C_2(t)|^2 \equiv 1$ .

The hopping rate  $\tau_h^{-1}$  given by eq 23 is proportional to  $J^2$ , as is the Marcus hopping rate,<sup>30</sup> but shows a singularity at  $\Delta E = 0$ . However, eq 23 is only valid when  $|2J| \ll |\Delta E|$ , since the derivation of the underlying eq 9 was limited to the first-order of perturbation theory. The applicability range of the Marcus rate is limited from the use of eq 9 as the



**Figure 2.** Charge carrier mobility as a function of site energy standard deviation,  $\tau_E = \tau_I = 1$  ps. Charge carrier lifetime  $\tau$  at localization sites was calculated according to eq 15, squares, dotted line; eq 22, circles, solid line; eq 23, triangles, dashed line.

starting point of the derivation and later the assumption that only states with  $\Delta E$  close to zero contribute to charge transport. Thus, eq 11 is only strictly valid for very small values of the charge transfer integral  $J$ .

## 5. Charge Carrier Hopping Simulations

In this section, simple simulations of charge transport by incoherent hopping based on eq 22 are presented. Charge transport along an infinite one-dimensional chain of localization sites is simulated as a random walk.<sup>21</sup> The results are compared to simulations based on approximate eqs 15 and 23.

Parameter values used in the simulations were not calculated for any specific material, but rather taken to be of the order of magnitude that is typical for conductive organic materials.<sup>7-9,13,14</sup> The distance  $a$  between neighboring localization sites (see Figure 1) was fixed at 1 nm. The site energies  $E_i$  and orbital couplings  $J_{i,i\pm 1}$  between the sites were initially (at time  $t = 0$ ) sampled from normal distributions with zero mean values.<sup>31</sup> The standard deviation  $\sigma_E$  in the site energy was varied between zero (all sites are equivalent) and 0.3 eV. The standard deviation  $\sigma_J$  in the coupling was taken to be 0.1 eV. Site energies and orbital couplings were assumed to vary in time due to random fluctuations with time scales  $\tau_E$  and  $\tau_J$  within the range from 1 to 100 ps, typical for organic molecules. Such fluctuation time scales are much slower than the charge carrier localization time  $\tau_h$ , which is below 100 fs for all mobility values found in these simulations. The temperature was assumed to be 293 K in all simulations.

The charge carrier was taken to be initially localized at the middle of a long 1D chain of localization sites. Hopping was only allowed between adjacent sites (nearest-neighbor hopping regime).<sup>50</sup> The expectation value for the charge carrier hopping time from one localization site to the next was assumed to be given by either eq 22 or one of the approximate eqs 15 and 23. Since eq 15 is only valid when  $\Delta E = 0$ , charge carrier hopping in simulations based on eq 15 was only allowed to states with  $|\Delta E| < k_B T$ .<sup>6,28</sup>

The mean squared displacement  $\langle r^2(t) \rangle$  of the charge carrier from its initial position as a function of time was recorded and averaged over 100 realizations of the simulation, which was found to be sufficient for convergence. The chain of localization sites was sufficiently long to avoid chain end effects;<sup>51</sup> thus, the diffusion coefficient of the charge could be found in the form  $D = (2t)^{-1} \langle r^2(t) \rangle$ . This diffusion coefficient was then introduced into eq 3 to obtain the DC charge carrier mobility.

Results of a typical hopping transport simulation are shown in Figure 2. It can be seen that when the energy disorder  $\sigma_E =$

0, the charge carrier mobility  $\mu_{H_2^+}$ , calculated on the basis of eq 15 stemming from  $H_2^+$  theory, is the same as the mobility  $\mu_{\text{gen}}$ , calculated on the basis of the generalized eq 22. However, as  $\sigma_E$  increases, the value of  $\mu_{H_2^+}$  quickly decays to zero (the probability of two neighboring charge carrier localization sites being close in energy at a given time is small). This decay becomes slower when the characteristic time  $\tau_E$  of energy fluctuations is decreased, meaning that charge transport can be hindered by vibrational kinetics in the system under consideration. This effect is particularly important for one-dimensional systems in the nearest-neighbor hopping regime, where only one pathway for charge transport exists.

It should be noted, that no kinetic effects are present in the traditional hopping rate derived from  $H_2^+$  theory, as it is normally assumed that eq 17 is valid.<sup>6,28</sup> However, the fraction of time  $t_c(\epsilon)t^{-1}$  spent by two charge carrier localization sites at energy  $\epsilon$  is only equal to the stationary probability  $dW(\epsilon)$  of finding both sites at that energy if the observation time  $t$  is infinitely long. On the time scale of charge transport, slow site energy fluctuations can be the limiting factor for resonant charge transfer. In doped inorganic crystalline semiconductors hopping is the dominant charge transport mechanism at low temperatures. Since in this case all site energies are close in energy and vibrations are relatively fast, the calculations based on  $H_2^+$  theory agree well with experimental data.<sup>6,28</sup>

It can also be seen from Figure 2 that at larger energy disorder,  $\sigma_E$ , the mobility  $\mu_M$ , calculated on the basis of eq 23, is almost identical to the mobility  $\mu_{\text{gen}}$ , calculated on the basis of the generalized eq 22. At lower  $\sigma_E$  values calculations on the basis of eq 23 overestimate the mobility.

It is interesting to note that, even though eq 23 is only strictly valid when  $|\Delta E| \gg |2J|$  (see section 4), it produces correct mobility values already when  $\sigma_E \sim |J|$ . This result is significant, as many materials of practical importance (such as discotic liquid crystals and  $\pi$ -conjugated molecular wires) have energy disorder parameters of the order of orbital couplings:  $|\Delta E| \sim |J|$ .<sup>13,52,53</sup> Incoherent hopping is often assumed to be the dominant charge transport mechanism in these materials, and Marcus theory is often used to predict their charge transport properties.<sup>13,31</sup> Just like the hopping time given by eq 23, the Marcus rate can be derived from eq 9, which is only valid when  $|\Delta E| \gg |2J|$ . Thus, its applicability for materials with  $|\Delta E| \sim |J|$  is, strictly speaking, doubtful. The good performance of eq 23 for such materials also indirectly validates the use of Marcus rate, which employs the same approximation in its derivation. However, Marcus rate is not a valid approximation if  $|\Delta E| \ll |2J|$ . When  $\Delta E = 0$ , the  $\Gamma_h \sim J^2$  dependence of the hopping rate on the charge transfer integral, eq 11, should be replaced by a  $\Gamma_h \sim |J|$  dependence, implied by eq 15.

Finally, it has been found that varying the time scales of localization site energy fluctuations  $\tau_E$  and charge transfer integral fluctuations  $\tau_J$  within the reasonable range from 1 to 100 ps has only a minor effect on the calculated charge carrier mobility. This agrees well with previously reported results.<sup>13,54</sup>

## 6. Conclusions

Expressions for the charge hopping rate were derived within the frameworks of Marcus theory and of hydrogen molecular ion theory. A system with two charge carrier localization sites was used for the derivation. The choice of this model system is justified by the fundamental assumption that has to be made whenever a hopping model is employed: the charge carrier should be sufficiently localized to describe hops between localization sites as independent. If this condition is not satisfied, a band-like model should be used instead.<sup>31</sup>

The applicability ranges of the rate expressions that follow from Marcus theory and from  $H_2^+$  theory were examined. The Marcus rate is strictly valid when instantaneous localization site energy disorder  $|\Delta E|$  is relatively small, but much greater than twice the charge transfer integral  $J$  absolute value:  $|\Delta E| \gg |2J|$ . However, even when  $|\Delta E| \sim |J|$  calculations based on the Marcus rate may still produce reasonable charge carrier mobility values. The importance of this finding stems from the fact that the Marcus rate has often been used in the past to describe charge transport in organic materials with  $|\Delta E| \sim |J|$ .

The applicability of hopping rates calculated on the basis of  $H_2^+$  theory, such as those discussed in refs 6 and 28, is determined by two major factors. First, the vibrations, which determine localization energy fluctuations, should be sufficiently fast, so that charge transport is not kinetically limited. Second, localization energy fluctuations have to be sufficiently small. Both of these conditions hold for doped inorganic crystalline semiconductors at low temperatures, which makes the model applicable to these materials.

A generalized expression for the charge carrier hopping time  $\tau_h(\Delta E)$  between two localized states with defined energies  $E$  and  $E + \Delta E$  (see Figure 1) was proposed. When  $\Delta E = 0$ , the generalized expression for the charge carrier hopping time coincides with that found from  $H_2^+$  theory. When  $|\Delta E| \gg |2J|$ , the generalized expression for the charge carrier hopping time is the same as that found on the basis of assumptions used in the derivation of the Marcus rate. Proof-of-principle hopping transport simulations were carried out using the proposed expression for the charge carrier hopping time  $\tau_h(\Delta E)$  and compared to simulations based on the hopping times calculated within the assumptions of Marcus theory and  $H_2^+$  theory.

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## References and Notes

- (1) Bässler, H. *Phys. Stat. Sol. B* **1993**, 175, 15.
- (2) Ambegaokar, V.; Halperin, B. I.; Langer, J. S. *Phys. Rev. B* **1971**, 4, 2612.
- (3) Poklonski, N. A.; Stelmakh, V. F. *Phys. Stat. Sol. B* **1983**, 117, 93.
- (4) Lunkenheimer, P.; Knebel, G.; Viana, R.; Loidl, A. *Solid State Commun.* **1995**, 93, 891.
- (5) Okutan, M.; Bakan, H. I.; Korkmaz, K.; Yakuphanoglu, F. *Physica B* **2005**, 355, 176.
- (6) Poklonski, N. A.; Vyrko, S. A.; Zabrodski, A. G. *Solid State Commun.* **2009**, 149, 1248.
- (7) Kirkpatrick, J.; Marcon, V.; Nelson, J.; Kremer, K.; Andrienko, D. *Phys. Rev. Lett.* **2007**, 98, 227402.
- (8) Kohary, K.; Cordes, H.; Baranovskii, S. D.; Thomas, P.; Wendorff, J.-H. *Phys. Stat. Sol. B* **2004**, 241, 76.
- (9) Lehmann, M.; Kestemont, G.; Gómez Aspe, R.; Buess-Herman, C.; Koch, M. H. J.; Debije, M. G.; Piris, J.; de Haas, M. P.; Warman, J. M.; Watson, M. D.; Lemaure, V.; Cornil, J.; Geerts, Y. H.; Gearba, R.; Ivanov, D. A. *Chem.—Eur. J.* **2005**, 11, 3349.
- (10) van de Craats, A. M.; Siebbeles, L. D. A.; Bleyl, I.; Haarer, D.; Berlin, Y. A.; Zharikov, A. A.; Warman, J. M. *J. Phys. Chem. B* **1998**, 102, 9625.
- (11) Cornil, J.; Lemaure, V.; Calbert, J.-P.; Brédas, J.-L. *Adv. Mater.* **2002**, 14, 726.
- (12) Choi, S. H.; Kim, B.; Frisbie, C. D. *Science* **2008**, 320, 1482.
- (13) Kocherzhenko, A. A.; Patwardhan, S.; Grozema, F. C.; Anderson, H. L.; Siebbeles, L. D. A. *J. Am. Chem. Soc.* **2009**, 131, 5522.
- (14) Wilson, T. M.; Tauber, M. J.; Wasilewski, M. R. *J. Am. Chem. Soc.* **2009**, 131, 8952.
- (15) Grozema, F. C.; Berlin, Y. A.; Siebbeles, L. D. A. *J. Am. Chem. Soc.* **2000**, 122, 10903.

- (16) Senthilkumar, K.; Grozema, F. C.; Fonseca Guerra, C.; Bickelhaupt, F. M.; Lewis, F. D.; Berlin, Y. A.; Ratner, M. A.; Siebbeles, L. D. A. *J. Am. Chem. Soc.* **2005**, *127*, 14894.
- (17) Bixon, M.; Giese, B.; Wessely, S.; Langenbacher, T.; Michel-Beyerle, M. E.; Jortner, J. *Proc. Natl. Acad. Sci.* **1999**, *96*, 11713.
- (18) Giese, B. *Acc. Chem. Res.* **2000**, *33*, 631.
- (19) Peyronneau, J.; Poirier, J. P. *Nature* **1989**, *342*, 537.
- (20) Xu, Y.; McCammon, C.; Poe, B. T. *Science* **1998**, *282*, 922.
- (21) Hughes, B. D. *Random Walks and Random Environments*; Oxford University Press: Oxford, U.K., 1995; Vol. 1.
- (22) Mott, N. F. *Phil. Mag.* **1969**, *19*, 835.
- (23) Marshall, J. M.; Main, C. J. *Phys.: Condens. Matter.* **2008**, *20*, 285210.
- (24) Kubo, R. *J. Phys. Soc. Jpn.* **1957**, *12*, 570.
- (25) Baranovskii, S. D.; Faber, T.; Hensel, F.; Thomas, P. *Phys. Stat. Sol. B* **1998**, *205*, 87.
- (26) According to ref 3, in the three-dimensional case the ratio of the diffusion coefficient for the holes (that move by incoherent hopping) and their mobility  $D/\mu_{dc} = \xi_h k_B T / e$  can somewhat exceed the Nernst–Einstein relation  $k_B T / e$ . Here  $\xi_h \geq 1$  reflects the fact that with the increase of the root mean square fluctuations,  $U$ , of the electrostatic potential in a material, the hopping conductivity of the holes,  $\mu_{dc}$ , decreases faster than their diffusion coefficient  $D$ . In particular, at low temperatures ( $U \gg k_B T$ ) the ratio  $D/\mu_{dc}$  depends on the bandwidth,  $U$ , of the band of quasilocalized states and on the degree to which it is filled with electrons, but only weakly depends on  $T$ . This conclusion correlates with the results of Monte Carlo simulations of the  $D/\mu_{dc}$  dependence on temperature for electrons at the tail of the conduction band density of states in crystals, ref 25. Also, according to ref 13, in the presence of structural disorder eq 3 is not valid, and the charge carrier mobility must be calculated using eq 2 and the mean squared displacement  $\langle r^2(t) \rangle$  obtained from numerical simulations.
- (27) Davydov, A. S. *Quantum Mechanics*; Pergamon Press: Oxford, U.K., 1976.
- (28) Poklonski, N. A.; Vyrko, S. A.; Zabrodski, A. G. *Phys. Solid State* **2005**, *47*, 2005.
- (29) Holstein, T. *Ann. Phys.* **1959**, *8*, 343.
- (30) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.
- (31) Grozema, F. C.; Siebbeles, L. D. A. *Int. Rev. Phys. Chem.* **2008**, *27*, 87.
- (32) Miller, A.; Abrahams, E. *Phys. Rev.* **1960**, *120*, 745.
- (33) Kenkre, V. M.; Knox, R. S. *Phys. Rev. Lett.* **1974**, *33*, 803.
- (34) Kenkre, V. M. *Phys. Rev. B* **1975**, *11*, 1741.
- (35) Kenkre, V. M.; Reineker, P. *Exciton Dynamics in Molecular Crystals and Aggregates*; Springer-Verlag: New York, 1982.
- (36) Silbey, R.; Munn, R. W. *J. Chem. Phys.* **1980**, *72*, 2763.
- (37) Pérez, S.; Imbert, A.; Engelsens, S. B.; Gruz, J.; Mazeau, K.; Jimenez-Barbero, J.; Poveda, A.; Espinosa, J.-P.; van Eyck, B. P.; Johnson, G.; French, A. D.; Kouwijzer, M. L. C. E.; Grootenuis, P. D. J.; Bernardi, A.; Raimondi, L.; Senderowitz, H.; Durier, V.; Vergoten, G.; Rasmussen, K. *Carbohydr. Res.* **1998**, *314*, 141.
- (38) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.
- (39) Hoofman, R. J. O. M.; de Haas, M. P.; Siebbeles, L. D. A.; Warman, J. M. *Nature* **1998**, *392*, 54.
- (40) Grozema, F. C.; Hoofman, R. J. O. M.; Candeias, L. P.; de Haas, M. P.; Warman, J. M.; Siebbeles, L. D. A. *J. Phys. Chem. A* **2003**, *107*, 5976.
- (41) Yang, X.; Li, Q.; Shuai, Z. *Nanotechnology* **2007**, *18*, 424029.
- (42) Deng, W.-Q.; Goddard, W. A. *J. Phys. Chem. B* **2004**, *108*, 8614.
- (43) Andrienko, D.; Kirkpatrick, J.; Marcon, V.; Nelson, J.; Kremer, K. *Phys. Stat. Sol. B* **2008**, *245*, 830.
- (44) Landau, L. D.; Lifshits, E. M. *Quantum Mechanics (Non-Relativistic Theory)*; 3ed.; Butterworth-Heinemann: Oxford, U.K., 1981.
- (45) Blumenfeld, L. A.; Gol'danskii, V. I.; Podgoretskii, M. I.; Chernavskii, D. S. *J. Struct. Chem.* **1967**, *8*, 770.
- (46) Whittle, P. *Probability via Expectation*; Springer: New York, 2000.
- (47) Cox, D. R.; Smith, W. L. *Queues*; Chapman & Hall/CRC: London, 1991.
- (48) Poklonski, N. A.; Lopatin, S. Y. *Phys. Solid State* **2001**, *43*, 2219.
- (49) Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; Wiley: New York, 2002.
- (50) Shklovskii, B. I.; Efros, A. L. *Electronic Properties of Doped Semiconductors*; Springer-Verlag: New York, 1984.
- (51) Prins, P.; Grozema, F. C.; Schins, J. M.; Siebbeles, L. D. A. *Phys. Stat. Sol. B* **2006**, *243*, 382.
- (52) Senthilkumar, K.; Grozema, F. C.; Bickelhaupt, F. M.; Siebbeles, L. D. A. *J. Chem. Phys.* **2003**, *119*, 9809.
- (53) Brédas, J.-L.; Beljonne, D.; Coropceanu, V.; Cornil, J. *Chem. Rev.* **2004**, *104*, 4971.
- (54) Prins, P.; Grozema, F. C.; Siebbeles, L. D. A. *J. Phys. Chem. B* **2006**, *110*, 14659.

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