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Charge dynamics through pi-stacked arrays of conjugated molecules: effect of dynamic disorder in different transport/transfer regimes

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We provide further computational evidence that the electronic coupling between pi-stacked molecules is strongly modulated by the thermal motions at room temperature, not only in supramolecular flexible systems (like DNA) but also in molecular crystals. The effect of this modulation on the charge dynamics is different for different transfer/transport mechanisms and depends on the modulation timescale. In the case of charge transfer (CT) between a donor and an acceptor, the effect of electronic coupling fluctuations introduces a corrective term in the expression of the rate constant (different for adiabatic and non-adiabatic CT). For the transport in molecular crystals, this fluctuation can be the limiting factor for the charge mobility. Although the fluctuation of the electronic coupling is similar in magnitude for all systems containing molecular pi-stacking, its importance for the charge dynamics increases with the decrease of the reorganization energy.

Keywords: Charge transfer; Organic semiconductor; Quantum dynamics; Electron-phonon coupling

1. Introduction

A large number of systems with useful and interesting electronic properties contain pi-stacked organic conjugated molecules. Molecular solids based on conjugated molecules constitute the most technologically relevant example, since they have been proposed as materials for the realization of large scale organic electronics devices [1–3]. Also DNA, regarded as an electronic material, offers the interesting possibility of charge transport along its pi-stacked nucleobases and it received great attention for its potential role in self-assembling circuits [4–6]. Other important classes of pi-stacked materials include discotic liquid crystals like hexabenzocoronene derivatives [7,8], which form columnar stacks, and highly ordered polymers like poly(3-hexylthiophene) that found application in thin film transistors [9]. The electronic structure of pi-stacked systems is largely determined by that of their molecular components since the energy splitting of the molecular levels is larger than the electronic coupling between the levels of close molecules. From a solid-state perspective, one can say that the molecule itself defines the band gap while the

intermolecular coupling defines the (always narrow) bandwidth. The weakness of the intermolecular interactions makes these materials quite different from inorganic semiconductors to which they have been often compared. It was noted many times [10] that, because of the small interaction between molecules, organic materials are very soft and the coupling between the electronic and vibrational degrees of freedoms is expected to be very high. In this paper we investigate the role of nuclear motions in the modulation of the intermolecular electronic coupling (off diagonal electron–phonon coupling) with particular emphasis on the effect that this modulation produces on the charge dynamics. We aim at providing a broad perspective on the effect of these fluctuations in the different cases of interest to physical chemistry (from biophysics to material science) and we will attempt a classification of the possible phenomenologies.

The study of nuclear motions modulating the intermolecular coupling is an important computational problem with dramatic consequences on the theoretical modeling of the charge transport/transfer. In literature, the computational and theoretical studies are usually

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presented in different papers, while, in this contribution, we will stress the strong relation between the two aspects. In the next section, we describe a computational approach used to evaluate the effect of molecular motions on the intermolecular coupling. The similitude between the previously published results on DNA and the new computation on organic semiconductors will be used to attempt a generalization for all materials containing organic pi-stacked molecules. Section 3 will focus instead on the theoretical consequences of these results on the charge dynamics: different transport mechanisms will be assumed and the effect of the electronic coupling modulation will be considered for each of them.

2. Fluctuation of the electronic coupling: computational assessment and some generalizations

The electronic coupling between one-electron states localized on different molecules is not an experimental observable but can be evaluated computationally using a variety of techniques. Many researchers that investigated computationally the dependence of the coupling on various system parameters found it extremely dependent on the system geometry [10,11]. One of the first systematic observations of this type was carried out by Kazmaier and Hoffmann [12] who were able to prove, with simple extended Hückel calculations, that the different electronic spectrum (and color) of a family of perylene derivatives is due to the different electronic coupling between molecules in the crystal. The sensitivity of the electronic coupling to the system geometry can be an essential component of the electron dynamics if the conformational space explored at room temperature causes large fluctuations in the intermolecular electronic coupling.

2.1 DNA

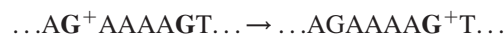
To assess the role of electronic coupling fluctuation in DNA at room temperature a standard classical molecular dynamics (MD) simulation was carried out on several DNA fragments and the electronic coupling between nucleobases was computed for snapshots of the MD simulation separated by 0.01 ps [13]. Assuming that the charge is carried by electron holes, which can be described by a linear combination of the HOMO orbitals of the nucleobases, one can write a Hamiltonian that includes the effect of intermolecular fluctuations as:

$$H = \sum_i \varepsilon_i |i\rangle\langle i| + \sum_{i \neq j} V_{ij}(t) |i\rangle\langle j| \quad (1)$$

Here the states $|i\rangle$ and $|j\rangle$ correspond to the HOMOs on different nucleobases and ε_i is the orbital energy. In equation (1), the effect of classical nuclear dynamics is incorporated into the time dependent couplings $V_{ij}(t)$ that summarize the effect of hundreds of possible nuclear modes, modulating the inter-base coupling.

The results of the MD/QC calculation [13] showed that the couplings $V_{ij}(t)$ between adjacent bases undergoes fluctuations of the same order of magnitude of their average value. For example, the computed average coupling between the central pair of adenines in the double helix sequence 5'-CAGAAAAGTG-3' was 150 cm^{-1} and its standard deviation was 700 cm^{-1} (A, C, G, T denote the four standard DNA bases). The large amplitude of the computed fluctuations in the Hamiltonian makes it difficult to consider the electronic structure of DNA anyhow related to that of an idealized or "averaged" structure. A similar observation was made also in other studies [14–16] and it is consistent with the variability of the intermolecular coupling computed using a set of crystallographic (static) structures [11].

The effect of these fluctuations on the electron dynamics depends on the charge transport mechanism, but there is not a consensus on the actual transport mechanism of positive charge in DNA and several contrasting hypotheses have been formulated [17–20]. The situation is clearer in some well-defined cases extensively investigated by Giese *et al.* [21]. In DNA sequences containing non-adjacent G bases, the charge transport can be seen as a series of charge transfer (CT) reactions (hopping) between a positively charged guanine (G^+) and a neutral close guanine. This is reasonable since the guanine has a lower ionization potential and the aqueous environment is able to localize the charge on the nucleobase where it is more stable [22]. The elementary process for the same sequence mentioned above can be written as



(examples where the above elementary reaction cannot account for the observations include CT through long DNA fragments not containing G or containing only GC pairs, and photo-induced charge separation processes). Assuming that a series of CT reactions actually take place, the appropriate rate constant for the process is the non-adiabatic thermal rate constant often written as: [23,24]

$$k_{CT} = \frac{2\pi}{\hbar} |V_{DA}|^2 \rho_{FCT} \quad (2)$$

where V_{DA} is the effective coupling between donor (D) and acceptor (A)—the two G bases in this case—, and ρ_{FCT} is the density of states weighted by the Franck-Condon factor and thermally averaged.

From the time dependent Hamiltonian of equation (1) one can compute the (time dependent) V_{DA} for the CT reaction considered above using, for example, the matrix partition method [25]. Two aspects of the $V_{DA}(t)$ computed in Ref. [13] are particularly striking: (i) the standard deviation of $V_{DA}(t)$ is much larger than its average value, and (ii) the average and standard deviation of $V_{DA}(t)$ seem to be determined by a minority of time points where the V_{DA} is several order of magnitudes larger than the most probable value (which is very close to zero).

2.2 Superexchange through a series of fluctuating couplings

Here we will put these observations in a more general context, valid for the electron tunneling between D and A through any one-dimensional array of N pi-stacked non-bonded molecules, each interacting only with its nearest neighbors. Assuming that D and A have the same energy, well below the energy of the bridging molecules, the effective tunneling matrix element between D and A is proportional to the product of the coupling between adjacent molecules according to the well known McConnell superexchange expression: [26]

$$V_{DA} \approx \frac{V_{D1} V_{NA}}{\Delta E^N} \prod_{i=1, N-1} V_{i, i+1} \quad (3)$$

ΔE is the energy difference between the bridge sites and the D (or A) energy † . The distribution probability of V_{DA} is therefore related to the distribution probability of its factors V_{D1} , V_{12} , V_{23} , ..., V_{ND} . We have seen how, at room temperature, pi-stacked molecules not connected by a rigid molecular bridge undergo large amplitude motions that introduce a modulation to the average intermolecular coupling. For simplicity one can build a model assuming that the coupling between two adjacent molecules V_{D1} , $\{V_{i, i+1}\}$, V_{ND} is normally distributed with the same distribution valid for any i , $i+1$ pair (see also next section for a justification of taking the normal distribution). It is not possible to express analytically the probability distribution of the product of two or more normally distributed variables (except if their average value is zero) [27]. The numerical evaluation of the probability distribution is done remembering that, if the variables X and Y are distributed according to the functions $P_X(x)$ and $P_Y(y)$, the product $Q = XY$ is distributed according to:

$$P_{XY}(q) = \int_{-\infty}^{+\infty} P_X(x) P_Y\left(\frac{q}{x}\right) \frac{1}{|x|} dx \quad (4)$$

In figure 1 the probability distribution of the superexchange coupling V_{DA} is shown, assuming it is determined by the product of several independent couplings normally distributed with the same average and standard deviation (equation (3)). When the standard deviation of $V_{i, i+1}$ is of the same order of magnitude of its average, the probability distribution of V_{DA} departs from the normal distribution and develops a tail for larger values of V_{DA} . The tail of the V_{DA} distribution is larger when the product of more independent couplings is considered, and the shape of the distribution departs more radically from the normal distribution when the ratio between the standard deviation and the average value is larger than ~ 0.5 . Above this threshold (e.g. in DNA) the most probable V_{DA} value is zero and the tail of the

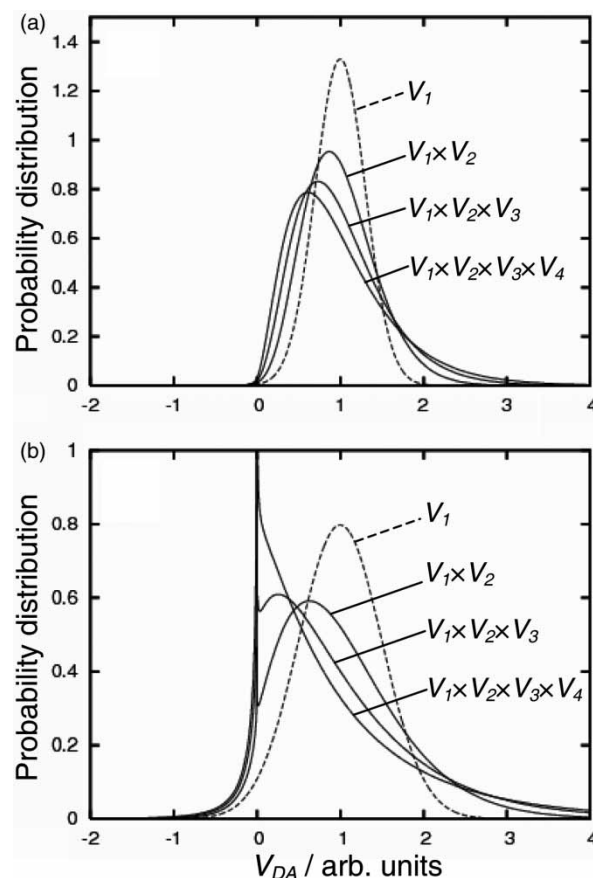


Figure 1. Probability distribution of the superexchange tunneling matrix element V_{DA} assuming it is proportional to the product of 2, 3 or 4 uncorrelated normally distributed individual couplings with average 1 (arbitrary units) and variance 0.3 (a) and 0.5 (b). The dashed line represents the distribution of each individual coupling. The distribution of V_{DA} acquires a tail for high coupling value. If the standard deviation is sufficiently large with respect to the average value, the most probable V_{DA} value becomes zero.

distribution is roughly proportional to $1/|x|^\alpha$ ($\alpha > 1$). This distribution seems to be typical of all tunneling phenomena through strongly fluctuating bridges and it has important consequences for the characterization of the electronic interaction in these systems. The calculation of V_{DA} in the equilibrium geometry or in few “representative” geometries is likely to give a completely misleading picture of the average coupling between donor and acceptor. In fact, the effective average coupling is determined by the tail of the distribution, i.e. by the less likely configurations. For this reason, an accurate sampling of the conformational space is an essential ingredient to characterize the coupling between configurations. This conclusion was reached independently by several groups that attempted the calculation of average couplings using conformational sampling from MD simulations including Balabin and Onuchic [28], Senthilkumar *et al.* [29], and Skourtis *et al.* [30].

† We have seen that, in DNA, the same qualitative behavior for V_{DA} is obtained using the approximate McConnell expression or the more rigorous matrix partition method.

2.3 Organic crystals

Discussing the dynamics of the electronic coupling between non-bonded molecules, it is natural to consider also the very important case of charge transport in molecular organic crystals [31]. These materials represent an ideal ground to study the effect of electronic coupling fluctuations because the other dynamical variables that can influence the charge carrier motions (conformational changes, counterions and solvent) are absent. As in the case of DNA, the nuclear dynamics of the crystal can be explored through classical MD simulations and the intermolecular electronic coupling can be evaluated for snapshots of the MD trajectory separated by fixed time intervals. An analysis of this type on anthracene, pentacene and pentacene derivatives was presented in Refs. [32] and [33]. We extend this study here to the electronic coupling fluctuations of sexithiophene, a molecule that can be considered a prototype for an entire class of organic semiconductors [9,34] and is therefore a reference also for many theoretical studies [35].

A supercell containing 48 molecules of sexithiophene was built replicating the crystal unit cell 2, 3 and 4 times, respectively, along the crystallographic axes a , b and c ($a = 44.70$ Å, $b = 7.81$ Å, $c = 6.03$ Å) [36]. The MD simulation at constant temperature [37] was run using the MM3 force field [38] with frozen C–H bond distances [39] and 2 fs integration step. Snapshots every 30 fs were considered for the quantum chemical study. For each snapshot the HOMO orbital of ten distinct molecules was computed with the INDO/S Hamiltonian and the coupling between 19 pairs of HOMOs was computed according to the method described in Ref. [40]. The quantum chemical evaluation of the intermolecular coupling was the computationally more demanding portion of this study and limited the analyzed trajectory to 30 ps (i.e. 1000 snapshots and 19,000 intermolecular coupling evaluations). The quality of the INDO/S Hamiltonian for this type of calculation was repeatedly checked against more accurate DFT calculations [41].

In figure 2 we showed the relative position of the molecular pairs that have the largest electronic coupling and we indicated them with A, B and C. The average coupling and standard deviation at 100 K resulting from this calculation is -167 ± 96 , 245 ± 104 and 189 ± 114 cm⁻¹ for A, B and C pairs, respectively, while the corresponding values for the simulation at 300 K are -158 ± 149 , 224 ± 161 and 197 ± 168 cm⁻¹. The probability distributions of the coupling A and B, shown in figure 2 for simulations at 300 and 100 K, can be considered a Gaussian to a fairly good approximation (this justifies the assumption of normal distribution made in figure 1). These results, together with previous reports, [32,33] confirm that the coupling fluctuation is an essential feature of organic solids. It is not easy to formulate a rigorous transport mechanism in the presence of such fluctuation in the intermolecular electronic coupling, but it can be safely stated that the band description of the

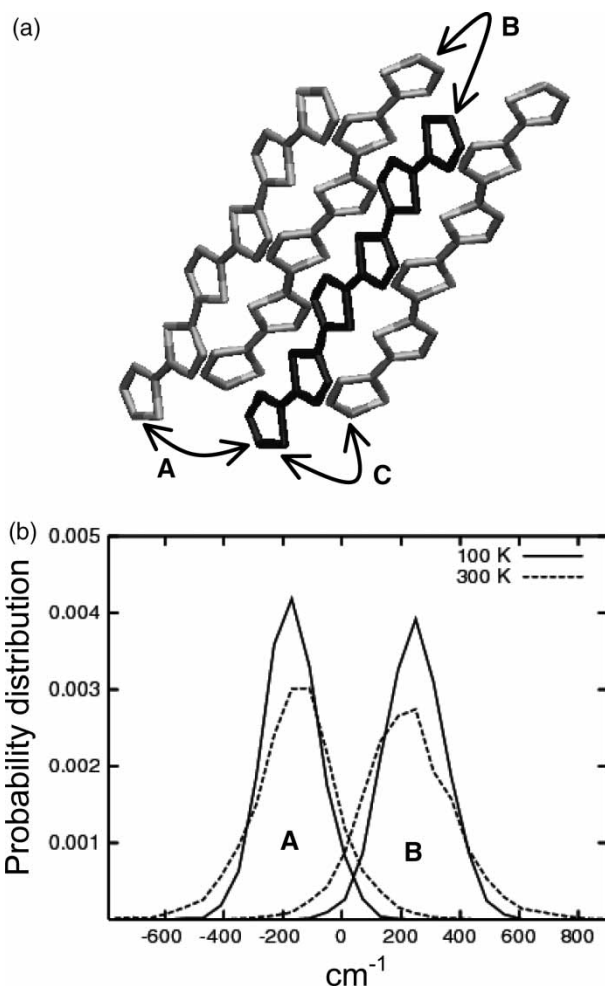


Figure 2. (top) Arrangement of sexithiophene molecules in the crystal and indication of the most strongly interacting pairs A, B, C. (bottom) Probability distribution at 100 and 300 K of the electronic couplings between the HOMO orbitals of the A and B pair (C is omitted for clarity).

electronic structure becomes inappropriate in these cases, because nuclear thermal motions destroy the translational symmetry of the electronic Hamiltonian. In the last section, we propose a numerical approach to describe the mobility in organic semiconductors characterized by thermal electronic disorder. It is important to characterize the typical timescale of the electronic coupling modulation, which ultimately determines its role on the transport mechanism. This timescale can be evaluated by inspecting $V_{ij}(t)$ or, more rigorously, performing a Fourier transform of the autocorrelation function $\langle V_{ij}(t)V_{ij}(0) \rangle$. The greatest contribution to the coupling fluctuation derives from vibrations with energy of ~ 50 cm⁻¹ (corresponding to an oscillation period of 60 fs) [32]. This justifies the approximation of treating the vibrations classically at room temperature ($\hbar\omega = k_bT$) and suggests that the snapshots of the MD simulation should be taken at intervals shorter than 60 fs.

2.4 Generalization

In all considered systems containing non-bonded pi-stacked molecules the computed intermolecular coupling

undergoes very large fluctuations at room temperature and it seems reasonable to ask whether this behavior is general or specific of the considered cases. The electron transport/transfer properties of all organic materials are dominated by the frontier orbital of their molecular constituents. Differently from the case of simple inorganic semiconductors, like silicon or germanium, the molecular frontier orbitals have a very complex shape and contain a large number of nodal planes. The HOMO orbital of a conjugated molecule with N sp^2 carbons will have approximately $N/2$ nodal planes and it is therefore very common that the overlap between two MOs localized on two adjacent molecules results from a complicated interference between positive and negative overlaps between the two orbitals. For this reason it is very difficult to rationalize the coupling between two orbitals only from their shape and relative orientation, and it is very common that the sign of the coupling changes if one molecule is displaced with respect to the other by a fraction of an Angstrom. A couple of conjugated molecules have the maximum intermolecular coupling if they are parallel to one another and the distance between the corresponding atoms in the two molecules is at its minimum (perfect pairing). This situation corresponds to a maximum in the coupling and, therefore, small molecular displacements do not modulate effectively the intermolecular coupling. However, in real crystals molecules do not pack in the maximum coupling geometry and, on the contrary, the relative position of the molecules is such that the intermolecular coupling is small, and very sensitive to the exact molecular position [33]. The subtle nature of the intermolecular interaction also explains why it has not been possible to find a simple relation between geometric and electronic structure of organic solids, notwithstanding more than three decades of systematic investigation.

3. Electron dynamics in pi-stacked systems with fluctuations

The electron dynamics in molecular systems is mainly determined by the relative magnitude of two energy parameters. When an excess charge (hole or electron) moves from one site (state) to another, the nuclei rearrange themselves into a new energy minimum. The energy reduction consequent to this nuclear relaxation is the reorganization energy (λ) and it measures the tendency of the system to localize its excess charge. The electronic coupling between localized electronic states (V) measures instead the tendency of the system to delocalize its electrons. Depending on the relative magnitude of electronic coupling and reorganization energy one can distinguish several limiting cases (we will describe them assuming first that V is constant in time):

- i) If there are two sites for the hole (or electron) and the reorganization energy is considerably larger than the coupling between these two sites, we are in the

non-adiabatic regime, by far the most common case considered in chemical quantum dynamics, and for which the theories of Marcus-Jortner-Hush can be applied [23]. In the discussion of electron dynamics through pi-stacked systems this situation can be found, for example, in the charge hopping between two guanine bases separated by several non-G nucleobases in DNA, or the charge hopping between two electronic traps in an organic crystal. It is common, in these cases, to identify one effective reaction coordinate (associated with the solvent coordinate in liquid phases) and to represent the energy of the two non-interacting states along the reaction coordinate as two intersecting parabolas. The coupling V between the two states causes a splitting (of $2|V|$) between the two potential energy curves.

- ii) Sometimes, the coupling between the two localized states is not very small, or the reorganization energy for the CT-reaction is modest. This is usually the case for molecules in direct contact (coupling of the order of 0.1–0.4 eV) and/or in the absence of polar solvent as in crystals. A prototypical case can be considered the charge hopping between two adjacent nucleobases in DNA or between two adjacent molecules in an organic crystal (assuming that the reorganization energy is strong enough to preserve some degree of localization [42]). This is an adiabatic CT-reaction, i.e. the system stays always in its ground state, in contrast with the non-adiabatic case when it is very probable for the system to cross the intersection between the two parabolas without changing electronic configuration. In solid-state literature the localized states of type (i) or (ii) are often called small polarons.
- iii) If the reorganization energy is very weak, as for large conjugated molecules in molecular crystals (e.g. pentacene and rubrene), the charge should be delocalized [43]. When this happens in solids the charge transport mechanism is usually said to be band-like but, as we will see, this statement is correct only at very low temperatures.

There are no neat boundaries between the three regimes, although there are traditionally different formalisms and languages used to approach each case. In particular, a great amount of work has been devoted to the coexistence of regime (ii) and (iii) in organic semiconductors [44]. It takes in fact a small change in the parameter space to go from the CT-reaction regime (familiar to physical chemists) to the delocalized regime (familiar to semiconductor physicists) and it is now acknowledged that the understanding of the charge dynamics in organic semiconductors will benefit from a synthesis between the two approaches. However, the study of electron transport/transfer in the intermediate regimes is particularly challenging also in the absence of coupling fluctuation and no general model is available. It is

therefore natural to study the two problems separately, i.e. considering intermediate regimes with constant coupling or a well-defined regime in the presence of coupling fluctuations. In the remainder of the section, we assume that one of the three regimes is appropriate and we consider the impact of electronic coupling fluctuation in each one of these regimes, neglecting the phenomenology for intermediate cases. Each case will involve a different set of approximations so that the accuracy of the resulting models cannot be directly compared. For reason of space we will stress the differences between regimes while we will refer the reader to the appropriate literature for other technical issues specific of each regime.

3.1 Charge transfer through fluctuating bridge in the non adiabatic limit

In the non-adiabatic limit and if the coupling between donor and acceptor states can be considered constant (Condon approximation) the appropriate expression of the rate is given by equation (2). Several researchers revisited the derivation of the non-adiabatic CT rate expression allowing for the presence of a time dependent $V_{DA}(t)$ coupling (non-Condon effects) and the readers is referred to these papers for a more complete overview of the current research [45–49]. Following, for example, Ref. [47], the rate constant from a particular vibrational state v of the donor to the vibrational manifold of the acceptor is given by,

$$k_v = \int_{-\infty}^{+\infty} J(E - E_v) \rho_{FCv}(E) dE \quad (5)$$

where the spectral density J contains the information on the fluctuation of the coupling V_{DA} and it is defined as a Fourier transform of the autocorrelation function of $V_{DA}(t)$:

$$J(E) = \frac{1}{\hbar^2} \int_{-\infty}^{+\infty} \langle V_{DA}(t) V_{DA}(0) \rangle e^{(i/\hbar)Et} dt \quad (6)$$

It is easy to verify that, if V_{DA} is constant in time, equation (6) gives $J(E) = 2\pi\delta(E)/\hbar$, which leads to the conventional golden rule in equation (2). An appealing property of this formalism is that it is possible to obtain a series expansion of the rate constant

$$k = k^{(0)} + k^{(1)} + k^{(2)} + \dots, \quad (7)$$

where the leading term coincides with the rate constant in the static limit

$$k^{(0)} = \frac{2\pi}{\hbar} \langle V_{DA}^2 \rangle \rho_{FCT} \quad (8)$$

and the remaining terms $k^{(1)}$, $k^{(2)}$, etc..., are the corrections due to the fluctuations of the coupling. If the nuclear modes are treated classically (numerical simulations show that only low frequency modes modulate the

electronic coupling), the first non zero correction is

$$k^{(2)} = \frac{\pi\hbar}{\tau_C^2} \langle (V_{DA} - \langle V_{DA} \rangle)^2 \rangle \rho_{FCT}'' \quad (9)$$

where τ_C is the characteristic timescale for the fluctuation of the coupling and ρ_{FCT}'' is the second derivative with respect to the energy of ρ_{FCT} . It is therefore possible to assess if it is meaningful to truncate the series expansion to the first term $k^{(0)}$, evaluating the magnitude of the correction in equation (9). Considering explicitly the expression for ρ_{FCT} derived by Marcus one finds:

$$k^{(0)} = \frac{\langle V_{DA}^2 \rangle}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\lambda + \Delta E^0)^2}{4\lambda k_B T}\right) \quad (10)$$

$$k^{(2)} = k^{(0)} 2 \frac{\hbar^2}{\tau_C^2} \left[\frac{(\lambda + \Delta E^0)^2 - 2\lambda k_B T}{(4\lambda k_B T)^2} \right] \times \left(1 - \frac{\langle V_{DA} \rangle^2}{\langle V_{DA}^2 \rangle} \right) \quad (11)$$

Several authors [16,29,30,40] have evaluated $k^{(0)}$ and $k^{(2)}$ from equations (10), (11) and found that the correction is typically very small ($k^{(2)} < 0.1k^{(0)}$). Therefore, the intuitive idea of substituting the coupling in equation (2) with its average value (equation (8)) is acceptable most of the times, and no major macroscopic deviation of the expected temperature dependence of the rate constant is expected for the presence of fluctuations of V_{DA} . However, it is important to point out that, because of the very broad distribution of V_{DA} that is found so frequently (see discussion in the previous section), it is very difficult to compute accurately $\langle V_{DA}^2 \rangle$ since the averaging requires an extensive exploration of the system conformational space.

3.2 Charge transfer in the presence of fluctuating coupling in the adiabatic limit

The adiabatic limit is not very often considered in the literature of CT because it is traditionally associated to the study of ground state reaction dynamics, which make use of a quite different set of methods and approximations. However, the adiabatic limit can be common when discussing the CT-reaction between adjacent pi-stacked molecules, since, in this case, the intermolecular coupling (typically between 80 and 2000 cm⁻¹) can be strong enough to split the potential energy surface of the two electronic states (figure 3(ii)), so that the reaction proceeds in the ground state. In DNA, for example, it is probable that the adiabatic and non-adiabatic CT models are appropriate for the CT-reaction between adjacent and non-adjacent nucleobases, respectively.

The effect of electron coupling fluctuations in adiabatic CT is considerably different. Since the splitting between the two states is twice $V_{DA}(t)^{\ddagger}$, indicating with $\delta V(t)$

[‡]To simplify the notation we have assumed $V_{DA} > 0$, but the same final result is obtained if $V_{DA} < 0$.

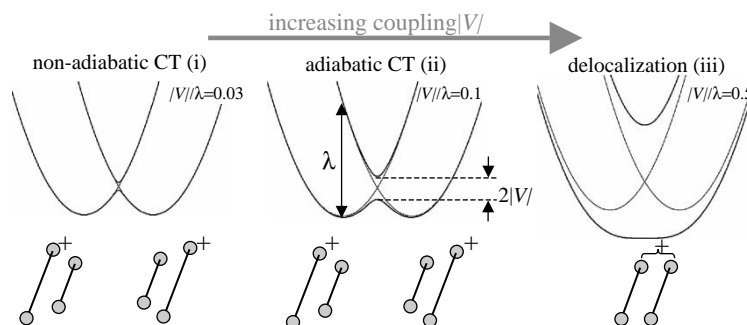


Figure 3. The three idealized CT/transport regimes encountered in systems containing pi-stacking interaction (see text for examples). The two displaced parabolas represent the potential energy surface of the states with the charge localized on two different molecules. From left to right the reorganization energy λ is kept constant while the coupling V increases. With strong coupling (regime iii) the charge is delocalized and a CT rate cannot be defined. Fluctuations of V have different effects in the three cases.

the difference $\delta V(t) = V_{\text{DA}}(t) - \langle V_{\text{DA}}(t) \rangle$, we find that the activation energy is modulated in time by $E_a(t) = \langle E_a \rangle - \delta V(t)$ (it must be $|\delta V(t)| < \langle E_a \rangle$ to be in this regime). One can therefore write an Arrhenius type expression of the rate constant with the activation energy being modulated by the fluctuating intermolecular coupling:

$$k(t) = A \exp\left(\frac{-\langle E_a \rangle - \delta V(t)}{k_B T}\right) \quad (12)$$

The previous equation is valid if the modulation $\delta V(t)$ is slow compared to the frequency modes along the reaction coordinate. This can be the case for reactions involving adjacent conjugated molecules, where the reorganization modes (reaction path) are a combination of fast C–C stretching modes, while the modes inducing the fluctuation in the electronic coupling are low frequency motions of one molecule with respect to the other. Under this condition, it makes sense to define an averaged rate constant as:

$$k^{\text{CT}} \equiv \langle k(t) \rangle = A \left\langle \exp\left(-\frac{E_a(t)}{k_B T}\right) \right\rangle \\ \approx A \exp\left(-\frac{\langle E_a \rangle}{k_B T}\right) \exp\left(\frac{\langle \delta V^2 \rangle}{2(k_B T)^2}\right), \quad (13)$$

where the last term was obtained using the cumulant expansion truncated to the second term:

$$\langle \exp(\alpha x) \rangle = \exp\left[\alpha \langle x \rangle + \frac{1}{2} \alpha^2 (\langle x^2 \rangle - \langle x \rangle^2) + \dots\right]. \quad (14)$$

If we define, as before, the zero order rate constant as the one in the absence of fluctuations $k^{(0)} = A \exp(-\langle E_a \rangle/k_B T)$, the effect of the fluctuation can be seen as a correcting factor to $k^{(0)}$ and equation (13) can be rewritten as

$$k^{\text{CT}} \equiv k^{(0)} \exp\left(\frac{\langle \delta V^2 \rangle}{2(k_B T)^2}\right). \quad (15)$$

This expression, like equations (7)–(9), relates the rate constant in the presence of coupling with the value of the rate constant in the frozen configuration (equation (15) is less general than equations (7)–(9) being valid only for

“slow” fluctuations). It is immediately clear that the effect can be substantial only if the amplitude of the fluctuation is large compared with $k_B T$. In both equations (9) and (15), the correction due to the coupling fluctuation leads to an increase of the effective rate with respect to an “averaged” situation.

We can build a small model system to predict the temperature dependence of the correcting factor, assuming that the coupling fluctuation is only due to a single harmonic nuclear degree of freedom q , which modulates V according to:

$$V(t) = \langle V \rangle + \alpha q(t). \quad (16)$$

Since $\langle \delta V^2 \rangle = \alpha^2 \langle q^2 \rangle$ and, for the equipartition principle, $\langle q^2 \rangle = k_B T / m \omega^2$ (being m and ω the mass and frequency of the oscillator), we get

$$k^{\text{CT}} = A \exp\left[-\frac{1}{k_B T} \left(\langle E_a \rangle - \frac{\alpha^2}{2m\omega^2}\right)\right] \quad (17)$$

Equation (17) implies that the main effect of fluctuations is a reduction of the apparent activation energy. However, it seems difficult to find a fingerprint of the fluctuation in measurements of the rate constant, although for the prediction of rate constants (as in the non-adiabatic case) it is again necessary to perform a good exploration of the conformational space to compute $\langle \delta V^2 \rangle$ accurately.

3.3 Charge transport in the “delocalized” case with fluctuating coupling

The consequence of electronic coupling fluctuation on the electron dynamics is particularly important in organic solids. In the solid-state, the reorganization energy is largely due to intramolecular vibrational modes while, in solution, the effect of the solvent is equivalently or more important. The intramolecular reorganization energy decreases monotonically increasing the size of conjugated molecules [50], while the typical intermolecular coupling (that do not follow a simple pattern) is of similar magnitude for any pairs of molecules in contact. For larger molecules the reorganization energy is so small

(e.g. 0.09 eV for pentacene) that it is not sufficient to localize the charge carriers (holes in the case of pentacene). We are in case (iii) pictured in figure 3: the electron should be delocalized and the charge transport described by a band model. In a band transport model, carriers delocalized over many unit cells are described by wavepackets with a given crystal momentum k and they are scattered to a new state k' by the interaction with phonons or impurities. It is possible to build a band transport model whose parameters are adjusted to reproduce the transport properties in organic materials [51]. However, if the fluctuation of intermolecular coupling is very strong, the electronic band structure (at 0 K) ceases to be a good description of the electronic states at room temperature, where the translational symmetry of the electronic Hamiltonian is completely broken by the dynamic disorder. It is easy to verify that, in the presence of such disorder, the charge carriers become localized over few unit cells. The dynamics of the charge carriers becomes intimately bound to the dynamics of the nuclei, since it is through the nuclear motions that the localized states are mixed one another and the carriers propagate through the lattice. It is essential to differentiate the localization due to the dynamic disorder (which is important when the reorganization energy is low and insufficient to localize the charge) and the localization due to the small polaron formation (which is found when the reorganization energy is sufficiently high).

The charge transport mechanism based on the dynamic localization has not been studied extensively in solid-state physics and no analytical treatment has been attempted so far. The following simplified model can be used to study numerically the basic features of the charge carrier motions in systems with dynamic disorder (figure 4a) [52]:

$$H = \sum_j (-\tau + \alpha(u_{j+1} - u_j))(|j\rangle\langle j+1| + |j+1\rangle\langle j|) + \sum_j \frac{1}{2} m \dot{u}_j^2 + \sum_j \frac{1}{2} K u_j^2. \quad (18)$$

A 1-dimensional array of molecules is considered, with a single nuclear mode u_j (harmonic, with mass m and force constant K) and a single orbital $|j\rangle$ per molecule. The coupling between two consecutive orbitals $|j\rangle$ and $|j+1\rangle$ is modulated by the classical nuclear modes according to the matrix element $-\tau + \alpha(u_{j+1} - u_j)$. The transport regime resulting from equation (18) depends on the set of chosen parameters. A typical set based on our recent calculation on the pentacene solid is given by $K = 14,500 \text{ amu ps}^{-2}$, $\tau = 300 \text{ cm}^{-1}$, $\alpha = 995 \text{ cm}^{-1}/\text{\AA}$, $m = 250 \text{ amu}$. We note that the model in equation (18) implies a Gaussian distribution of the intermolecular coupling at any given temperature deriving from the Gaussian distribution of the displacements u_j .

Details on the numerical integration of equation (18) are given in Ref. [52] and a similar model is discussed in the context of DNA transport by Senthilkumar *et al.* [29].

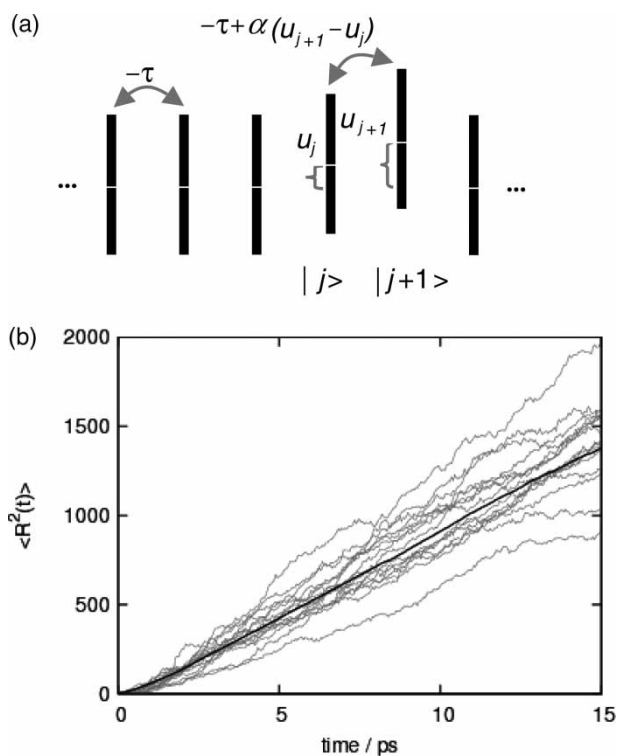


Figure 4. (a) Schematics of the model Hamiltonian of equation (18): molecules in a 1-dimensional stack interact with their nearest neighbors through a coupling $-\tau$ modulated by the displacements u_j of each molecule from its equilibrium position. (b) Time evolution of the spread of the wavefunction (defined in equation (19)). Gray lines refer to 15 independent trajectories, while the black line corresponds to the average over 125 trajectories at 300 K.

The initial wavefunction, taken to be one of the Hamiltonian eigenfunctions at $t = 0$, is localized on few molecular sites (with the considered parameter set at room temperature). Because of the dynamic coupling between adjacent molecules, the initial wavefunction spreads over the lattice and its time dependent diffusion can be monitored evaluating the quantity

$$R_n^2(t) \equiv \langle \psi_n(t) | r^2 | \psi_n(t) \rangle - \langle \psi_n(t) | r | \psi_n(t) \rangle^2. \quad (19)$$

Many trajectories can be computed starting from different initial wavefunctions $\psi_n(t=0)$ (and energy E_n) and the average $\langle R^2(t) \rangle$ can be computed by Boltzman averaging the quantity $R_n^2(t)$ over different trajectories. Figure 4b shows the behavior of $R_n^2(t)$ for selected starting wavefunctions $\psi_n(t=0)$ and the average $\langle R^2(t) \rangle$ computed from 125 trajectories at 300 K. As discussed elsewhere [52], this model describes quite accurately the main features of the charge transport in crystals of large conjugated molecules but it is probably too simple to be considered valid for a generic molecular semiconductor. First, one needs to include the effect of dephasing on the evolution of the wavefunctions that now evolves only coherently in the lattice (the current model is valid if the dephasing time is slower than the intermolecular vibrations). Secondly, it is also important to incorporate the effect of reorganization energy that is neglected

in equation (18) (this is expected to be important for smaller conjugated molecules like naphthalene) [43].

Despite its limitations, the model in equation (18) illustrates quite clearly an important point: the fluctuations of the intermolecular coupling are the factor that determines (and limit) the mobility in organic semiconductors, i.e. they are not a correction on the charge dynamics observed in their absence (as in the case of non-adiabatic and adiabatic CT reactions).

4. Conclusion

We have provided further evidence that the electron coupling between pi-stacked molecules presents typically strong fluctuations due to thermal motions. The effects of these fluctuations are different and depend of the regime of charge transport/transfer that is being considered. Usually, the stronger is the charge localization due to the reorganization energy the weaker is the effect of the coupling fluctuation on the electron dynamics. In the case of non-adiabatic CT reactions (strong reorganization energy and weak coupling), the fluctuations cause a small additive correction to the expression of the rate constant, which can be accurately evaluated using the squared averaged electronic coupling between donor and acceptor. In the case of adiabatic CT reactions (reorganization energy strong enough to localize the charge but comparable with the donor-acceptor coupling) the effect is larger, and the correction due to the fluctuation of the coupling appears as a multiplicative correction to the rate constant. For both cases where the reorganization energy is sufficient to localize the charge, the presence of fluctuations has a greater impact on the computational modeling than on the analysis of the experimental data. In fact, while it is difficult to find evidence of the coupling fluctuations from the experiments, the computation of the electronic coupling needed to interpret the experiments requires an accurate average over the broad region of conformational space explored by the system. A much stronger effect of the fluctuation of the electronic coupling is found when the reorganization energy is small compared to the intermolecular coupling and the conventional models would suggest that the charge carriers are delocalized. In this case, the fluctuation causes dynamic localization of the charge and determines the transport mechanism instead of introducing a small correction.

The present description of the effects of coupling fluctuation has neglected the existence of intermediate regimes and focused mainly on highly idealized systems. Currently, in the absence of simple phenomenological models for intermediate regimes with fluctuating electronic coupling, these complicated cases can be studied only through fully numerical simulations involving a suitable extension of the Hamiltonian in equation (18). Additional theoretical and computational work is necessary to translate these ideas into a practical set of

computational tools for the prediction of the charge dynamics in materials containing non-bonded pi-stacked molecules.

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References

- [1] C.D. Dimitrakopoulos, P.R.L. Malenfant. Organic thin film transistors for large area electronics. *Adv. Mater.*, **14**, 99 (2002).
- [2] O.D. Jurchescu, J. Baas, T.T.M. Palstra. Effect of impurities on the mobility of single crystal pentacene. *Appl. Phys. Lett.*, **84**, 3061 (2004).
- [3] V. Podzorov, E. Menard, J.A. Rogers, M.E. Gershenson. Hall effect in the accumulation layers on the surface of organic semiconductors. *Phys. Rev. Lett.*, **95** (2005).
- [4] D. Porath, G. Cuniberti, R. Di Felice. *Long-range Charge Transfer in DNA II*, vol. 237, pp. 183 (2004).
- [5] R.G. Endres, D.L. Cox, R.R.P. Singh. Colloquium: the quest for high-conductance DNA. *Rev. Mod. Phys.*, **76**, 195 (2004).
- [6] Y.A. Berlin, I.V. Kurnikov, D. Beratan, M.A. Ratner, A.L. Burin. *Long-range Charge Transfer in DNA II*, vol. 237, pp. 1 (2004).
- [7] A. Fechtenkotter, K. Saalwacher, M.A. Harbison, K. Mullen, H.W. Spiess. Highly ordered columnar structures from hexa-peri-hexabenzocoronenes—synthesis, X-ray diffraction, and solid-state heteronuclear multiple-quantum NMR investigations. *Angew. Chem. Int. Edit.*, **38**, 3039 (1999).
- [8] A.M. van de Craats, N. Stutzmann, O. Bunk, M.M. Nielsen, M. Watson, K. Mullen, H.D. Chanzy, H. Sirringhaus, R.H. Friend. Meso-epitaxial solution-growth of self-organizing discotic liquid-crystalline semiconductors. *Adv. Mater.*, **15**, 495 (2003).
- [9] H. Sirringhaus. Device physics of solution-processed organic field-effect transistors. *Adv. Mater.*, **17**, 2411 (2005).
- [10] J.L. Bredas, J.P. Calbert, D.A. Da Silva Filho, J. Cornil. Organic semiconductors: a theoretical characterization of the basic parameters governing charge transport. *Proc. Natl. Acad. Sci. USA*, **99**, 5804 (2002).
- [11] A. Troisi, G. Orlandi. The hole transfer in DNA: calculation of electron coupling between close bases. *Chem. Phys. Lett.*, **344**, 509 (2001).
- [12] P.M. Kazmaier, R. Hoffmann. A theoretical-study of crystallochromy—quantum interference effects in the spectra of perylene pigments. *J. Am. Chem. Soc.*, **116**, 9684 (1994).
- [13] A. Troisi, G. Orlandi. Hole migration in DNA: a theoretical analysis of the role of structural fluctuations. *J. Phys. Chem. B*, **106**, 2093 (2002).
- [14] A.A. Voityuk, K. Siriwong, N. Rosch. Charge transfer in DNA. Sensitivity of electronic couplings to conformational changes. *Phys. Chem. Chem. Phys.*, **3**, 5421 (2001).
- [15] A.A. Voityuk, K. Siriwong, N. Rosch. Environmental fluctuations facilitate electron-hole transfer from guanine to adenine in DNA pi stacks. *Angew. Chem. Int. Edit.*, **43**, 624 (2004).
- [16] T. Cramer, T. Steinbrecher, A. Labahn. Static and dynamic aspects of DNA charge transfer: a theoretical perspective. *Phys. Chem. Chem. Phys.*, **7**, 4039 (2005).
- [17] E.M. Conwell. Charge transport in DNA in solution: the role of polarons. *Proc. Natl. Acad. Sci. USA*, **102**, 8795 (2005).
- [18] M.A. O'Neill, J.K. Barton. DNA charge transport: conformationally gated hopping through stacked domains. *J. Am. Chem. Soc.*, **126**, 11471 (2004).
- [19] Y.A. Berlin, A.L. Burin, M.A. Ratner. Elementary steps for charge transport in DNA: thermal activation vs. tunneling. *Chem. Phys.*, **275**, 61 (2002).
- [20] A. Joy, G.B. Schuster. Long-range radical cation migration in DNA: investigation of the mechanism. *Chem. Commun.*, 2778 (2005).

- [21] B. Giese, S. Wessely, M. Spormann, U. Lindemann, E. Meggers, M.E. Michel-Beyerle. On the mechanism of long-range electron transfer through DNA. *Angew. Chem. Int. Edit.*, **38**, 996 (1999).
- [22] I.V. Kurnikov, G.S.M. Tong, M. Madrid, D.N. Beratan. Hole size and energetics in double helical DNA: competition between quantum delocalization and solvation localization. *J. Phys. Chem. B*, **106**, 7 (2002).
- [23] M.A. Ratner. Bridge-assisted electron-transfer—effective electronic coupling. *J. Phys. Chem.*, **94**, 4877 (1990).
- [24] M.D. Newton. *Electron Transfer-from Isolated Molecules to Biomolecules, Pt 1*, vol. 106, pp. 303 (1999).
- [25] S.S. Skourtis, D.N. Beratan. *Electron Transfer-from Isolated Molecules to Biomolecules, Pt 1*, vol. 106, pp. 377 (1999).
- [26] A. Nitzan. Electron transmission through molecules and molecular interfaces. *Annu. Rev. Phys. Chem.*, **52**, 681 (2001).
- [27] J.K. Patel, C.B. Read. *Handbook of the Normal Distribution*, Dekker, New York (1982).
- [28] I.A. Balabin, J.N. Onuchic. Dynamically controlled protein tunneling paths in photosynthetic reaction centers. *Science*, **290**, 114 (2000).
- [29] K. Senthikumar, F.C. Grozema, C.F. Guerra, F.M. Bickelhaupt, F.D. Lewis, Y.A. Berlin, M.A. Ratner, L.D.A. Siebbeles. Absolute rates of hole transfer in DNA. *J. Am. Chem. Soc.*, **127**, 14894 (2005).
- [30] S.S. Skourtis, I.A. Balabin, T. Kawatsu, D.N. Beratan. Protein dynamics and electron transfer: electronic decoherence and non-condon effects. *Proc. Natl. Acad. Sci. USA*, **102**, 3552 (2005).
- [31] M. Pope, C.E. Swenberg. *Electronic Processes in Organic Crystals and Polymers*, 2n ed., Oxford University Press, New York (1999).
- [32] A. Troisi, G. Orlandi. Dynamics of the intermolecular transfer integral in crystalline organic semiconductors. *J. Phys. Chem. A*, **110**, 4065 (2006).
- [33] A. Troisi, G. Orlandi, J.E. Anthony. Electronic interactions and thermal disorder in molecular crystals containing cofacial pentacene units. *Chem. Mat.*, **17**, 5024 (2005).
- [34] A. Facchetti, M. Mushrush, M.H. Yoon, G.R. Hutchison, M.A. Ratner, T.J. Marks. Building blocks for n-type molecular and polymeric electronics. Perfluoroalkyl-versus alkyl-functionalized oligothiophenes (nT; $n = 2-6$). Systematics of thin film microstructure, semiconductor performance, and modeling of majority charge injection in field-effect transistors. *J. Am. Chem. Soc.*, **126**, 13859 (2004).
- [35] J. Cornil, J.P. Calbert, D. Beljonne, R. Silbey, J.L. Bredas. Charge transport versus optical properties in semiconducting crystalline organic thin films. *Adv. Mater.*, **12**, 978 (2000).
- [36] G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J.L. Fave, F. Garnier. Growth and characterization of sexithiophene single-crystals. *Chem. Mat.*, **7**, 1337 (1995).
- [37] H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. Di Nola, J.R. Haak. *J. Chem. Phys.*, **81**, 3684 (1984).
- [38] N.L. Allinger, F. Li, L. Yan, J.C. Tai. Molecular mechanics (MM3) calculations on conjugated hydrocarbons. *J. Comput. Chem.*, **11**, 868 (1990).
- [39] H.C. Andersen. RATTLE—A velocity version of the chake algorithm for molecular-dynamics calculations. *J. Comput. Phys.*, **52**, 24 (1983).
- [40] A. Troisi, M.A. Ratner, M.B. Zimmt. Dynamic nature of the intramolecular electronic coupling mediated by a solvent molecule: a computational study. *J. Am. Chem. Soc.*, **126**, 2215 (2004).
- [41] J.L. Bredas, D. Beljonne, V. Coropceanu, J. Cornil. Charge-transfer and energy-transfer processes in pi-conjugated oligomers and polymers: a molecular picture. *Chem. Rev.*, **104**, 4971 (2004).
- [42] A.A. Voityuk. Charge transfer in DNA: hole charge is confined to a single base pair due to solvation effects. *J. Chem. Phys.*, **122** (2005).
- [43] K. Hannewald, P.A. Bobbert. *Ab initio* theory of charge-carrier conduction in ultrapure organic crystals. *Appl. Phys. Lett.*, **85**, 1535 (2004).
- [44] S. Fratini, S. Ciuchi. Dynamical mean-field theory of transport of small polarons. *Phys. Rev. Lett.*, **91**, 256403 (2003).
- [45] J. Tang. Effects of a fluctuating electronic coupling matrix element on electron-transfer rate. *J. Chem. Phys.*, **98**, 6263 (1993).
- [46] E.S. Medvedev, A.A. Stuchebrukhov. Breakdown of the Born-Oppenheimer-Condon-Marcus approximation in long distance electron transfer. *Chem. Phys.*, **296**, 181 (2004).
- [47] A. Troisi, A. Nitzan, M.A. Ratner. A rate constant expression for charge transfer through fluctuating bridges. *J. Chem. Phys.*, **119**, 5782 (2003).
- [48] S.J. Jang, M.D. Newton. Theory of torsional non-Condon electron transfer: a generalized spin-boson Hamiltonian and its nonadiabatic limit solution. *J. Chem. Phys.*, **122** (2005).
- [49] A. Teklos, S.S. Skourtis. Electron transfer through time dependent bridges: differences between Franck-Condon and Born-Oppenheimer breakdown. *Chem. Phys.*, **319**, 52 (2005).
- [50] V. Coropceanu, M. Malagoli, D.A. Da Silva Filho, N.E. Gruhn, T.G. Bill, J.L. Bredas. Hole- and electron-vibrational couplings in oligoacene crystals: intramolecular contributions. *Phys. Rev. Lett.*, **89**, 275503 (2002).
- [51] V.M. Kenkre, J.D. Andersen, D.H. Dunlap, C.B. Duke. Unified theory of the mobilities of photoinjected electrons in naphthalene. *Phys. Rev. Lett.*, **62**, 1165 (1989).
- [52] A. Troisi, G. Orlandi. Charge-transport regime of crystalline organic semiconductors: diffusion limited by thermal off-diagonal electronic disorder. *Phys. Rev. Lett.*, **96** (2006).