Coherent electron tunnelling dynamics in polyacetylene

D. Psiachos

Abstract

We examine, theoretically, using a mixed classical-quantum electron-lattice dynamics model, electron transfer in a molecular junction system with a polyacetylene wire at its centre. We identify two qualitatively-different transfer regimes: hopping and tunnelling. We discuss the criteria for achieving each one and for minimizing inelastic scattering and decoherence arising from the coupling to the lattice, and we connect our main results to quantities derived from electron dynamics in simpler, three-state model systems. We identify the requirements to have near-ballistic transfer.

PACS numbers: 73.22.-f,73.63.NM,63.20.kd
I. INTRODUCTION

Electron transport through organic molecules or chains of molecules has been an active area of fundamental research because of its potential applications to molecular electronics. Recently, measurements of the conductance of single molecules or atomic wires attached to leads have become very refined\(^1\). A simple expression for the electronic conductance through a molecule is provided by the Landauer formula, which states that the conductance between two leads is proportional to the transmission, which is assumed to be constant for the narrow energy range covered by the leads. The actual behaviour of the transmission depends on the scattering processes involved. Some of the methods used to describe the scattering include Green’s function methods, transfer matrix approaches such as the electron scattering quantum chemistry (ESQC) method\(^2\), or the use of Lippmann-Schwinger scattering operators for mapping the non-equilibrium system onto an equilibrium one\(^3\). All of these methods are time-independent, thus enabling the use of the Landauer or, in the case of several leads, the Landauer-Büttiker formula, to evaluate the current. Time-dependent methods include non-equilibrium Green’s function-based approaches or approaches based on the time-dependent Schrödinger equation applied to the key parts of the system, \textit{i.e.} the tunnelling electron, \textit{etc}. and enable a direct evaluation of the transmission and the current.

The treatment of the electron-lattice interaction within semi-empirical formalism assumes the validity of one of two regimes: strongly or weakly-localised electron-lattice interaction. The Marcus theory\(^6\) treats electron transfer non-adiabatically with a rate expression involving the initial, donor, and final, acceptor, states and geometries expressed in terms of two key quantities, presumed to be separable owing to the slow intermolecular vibrations compared to the fast electron transfer rate: the difference in energy of the ground-state configurations before and after electron transfer, and the non-adiabatic contribution, called the reorganization energy, which is defined as the electronic excitation energy of the initial state in its ground-state configuration. As in the Marcus assumption of distinct donors/acceptors, the Holstein model\(^7\) also treats the electron as being highly localised in space. These techniques are most appropriate for non-homogeneous systems or systems containing defects or other strong scattering centres where there is a clear distinction between donor and acceptor and the transfer is accomplished by hopping between these two species. In more homogeneous systems, there tends to be a more delocalised electron-lattice interaction, leading to
relatively adiabatic electron transfer.

The different models for electron transfer have been developed with the goal of describing polaron motion in oligomers. The Holstein model describes “small-polaron” formation, or localised interaction with a particular molecule (site) and the electron conduction is accomplished by distinct hopping, a non-adiabatic process. The structural perturbation is similarly highly localised. Another regime, the “large-polaron” model, which leads to a longer-ranged structural distortion and at the same time, a long-ranged electronic effect, is suitable for periodic systems. The best-known description for large-polaron formation is the SSH model. Polaron transport in oligomer chains using the SSH model driven by an electric field has been studied extensively. The main result of these studies is that at high field strengths polaron dissociation occurs because of a complete decoupling of electron and lattice motion time scales for highly-energetic electrons, which leads to increased charge mobility as the carrier becomes a free electron.

Recently, the Holstein and SSH models have been combined, in order to describe both the inter- and intra-molecular interactions respectively of a crystal formed of pentacene chains. While the inter-molecular interactions, originating from Van der Waals forces, are weak, they are not neglected because in realistic molecular crystals there is a high degree of disorder in the molecules’ arrangements, and this was found to play a significant role in determining the type of charge transport at nonzero temperatures - going from bandlike to diffusive hopping transport as the disorder increases.

In our work, we work with a single chain of atoms only, and as such within the “large-polaron” regime. Specifically, we study the influence of electron-lattice coupling on electron transfer in a polyacetylene (PA) chain. Rather than using an electric field, we consider electrons coming from a reservoir of varying chemical potential, and study the influence of this as well as the coupling to the PA chain on the electron-lattice dynamics timescales and the charge propagation through the chain.
II. METHODOLOGY

A. The SSH Hamiltonian

We use the SSH Hamiltonian\textsuperscript{10} to describe the electronic and structural properties of the PA chain. This model uses a basis of site-centred π orbitals in the tight-binding approximation to describe the electronic properties, while the lattice is treated classically. Regardless of the number of electrons, the basis size is fixed to the number of atomic sites, as per the LCAO approximation. Explicitly, the Hamiltonian is split into electronic and ionic parts:

\[ \hat{H} = \hat{H}_{el} + \hat{H}_{ion} \]  

where

\[ \hat{H}_{el} = -\sum_{n,\sigma} t_{n+1,n} \left( c_{n+1,\sigma}^\dagger c_{n,\sigma} + c_{n,\sigma}^\dagger c_{n+1,\sigma} \right) + \sum_{n,\sigma} \epsilon_n c_{n,\sigma}^\dagger c_{n,\sigma} \]  

is the electronic part where, the operator \( c_{n,\sigma}^\dagger \) adds an electron of spin \( \sigma \) to site \( n \) and where in the SSH model, the site energies \( \epsilon_n \) are set to zero and \( t_{n+1,n} = t_0 - \alpha (u_{n+1} - u_n) \) describes the hopping of the electron. The hopping is modified by the electron-phonon coupling parameter \( \alpha \) according to the displacements \( u_n \) of the ions, from their positions in a perfect, undimerised chain and its range is confined to nearest neighbours.

The lattice part,

\[ \hat{H}_{ion} = \hat{V}_{ion} + \hat{T}_{ion} = \frac{1}{2} \sum_n K (\hat{u}_{n+1} - \hat{u}_n)^2 + \sum_n \frac{\hat{p}_n^2}{2M} \]  

consists of a harmonic potential energy operator with spring constant \( K \) and a kinetic energy operator. The set of parameters used is standard in the SSH model literature as applied to PA chains\textsuperscript{10}. \( t_0=2.5 \text{ eV}, \alpha=4.1 \text{ eV/Å}, K=21 \text{ eV/Å}^2, \text{ and } M=1349.14 \text{ eV fs}^2/\text{Å}^2. \) The electronic and ionic Hamiltonians are thus linked by the ionic displacements \( u_n \).

We include the site-energy term in Eq. 2 because we will consider a chain where each end is coupled to a molecular level with energy \( \epsilon_{end} \). All other \( \epsilon_n \) are set to zero. In addition, we will modify the coupling between the molecular level and the chain to a value \( t_{end} \). We will take the molecular levels and couplings at both ends to be the same. A schematic of a chain with its end sites coupled to molecular levels is shown in Fig. 1. The coupling to the electrode \( t_{end} \) is fixed and does not depend on the distortion of the chain’s end sites.
FIG. 1: Chain with nearest-neighbour hoppings based on the site distortions $u$ (see Eq. 3), coupled to molecular levels. The total number of sites including the molecules at the ends is $N$.

B. Solving the coupled ion-electron system

We use the Ehrenfest approximation\textsuperscript{13,15–18}, a non-adiabatic semi-classical scheme in which the ions undergo classical motion while the electrons are treated quantum-mechanically, evolving in time. The adiabatic approximation, also known as Born-Oppenheimer (BO) dynamics, a simpler scheme in which the electron orbitals are treated time-independently, affected only by changes in the ionic potential, and thus not deviating from their initial superpositions of Hamiltonian eigenstates, would not lead to electron transfer which is what we want to study here. To that end, the equation of motion of the electrons $|\psi_k(t)\rangle$ of state $k$ is given by

$$i\hbar \frac{d|\psi_k(t)\rangle}{dt} = \hat{H}_{el} |\psi_k(t)\rangle$$

while that for the $n$th ion is

$$M \frac{d^2 u_n}{dt^2} \equiv F_n = -\left\langle \frac{d}{du_n} \hat{H} \right\rangle = -\sum_{k,occ} \left\langle \psi_k(t) \left| \frac{d}{du_n} \hat{H}_{el} \right| \psi_k(t) \right\rangle - \frac{d}{du_n} V_{ion},$$

which we integrate using the velocity-Verlet algorithm

$$u_n(t + \tau) = \frac{\tau^2}{M} F_n + 2u_n(t) - u_n(t - \tau)$$

for a sufficiently-small timestep $\tau$ with which to maintain energy conservation - e.g. a $\tau$ of 0.02 fs conserves the total energy to within 0.13 meV/site over 1 ps. In Eqn. 6 we use the definition of the Hellman-Feynman force because it is this and not the derivative of the negative of the electronic energy which yields the expectation values of the ionic trajectories. In practice however, we found virtually no difference between the results obtained by the two force expressions for systems as large as the ones we studied.

Letting the electronic eigenstates arising from a solution to the time-independent Schrödinger equation

$$\hat{H}_{el} |\chi_m\rangle = \epsilon_m |\chi_m\rangle,$$
where $\hat{H}_{el}$ implicitly depends on the ionic configuration $\{u_n\}$, be represented by the set $\{\chi_m\}$, the wavefunctions of all the electrons $k$ can be written as superpositions of the eigenstates as

$$|\psi_k(t)\rangle = \sum_m g_{m,k}(t) |\chi_m\rangle$$

(9)

The initial conditions of the problem are divided conceptually into two types: the first type of initial condition is $g_{m,k}(0) = \delta_{mk}$ and is imposed on the $N$ wavefunctions of the $N$-site system, while the extra electron is set up in a superposition state in general. Thereafter, all of the $\psi_k(t)$ evolve according to Eq. 5 along with the boundary condition that they are continuous across time-steps, and become non-stationary states, written in terms of the eigenstates corresponding to the current $\{u_n\}$.

In all of the results presented in this paper, we treat all of the electronic wavefunctions with the Ehrenfest method. Before an extra electron is added to the system, the ground state of the neutral chain, whether coupled to a junction or not, is determined. This is done via the procedure described above with the ionic velocities held to zero. Here, the ends, which may correspond to coupled molecules, are free to move while a total length constraint is imposed on the system. The purpose of this is to obtain displacement values for the ends which are consistent with the parameters of the Hamiltonian, thereby minimising the finite-length effects. Afterwards, for the dynamics, the length constraint is removed and the end states are held fixed to their relaxed values because keeping the length constrained instead of fixing the ends led to the plots of displacement $u$ versus site number being tilted, as the chain would translate, and this made the results difficult to compare and analyze. Imposing no boundary conditions whatsoever results in highly-distorted ground-state structures due to the finite length of the chains, obscuring the phenomena which we would like to study.

### III. SYSTEMS STUDIED

**A. Isolated PA chain**

Two types of open neutral chains were studied as starting points: with an even or an odd number of sites. The ground state of the even chain leads to the well-known dimerisation pattern, shown in Fig. 4a, while that of the odd chain contains a soliton, again as expected.
After obtaining these ground states, an electron was prepared in either the LUMO, or in a non-stationary state at one end, and the dynamics were performed. In the even-site chain, the case of the LUMO preparation leads to a polaron, a structural deformation consisting of a soliton/anti-soliton pair moving in tandem with the electron localisation. We focused on even-site chains in order to avoid considering soliton dynamics along with the transfer of the extra electron. The effect of the Ehrenfest approximation as opposed to the BO one is clear from Fig 2. The energy of the extra wavepacket, initially prepared in the LUMO, closely follows the LUMO but nonetheless deviates from it at times.

![Graph](image)

**FIG. 2**: The energy of the added electron deviates from the LUMO, in Ehrenfest dynamics.

For the electron prepared at one end, the charge density oscillated back and forth (see Fig. 3a). This oscillation was virtually all due to the extra electron - the other electrons in the chain had practically no contribution to it. However, the chain distortions were very large, several times greater than those corresponding to the dimerisation (∼ ±0.04Å, see Fig. 4a), and in practice, would require anharmonic potentials to treat, and may lead to chain breakup. It is important to note that as the electron wavefunction oscillates back and forth, it distinctly passes through all sites between the two ends. Therefore, this is a hopping transfer regime as opposed to a tunnelling one.

In order to determine the effect of the lattice on the electron propagation, we compare the propagation with that for the case of a frozen lattice (Fig. 3b). In a frozen lattice, the propagation is quasi-periodic, owing to the non-commensurability of the eigenvalues in the eigenstate superposition comprising the wavefunction of the propagating electron. For increasingly longer times, according to the Poincaré theorem applied to quantum superpositions of eigenstates with non-commensurate eigenvalues, the oscillations will approach the original value increasingly faithfully and eventually lead to a value near 1. This is the reason why the value of 1 is not reached during the few ps of the simulations for the frozen ion case. Beyond that, the electron-lattice interaction destroys the coherences (off-diagonal entries of
the density matrix), which manifests itself in a decrease in site populations in Fig. 3b for
the simulation with full dynamics, as compared with the frozen-ion case. The off-diagonal
entries of the density matrix appear in the electron density due to the extra electron as a
result of interferences from the eigenstate superposition.

FIG. 3: (a) The populations of the two end sites 1, 60 and the middle site, 30, for electron-ion
dynamics for a chain not coupled to molecular junctions where an extra electron was added at site
1 at t=0. (b) Comparison with the frozen ion case. The population shown is only due to the extra
electron (see text for an explanation).

B. Chain within molecular junctions

The molecular junction coupling parameters $t_{\text{end}}$ and $\epsilon_{\text{end}}$ were varied across a wide range
of values in order to search for an optimal set which would lead to low electron decoherence,
meaning a small influence of the lattice on the electron transfer. This required first obtaining
a relaxed ground-state structure for the lattice, and then performing dynamics using the
added wavepacket. We only performed dynamics for cases which looked promising based
on the frozen-lattice transfer calculations. The ground-state structure for a chain coupled
to a molecule at each end deviates significantly from that of a dimerised chain (Fig. 4a).
Most notable, apart from the end effects, are the kinks introduced at large $\epsilon_{\text{end}}$ and small
$\epsilon_{\text{end}}$, (Fig. 4b) which migrate towards the ends for smaller $\epsilon_{\text{end}}$ and larger $t_{\text{end}}$ (Fig. 4b).
Usually, the site population over time can be approximately represented by a single Rabi
FIG. 4: (a) Ionic distortions $u(n)$ in Å for a chain with no coupling to a molecular junction at its ends, (b) $\epsilon_{\text{end}}=0.3$ eV and $t_{\text{end}}=1.0$ eV, and (c) $\epsilon_{\text{end}}=0.8$ eV and $t_{\text{end}}=0.4$ eV.

frequency, the frequency of oscillation for an electron in a three-state quantum system, by a projection technique$^{20}$. Characteristics such as short Rabi oscillation timescales with a single dominant Rabi frequency, usually led to the most unaffected by the lattice vibrations transfer (see later in Sec. III C). The reverse is found to be the case as well: the electron oscillation did not affect the structure a lot, which is a different result than the one found by Ness and Fisher$^{21}$ who used a model with quantized phonon modes. What completely destroyed the electron oscillations was the presence of noise which competed with the main Rabi frequency and led to destructive interference in the oscillations.

Regarding the charge density oscillations, as with the case of the chain not coupled to any junction, only the extra electron reached the other side. The other electrons nevertheless caused a significant amount of charge-density oscillation, which was correlated with the evolution of the lattice deformation. In Fig. 5 we show a case also in the “hopping” regime, albeit not as extreme as the case of Fig. 3 which had equal occupation of all sites. Still, there is a non-negligible occupation of all of the interior chain sites (only a central site is shown in the figures), and as discussed below, numerous Rabi frequencies, which do not show up at the small times in which coherent oscillation is maintained.

It is important to note that distinct hopping across the chain by the extra electron was not always found to occur - we also identified another limit: that of tunnelling. In Fig. 6 we
FIG. 5: (a) The populations of the two end sites 1, 60 and a central site, 30, for electron-ion dynamics for a chain coupled to end molecules with energy $\epsilon_{\text{end}} = 2.0$ eV and coupling to chain $t_{\text{end}} = 1.1$ eV where an extra electron was added at site 1 at $t=0$. (b) Comparison with the frozen ion case. Only the contribution from the extra electron is shown (see text for an explanation).

show a case in the “tunnelling” regime which had relatively low scattering of the electron by the lattice. It is called tunnelling because there is almost no occupation of the chain sites, with one dominant electron oscillation frequency connecting the defect levels arising from the end states (see Sec. III C).

An interesting case, where the electron oscillation frequency changes dramatically with the dynamics, is shown in Fig. 7. Also, the oscillations are incredibly persistent over very long times. Generally, the electron oscillations are stable over long times throughout the tunnelling regime because the electron tunnels between the two fixed end molecules with minimal impact from any structural distortions which may be occurring in the chain.

C. Rabi frequencies

We systematically studied the oscillation of an electron in a frozen lattice by varying different fundamental quantities: the lattice vibration parameter $K$, the electron-phonon coupling parameter $\alpha$, and the electronic parameters $t_{\text{end}}$ and $\epsilon_{\text{end}}$ of the end molecules. We determined the contribution of the pair of eigenstates comprising each Rabi frequency to the electron oscillation by projecting the eigenstates onto the end-molecule wavefunctions.
Explicitly, this weight for the \((n,m)\) pair of eigenstates is equal to

\[
D_{nm} = \langle \phi_1 | \hat{P}_n | \phi_{\text{end}} \rangle \langle \phi_{\text{end}} | \hat{P}_m | \phi_1 \rangle \tag{10}
\]

where the operator \(\hat{P}_i = | \chi_i \rangle \langle \chi_i |\) is the projector of eigenstate \(i\) and the two electrode sites are labelled \(\phi_1\) and \(\phi_{\text{end}}\). The quantity in Eq. 10 is actually the maximum value, as the weight oscillates in time according to the Rabi frequency. In three-state quantum systems there is a relationship of inverse proportionality between the Rabi frequency and the weight (see Eq. 3 in Ref. 22) which we exploit in our analysis of Sec. IV B. We focused on varying the end-molecule parameters \(t_{\text{end}}\) and \(\epsilon_{\text{end}}\) in our analysis of the Rabi frequencies.

The hopping case (Fig. 3 and 5) is characterised by the presence of a large number of competing Rabi frequencies while in tunnelling (e.g. Fig. 6), just one or two frequencies dominate the oscillations. However, even in hopping, at small times there seems to be just one main frequency present, corresponding to a fast time scale, on which there is superimposed noise from an even faster one. The other frequencies, with a longer period, eventually show up, and lead to an indistinct oscillation but by that time, the oscillation is already destroyed by the electron-lattice interaction. In Sec. IV A we discuss which choices of parameters lead to these different regimes and how the transmission occurs.
FIG. 7: (a) The populations of the two end sites 1, 60 and a central site, 30, for electron-ion dynamics for a chain coupled to end molecules with energy $\epsilon_{\text{end}} = 0.7$ eV and coupling $t_{\text{end}} = 0.4$ eV where an extra electron was added at site 1 at $t=0$. (b) Comparison with the frozen ion case. Only the contribution from the extra electron is shown (see text for an explanation).

IV. ANALYSIS

A. Defect states

The perfect dimerized chain has a double bond at both ends and an energy gap of 1.39 eV. When $t_{\text{end}}$ is significantly different from $t_{\text{0}}$, defect states appear in the gap. If the chain is still well-dimerized, as for the case of Fig. 4b, there are only two defect states, one filled and one empty, degenerate and at nearly the energy $\epsilon_{\text{end}}$; otherwise there are two additional defect states, split off from the valence and conduction band respectively, consistent with a bi-polaronic distortion such as that shown in Fig. 4c. The latter case is the most usual, as the case of only two defect states is confined to marginal cases (very small $\epsilon_{\text{end}}$). Fig. 8 shows the one-electron energy level structure of the system attached to end molecules, for the most common case, that of a bi-polaronic distortion. For low $t_{\text{end}}$ the empty-state defect levels are nearly degenerate and approximately equal to $\epsilon_{\text{end}}$. The bi-polaronic distortion is gradually lost for $t_{\text{end}} > \epsilon_{\text{end}}$ and progresses to the ends for $t_{\text{end}} \gg \epsilon_{\text{end}}$, and for sufficiently large $t_{\text{end}}/\epsilon_{\text{end}}$, there are no defect states at all in the gap.

The closeness in energy of the empty states for low $t_{\text{end}}$ means that the Rabi oscillation period is very long. This is also the pure “tunnelling” regime because there are virtually no
FIG. 8: Schematic of the energy levels for a system with two kinks in the distortion \( u(n) \), e.g. Fig. 4c. In a case such as Fig. 4b, there is no longer a dominant Rabi frequency \( \Omega \) and transmission takes place through many levels, including those in the conduction band (CB), filled defect levels, and valence band (VB).

other contributions from other pairs of eigenstates to the electron oscillation between the ends.

For \( t_{\text{end}} \ll \epsilon_{\text{end}} \), the defect levels are present, owing to the bi-polaronic distortion through the lattice, but only the filled ones are in the gap while the empty ones are located in the CB, assuming that \( \epsilon_{\text{end}} \) is large enough that it is in the CB. A very low \( t_{\text{end}} \) combined with a large \( \epsilon_{\text{end}} \) leads to a very small Rabi frequency, or very slow electron oscillation, which may be undesirable. Nevertheless, this is the pure tunnelling regime, as these defect energy levels are highly localised at the end molecules. However, as \( t_{\text{end}} \) increases, more CB states around the energy \( \epsilon_{\text{end}} \) suddenly become involved in the transfer leading to a noisy spectrum. Thus, a large \( \epsilon_{\text{end}} \) which leads to defect states in the CB is not very practical for achieving stable coherent oscillations. On the other hand, for \( t_{\text{end}} \gg \epsilon_{\text{end}} \), there are no defect levels as the chain is dimerised and the transfer occurs through a large number of levels, both filled and empty. The extreme case is that of Fig. 3. For both of these situations, the system is in the hopping regime as the tunnelling through numerous energy levels implies that the wavefunction of the extra electron has a non-negligible projection onto the chain sites. However, for intermediate values of \( t_{\text{end}} \) and \( \epsilon_{\text{end}} \), we are able to obtain tunnelling and a fairly large, single dominant oscillation frequency, which is stable under the effect of lattice dynamics for at least a few cycles, over a wide range of molecular-junction parameters.
B. Effect of dynamics on Rabi frequencies

Here, we describe the effect of ion dynamics on the Rabi frequencies, in order to explain the decoherence mechanism. A recent study\textsuperscript{23} examined the decoherence mechanism for electron wavepackets added to chains and determined that for long chains, decoherence is caused by population transfer into other states due to the dense energy level structure. Our results, which show a decay in population of the initial wavefunction superposition, especially in the case of the defect levels located in the conduction band, agree with this explanation.

FIG. 9: Variation of key quantities with time for the case $t_{\text{end}}=0.4$ eV and $\epsilon_{\text{end}}=0.7$ eV. The top panel shows the eigenvalues, L: LUMO, L1: LUMO$+1$, L2: LUMO$+2$. The middle panel shows the inverse of the Rabi frequency, $T(t) \equiv 1/\Omega(t)$ for the two competing Rabi frequencies formed by the two pairs of energy levels shown. The bottom panel shows the variation with time of the weights of these Rabi frequencies. For clarity, the data shown is a running average over 100 fs.

In addition, we find that when multiple Rabi frequencies compete, they interfere. As well, in the hopping regime, the electronic oscillation is substantially degraded by the ionic dynamics, as mentioned earlier at the end of Sec. IV A. However, for several cases of two competing Rabi frequencies, we find that the electron dynamics exhibit exceptional stabil-
ity, particularly when the two Rabi frequencies contribute roughly equally to the oscillation. The reason is that their weights oscillate out of phase with each other. In Fig. 9 we show the time dependence of the energy levels involved in the oscillation, the inverse Rabi frequencies derived from these energy levels, and the maximum weights of the latter, for a case which had great stability in the electron oscillation. As mentioned earlier in Sec. III C, the quantities $T(t)$ and $D(t)$ are correlated. We create a simple model for combining the two Rabi oscillations, omitting the time dependence from $T(t)$ as it is already found in $D(t)$. If we denote the average value of the $i$th inverse Rabi frequency (connecting two particular energy levels) as $T_i \equiv 1/\Omega_i$, and its maximum weight $D_i(t)$ (see Eq. 10), oscillating with a frequency $\omega_0$, we may write

$$T_1(t) = T_1$$
$$D_1(t) = D_1 + B_1 \cos(\omega_0 t)$$
$$T_2(t) = T_2$$
$$D_2(t) = D_2 - B_2 \cos(\omega_0 t) \quad (11)$$

and the combined oscillation period becomes:

$$T_{net}(t) = \frac{T_1 D_1(t) + T_2 D_2(t)}{D_1(t) + D_2(t)} \quad (12)$$

We found that this expression represents the electron oscillation period very well. The main cause of any deviation from the prediction of Eq. 12 and the data is due to other secondary inverse Rabi frequencies, which are smaller and tend to bring the actual value down. The time-dependence in Eq. 12 is generally quite weak, owing to the opposite signs in the time-dependent quantities of Eq. 11 and this leads to the exceptional stability seen in Fig. 7. We determined the average value $T_{av}$ of $T_{net}(t)$ and compared it with the main oscillation period for several cases, which we show in Table I. Regarding the oscillation frequencies $\omega_0$, they mainly corresponded to the bare (without the extra electron) lowest phonon modes of the respective system but not always, and importantly, no relation was seen between the matching or not of the $\omega_0$ with a bare phonon frequency and the stability of electron oscillations in the respective system.
\[ \epsilon_{\text{end}}(eV) \quad T(0) \quad \mathcal{T} \quad \mathcal{D} \quad B \quad 2\pi/\omega_0 \quad T_{av} \quad T_{actual} \]

| \epsilon_{\text{end}}(eV) | T(0) | \mathcal{T} | \mathcal{D} | B | 2\pi/\omega_0 | T_{av} | T_{actual} |
|-----------------|------|---------|--------|---|-------------|-------|-----------|
| 0.6             | 6239 | 4286    | 0.116  | 0.012 | 172, 300, 250 | 4286  | 3879      |
| 0.62            | 5274 | 3218    | 0.132  | 0.011 | 211          | 3218  | 3100      |
| 0.64            | 4331 | 2229    | 0.119  | 0.011 | 269          | 2229  | 1900      |
| 0.65            | 3900 | 2014    | 0.113  | 0.010 | 303, 160     | 2014  | 1520      |
| 0.67            | 3158 | 1004    | (483)  | 0.073 (0.069) | 0.007 (0.006) | 443   | 751       |
| 0.7             | 2231 | 882     | (495)  | 0.072 (0.081) | 0.025 (0.025) | 328   | 678       |
| 0.72            | 1681 | 863     | (521)  | 0.073 (0.090) | 0.036 (0.034) | 278   | 674       |
| 0.75            | 1110 | 639     | (593)  | 0.056 (0.106) | 0.016 (0.036) | 250   | 609       |
| 0.77            | 853  | 513     | (611)  | 0.044 (0.115) | 0.009 (0.025) | 216   | 584       |
| 0.8             | 586  | 672     | 0.120  | 0.022 | 169          | 672   | 586       |
| 1.0             | 440  | 505     | 0.114  | 0.023 | 125          | 505   | 469       |

TABLE I: Parameters of Eq. 11 for several cases of \( \epsilon_{\text{end}} \) (in eV) for fixed \( t_{\text{end}}=0.4 \) eV, as deduced from the dynamics, for comparison with the average value \( T_{av} = \frac{T_{\text{net}}(t)}{T_{actual}} \) and with the main electron oscillation period \( T_{actual} \). Note that \( T(0) \) is the frozen inverse frequency. If two inverse Rabi frequencies compete, the values corresponding to both are given, the same one always in parentheses. All times are in fs.

V. CONCLUSIONS

In summary, we investigated the inelastic electron transfer in a polyacetylene wire within molecular junctions and we found that under certain conditions, which we identify, there is near-ballistic transfer, in two distinct regimes: tunnelling and hopping. The tunnelling case resulted when the defect levels from the electrodes were in the band gap of the chain whereas when they are in the conduction or valence band, tunnelling occurs through multiple energy levels leading to a non-negligible occupation of the chain sites, a regime which we term hopping. Ness and Fisher\(^{21}\) have calculated tunnelling electron transport for a chain coupled to metallic leads, using a model incorporating a quantized description of the main phonon modes, and find a clear indication of polaron transport, or a distortion of the lattice which propagates along with the electron. On the other hand, another study\(^4\), based on the SSH model with a classical, single-oscillator description of lattice vibrations, does not find
any polaron transport. It does find however, that energy levels arising from a pre-existing polaronic distortion aid in the tunnelling process. Our work suggests that not polaronic *per se*, but defect levels in the energy gap, produce tunnelling transfer. We expect that there will be dramatic changes in the transport characteristics, particularly for the cases in which the defect levels are located in the conduction band, if we consider electron-electron interactions, and this extension is presently under investigation. We do not expect that a full treatment of transport from the coupling of the system to metallic leads will lead to qualitative changes. While we find that multiple competing Rabi frequencies lead to hopping and a destruction of the electron oscillations because of their different behaviour under the dynamics, we find a large stable regime where two competing Rabi frequencies interfere destructively in order to yield exceptionally-stable electron oscillations at a faster rate than if the ions were completely static. Generally in the tunnelling regime, we predict that when connected to a source of current, the conductivity will increased as a result of the ion-electron interactions.

1 Y. Okawa, S. K. Mandal, C. Hu, Y. Tateyama, S. Goedecker, S. Tsukamoto, T. Hasegawa, J. K. Gimzewski, and M. Aono. Chemical wiring and soldering toward all-molecule electronic circuitry. *J. Am. Chem. Soc.*, 133:8227–8233, 2011.
2 P. Sautet and C. Joachim. Electronic transmission coefficient for the single-impurity problem in the scattering-matrix approach. *Phys. Rev. B*, 38:12238–12247, 1988.
3 J. E. Han. Quantum simulation of many-body effects in steady-state nonequilibrium: Electron-phonon coupling in quantum dots. *Phys. Rev. B*, 73:125319–1–9, 2006.
4 Z. G. Yu, D. L. Smith, A. Saxena, and A. R. Bishop. Green’s function approach for a dynamical study of electron transport in metal/organic/metal structures. *Phys. Rev. B*, 59:16001–16010, 1999.
5 N. Renaud, M. Ratner, and C. Joachim. A time-dependent approach to electronic transmission in model molecular junctions. *J. Phys. Chem. B*, 115:5582–5592, 2011.
6 R. A. Marcus. Electron transfer reactions in chemistry. theory and experiment. *Rev. Mod. Phys.*, 65:599–610, 1993.
7 T. Holstein. Studies of polaron motion part i. the molecular-crystal model. *Annals of Physics*,
8 A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su. Solitons in conducting polymers. Rev. Mod. Phys., 60:781–850, 1988.
9 W. P. Su and J. R. Schrieffer. Soliton dynamics in polyacetylene. Proc. Natl. Acad. Sci. USA, 77:5626–5629, 1980.
10 W. P. Su, J. R. Schrieffer, and A. J. Heeger. Soliton excitations in polyacetylene. Phys. Rev. B, 22:2099–2111, 1980.
11 S. V. Rakhmanova and E. M. Conwell. Polaron dissociation in conducting polymers by high electric fields. Appl. Phys. Lett., 75:1518–1520, 1999.
12 S. V. Rakhmanova and E. M. Conwell. Nonlinear dynamics of an added carrier in trans-polyacetylene in the presence of an electric field. Synth. Met., 110:37–45, 2000.
13 Å. Johansson and S. Stafström. Polaron dynamics in a system of coupled conjugated polymer chains. Phys. Rev. Lett., 86:3602–3605, 2001.
14 H. Ishii, K. Honma, N. Kobayashi, and K. Hirose. Wave-packet approach to transport properties of carrier coupled with intermolecular and intramolecular vibrations of organic semiconductors. Phys. Rev. B, 85:245206–1–9, 2012.
15 J. C. Tully. Mixed quantum-classical dynamics. Faraday Discuss., 110:407–419, 1998.
16 E. J. Mele. Transient structural response to photoexcitation in polyacetylene. Phys. Rev. B, 26:6901–6908, 1982.
17 H. W. Streitwolf. Dynamics of a bond-disordered peierls chain and mixed gap states. Phys. Rev. B, 58:14356–14363, 1998.
18 R. E. Allen. Electron-ion dynamics: A technique for simulating both electronic transitions and ionic motion in molecules and materials. Phys. Rev. B, 50:18629–18632, 1994.
19 S. R. Phillpot, D. Baeriswyl, A. R. Bishop, and P. S. Lomdahl. Interplay of disorder and electron-phonon coupling in models of polyacetylene. Phys. Rev. B, 35:7533–7550, 1987.
20 C. Joachim. Ligand-length dependence of the intramolecular electron transfer through-bond coupling parameter. Chem. Phys., 116:339–349, 1987.
21 H. Ness and A. J. Fisher. Quantum inelastic conductance through molecular wires. Phys. Rev. Lett., 83:452–455, 1999.
22 P. Sautet and C. Joachim. The switching ability of a three-level tight-binding system: the isolated and embedded case. J. Phys. C: Solid State Phys., 21:3939–3957, 1988.
I. Franco and P. Brumer. Electronic coherence dynamics in trans-polyacetylene oligomers. *J. Chem. Phys.*, 136:144501–1–10, 2012.