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Electron Dynamics in Tight-Binding Approximation - the Influence of Thermal Anharmonic Lattice Excitations

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We study here several basic problems of the quantum mechanics of electrons which are embedded into a one-dimensional (1D) nonlinear, thermally excited lattice. Our approach uses the tight-binding model for the dynamics of the electrons. Through coupling terms in the Hamiltonian the electron quantum dynamics is connected with the classical dynamics of the lattice endowed with Morse interactions. First it is shown that the electron forms bound states with the solitonic excitations in the lattice. These so-called solectrons may move with supersonic speed. Then we study the effects of interference of solectrons with solitons. Finally we study the interference between thermal excitations on tunneling between two minima.

1 Introduction

The aim of this work is the study of several basic problems of the quantum-mechanical motion of electrons in one-dimensional plasmas. In previous notes [1–6] we studied the influence of nonlinear lattice excitations on electron transfer by using a semiclasical approach. It was shown that electron trapping by solitons and a new form of electric conduction mediated by solitons are possible in an anharmonic one-dimensional (1D) lattice. In subsequent work corresponding results were obtained by treating the electrons quantum-mechanically [7–10]. There and here the electron-lattice interaction is considered within the tight binding approximation [11], while the lattice dynamics is treated classically. The lattice interactions are of Toda or Morse type akin to the Lennard-Jones interaction, hence allowing for phonon - and soliton - longitudinal vibrations with compressions governed by the repulsive part of the potential. Building upon this we here study the interference between electron tunneling from potential well to potential well with thermally excited solitons. There is detailed data on the long-range electron tunneling through biomolecules such as proteins and DNA [12–16] for which our theory may offer a plausible explanation.

2 Hamiltonian and electron-lattice dynamics

Our model is based in the quantum mechanical "tight binding" approximation (TBA) for electrons which are moving on the background of a lattice with Morse interactions,

$$H = H_{electron} + H_{lattice} \tag{1}$$

with

$$H_{lattice} = \sum_n \left\{ \frac{p_n^2}{2M} + D\left(1 - \exp\left[-B\left(q_n - q_{n-1}\right)\right]\right)^2 \right\}, \tag{2}$$

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and

$$H_{el} = \sum_n E_n c_n^* c_n - \sum_n V_{nn-1}\left(q_k\right)\left(c_n^* c_{n-1} + c_n c_{n-1}^*\right), \tag{3}$$

where $|c_n|^2$ gives the probability of finding the electron residing at the site n. The quantity V_{nn-1} defines the transfer matrix element responsible for the hopping of the electron along the chain (considering only nearest neighbors). This matrix is the key ingredient, allowing for the coupling of the electron to the lattice displacements, and hence to the lattice vibrations, phonons or solitons. A reasonable choice for V_{nn-1} is [7, 10]

$$V_{nn-1} = V_0 \exp\left[-\alpha\left(q_n - q_{n-1}\right)\right], \tag{4}$$

where the parameter α accounts for the strength of the coupling. This is a rather crude model of the electron dynamics. However because of its relative simplicity we are able to study the influence of thermal excitations of the electron dynamics in some detail.

We assume that the electrons are in 3D though the (ion)lattice is 1D. Further we have considered the whole system in a "thermal bath" characterized by a Gaussian white noise, ξ_j , of zero mean and delta correlated. The bound state energy at site n may depend on the position n.

For a "universal" description it is best to rescale quantities and consider the corresponding dimensionless problem. We take as unit of time Ω_{Morse}^{-1}, where $\Omega_{Morse} = \left(2DB^2/M\right)^{1/2}$ denotes the frequency of harmonic oscillations (linear, first-order approximation to the Morse exponential). As unit of energy we take $(2D)$. For displacements we take B^{-1} as the unit. For momenta we take $(2MD)^{1/2}$, hence for the interaction force we have $\alpha V_0/2BD$, and α is measured in $\left(B^{-1}\right)$ units. Then, expecting no confusion in the reader, denoting the new dimensionless quantities with the same symbols as the old ones, the dynamics of the Hamiltonian system (1,2,3,4) is given by the following equations for the electron probability density, c_n, and lattice vibrations, q_n ,

$$i\frac{dc_n}{dt} = \epsilon_n c_n - \tau\left[\exp\left[-\alpha\left(q_{n+1} - q_n\right)\right] c_{n+1} - \exp\left[-\alpha\left(q_n - q_{n-1}\right)\right] c_{n-1}\right], \tag{5}$$

$$\begin{aligned}\frac{d^2 q_n}{dt^2} = &\left\{1 - \exp\left[-\left(q_{n+1} - q_n\right)\right]\right\}\exp\left[-\left(q_{n+1} - q_n\right)\right] - \\ &- \left\{1 - \exp\left[-\left(q_n - q_{n-1}\right)\right]\right\}\exp\left[-\left(q_n - q_{n-1}\right)\right] - \\ -\alpha V\left\{\left(c_{n+1}^* c_n + c_{n+1} c_n^*\right)\exp\left[-\alpha\left(q_{n+1} - q_n\right)\right] + \left(c_n^* c_{n-1} + c_n c_{n-1}^*\right)\exp\left[-\alpha\left(q_n - q_{n-1}\right)\right]\right\},\end{aligned} \tag{6}$$

where $\epsilon_n = (E_n/\Omega_{Morse}\hbar)$, $\tau_0 = (2D/\Omega_{Morse}\hbar)$, $\tau = (V_0/\Omega_{Morse}\hbar)$ and $V = V_0/2D$. Needless to say, in general the two time scales in (5) and (6) are not the same (which in frequency terms refer to ultraviolet/electronic *versus* infrared/acoustic), for most cases with electrons and phonons. For purposes of mere illustration we shall use the following parameter values: $B = 4.45\mathring{A}^{-1}$, $\alpha = 1.75B$, $D = 0.1eV$, $V_0 = 0.2eV$ $\Omega_{Morse} = 3.04 \cdot 10^{12}s^{-1}$, $\Omega_{electron} = V_0/\hbar = 0.608 \cdot 10^{14}s^{-1}$, and $\tau = 10$. These numerical values are relevant, e.g., for electron transport along hydrogen bonded polypeptide chains such as α-helices and other biomolecules.

3 Interference between electron and lattice dynamics

Let us begin with the simplest situation, the electron transfer (ET) from a "donor" lattice unit to an "acceptor" lattice unit. In Fig. 1 we display typical evolving electron distributions (upper part) and solitonic excitations the lattice, which evolve alien to the electrons (lower part). Next we estimate how the path of an electron may be influenced by a soliton which was generated by a perturbation of the lattice (see Fig. 2). We show the interaction of an electron emitted at site 100 with a soliton moving on the cold lattice of 200 Morse particles (see also [7,8]). We see clearly that the electron is attracted by the soliton. Both particles are forming a bound state (solectron) and travel together.

Let us consider now the solectron stability and the interaction of electrons with solitons. The added, excess electron is placed at $t = 0$ at a "donor" located at site $n = 100$ at time $t = 0$, Fig. 2 shows our findings. Due to the electron-lattice interaction ($\alpha = 1, 75$) we observe soliton-mediated ET.

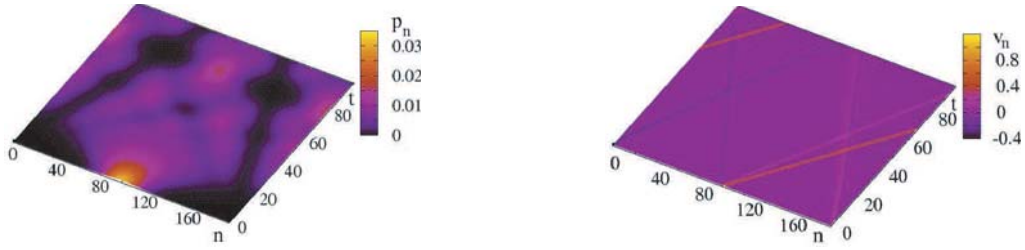


Fig. 1 Morse lattice of $N = 200$ particles. Left: Evolution of a free electron started at position 100. Right: a free soliton started at position 100. No interaction is taken into account. (Online colour: www.cpp-journal.org)

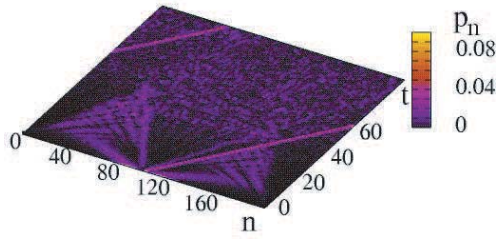


Fig. 2 Morse lattice of $N = 200$ particles. Influence of electron-soliton interaction on the electron. (Online colour: www.cpp-journal.org)

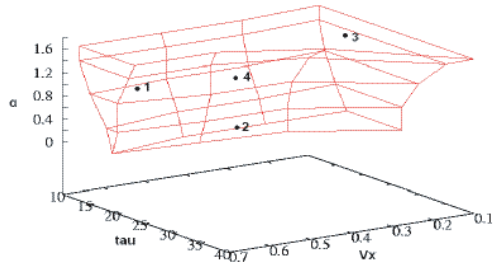


Fig. 3 Morse lattice. Parameter region were bound states of electrons and solitons, hence solectrons, are observed. Recall that α is measured in units B^{-1} (the inverse of the stiffness constant of the Morse potential).

The electron is dynamically bound to the soliton thus creating the travelling, generally supersonic solectron excitation. The region of stability of solectrons is shown in Fig. 3. Indeed when the electron-lattice interaction is operating, we see that the electron moves with the soliton with a slightly supersonic velocity $v_{el} = (100/70)v_{sound}$ and is running to the right border of the square plot. Let us assume that there the "acceptor" is located. This means that the electron is guided by the soliton from "donor" to "acceptor". In reality the electron cannot ride on just a single soliton from donor to acceptor. Several solitons should be involved in transport. Therefore the above given soliton velocity is an upper bound for ET. As the result of a second experiment we show a color-coded plot starting with an electron and a soliton initially at different positions (see Fig. 4a).

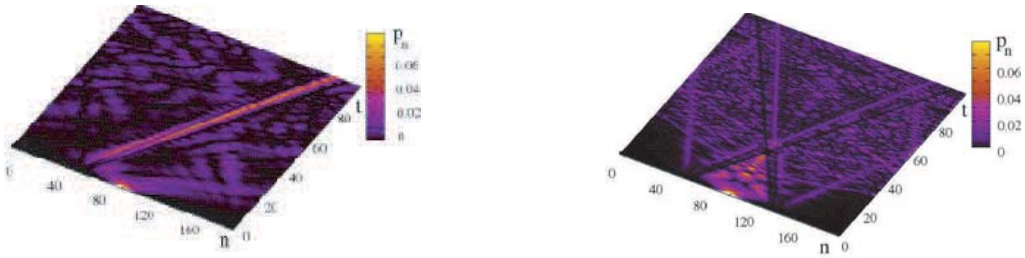


Fig. 4 Morse lattice. Evolution of one electron density starting at position 100. Parameters: $V = 0.1, \tau = 20$. Left panel: One soliton starts at position 50 and influences the electron density. The electron is beginning from 10-20 time units after the start catched by the soliton and forms with it a bound state which moves with slightly supersonic velocity. Right panel: The elctron density is influenced by two solitons emitted at positions 60 and 140. The (quantum) electron probability density splits between the two solitons. (Online colour: www.cpp-journal.org)

In order to study the superposition of several solitons acting on one electron we carried out a third experiment to see the evolution of an electron in the field of two solitons (Fig. 4b). The outcome is a splitting of the (quantum) electron probability density as noted in an earlier publication [8, 9]. The solitons which we considered so far, were of external origin, as the solitons were launched (as an initial condition) at some place of the lattice at $t = 0$ and simultaneously we placed somewhere else an electron.

4 Solectrons in thermal lattices

Let us study now a lattice heated to temperature T. Then solitons are excited due to the influence of the thermal embedding. However we do not have just one or two solitons, but many of them generated by the heat bath [17,18]. Indeed we see up to the range of physiological temperatures many relatively small solitons in the system which have a finite life-time up to a few picoseconds. The general picture is now that the electron density is concentrated in the local "hot spots" created by the local solitonic thermal excitations. In order to study the influence of this effect on "donor-acceptor" ET in more detail we performed a series of computer simulations.

In this series of experiments we released an electron on a previously thermally heated lattice by means of the friction and noise sources. These sources are switched off at $t = 0$. Then the electron starts moving. The result is shown in Fig. 5. In Fig. 5 we represent in the left panel the electron density developing in a lattice heated up to $T = 0.05$ which, using the parameter values earlier given, corresponds to about 100K. We see that the electron density is confined more or less in a cone. For $T = 0.5$, represented in the right panel the cone narrows (Fig. 5). Note that such a high temperature is taken here as an upper level for illustration in our computer simulations with no physical meaning. In real life we must not reach the melting point of the material.

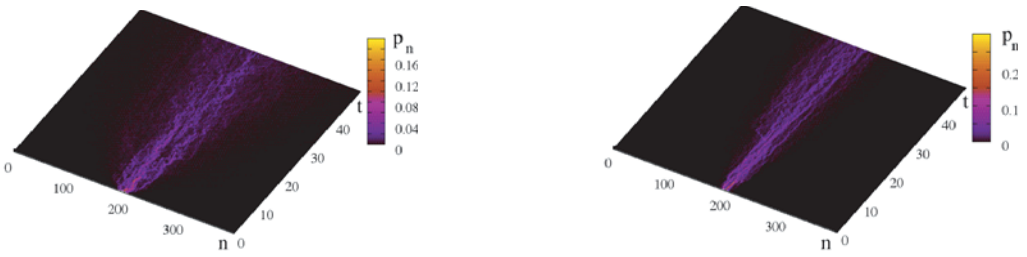


Fig. 5 Morse-lattice. The density of an electron released on a thermal lattice ($\tau = 10$, $\alpha = 1.75$) gets concentrated at places of local solitonic excitations (with a size up to 10 lattice sites) and survives there a finite time (about a few picoseconds) then it moves to another "hot spot". Left panel: $T = 0.05$, the cone filled by the density is still relatively wide. Right panel $T = 0.5$, the cone gets more narrow. (Online colour: www.cpp-journal.org)

What we see in Figs. 5 is that the electron probability density splits into many small spots which are localized at thermal solitons. These "hot spots" of size up to $50\mathring{A}$ may comprise up to 10 lattice sites and have only a relatively short lifetime which is in the range of a few picoseconds.

The little maximum of the electron density "dies" with the soliton and moves eventually to the next local soliton. The whole process is dynamic, hence time-dependent as the "hot spots" are created and annihilated in the thermal process. Note that the spots denote only probability densities, but in reality the electron is localized at one of the spots. In Fig. 5 we see that at higher temperatures ($T = 0.5$) the development of the electron density in a lattice splits into rather narrow spots. Again the electron density is confined to a cone.

5 Interference between electron tunneling and thermal solitons

So far we studied the motion of free (non-interacting) electrons on the lattice. Now we will consider the more difficult problem of transitions between two potential wells by tunneling and/or thermal activation. We assume that we have a Morse lattice with $N = 200$. The first Morse particle placed at $n = 100$ and its (Gaussian) neighborhood form the "donor" and the Morse particle (at $n = 185$) and (Gaussian) surrounding represent the "acceptor" (see Fig. 6). We assume that at these places the electrons are sitting in deep Gaussian wells, the acceptor level being lower than the donor level (see Fig. 6).

A well of the electron energy includes not just one site but in addition to the central site also some (Gaussian) surrounding. In between the wells are normal Morse sites with constant electron energies $E_n \sim 0$. This forms the nuclear landscape as postulated by Marcus [12, 13]. Due to our periodic boundary conditions we have a ring structure, where donor and acceptor are sitting at approximately opposite sites.

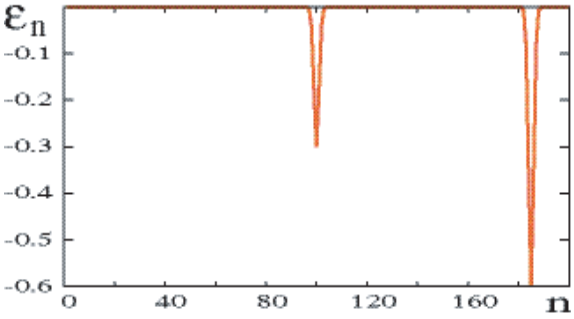
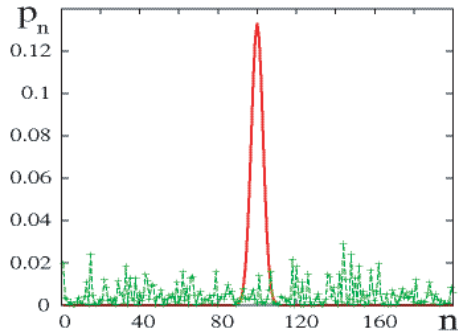


Fig. 6 Structure of the two Gaussian potential wells of the electron energies, ϵ_n, corresponding to "donor" (left at position 100) and "acceptor" (right at position 185) . Note that in TBA the landscape of the electron energies is discrete. We have one energy state per site.



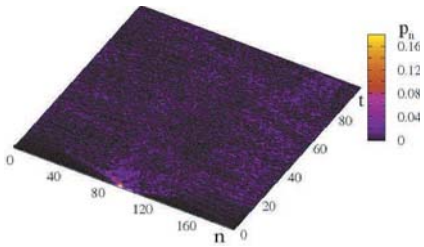


Fig. 7 Evolution of the tunneling electron density at a very low temperature T = 0.01. Left: Distribution at the initial and the final time. Right: Representation in time and space. The electron seems to feel already the deeper well in large distance at position 185, since the electron density is asymmetric, but tunneling is still rather weak. (Online colour: www.cpp-journal.org)

As shown in Fig. 7, at relatively low temperatures, the electron initially placed at the "donor" site well is practically unable to leave it. Increasing the temperature, the tunneling is supported by thermal activation. We see in Fig. 8, that in spite of the fact that the threshold is still three times higher than the thermal energy, a substantial part of the electron density is able to leave the well, to travel along the bridge and to find the deeper well which is located at a quite large distance at position 185. The thermal solitons play an important role for the traveling along the bridge, however the details of the interference between thermal processes and tunneling is still to be explored. At the highest which we explored, at $T = 0.5$, many thermal solitons are excited, and the soliton-assisted transfer of the electron density along the bridge is very fast bringing the electron quickly to the deeper well (see Fig. 9).

As we see, there is a whole spectrum of processes between the tunneling-dominated well-to-well-transition at low temperatures (here demonstrated for $T = 0.01$) over a combination between tunneling and thermal activations (demonstrated here for $T = 0.1$) to the case of higher temperatures (here demonstrated for $T = 0.5$), where thermal activation clearly dominates. The details of the combination of tunneling and thermal activation are still to be explored, in particular the role of the thermal solitons. Anyhow we may already express the hope that this will contribute to the further exploration of the understanding of the observed electron transfer (ET) in biomolecules over long distances [14–18].

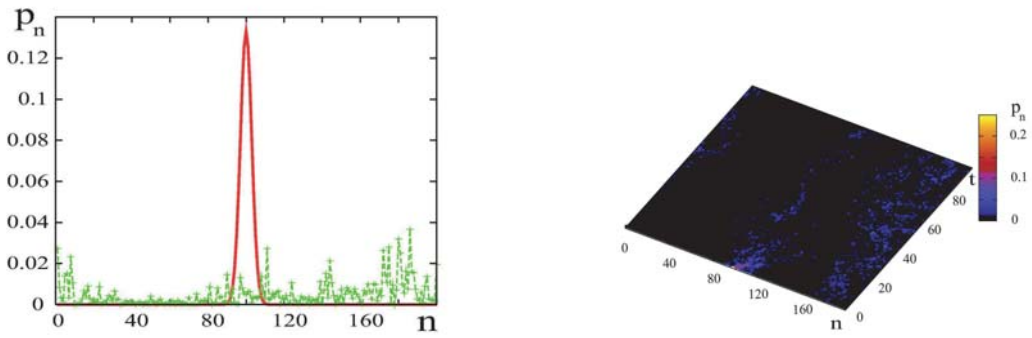


Fig. 8 Evolution of the tunneling electron density at an intermediate temperature T = 0.1. Left: Distribution at the initial and the final time. Right: Representation in time and space. Tunneling is supported by thermal activation. A considerable part of the electron density travels along the bridge to the deeper well located in large distance at position 185. (Online colour: www.cpp-journal.org)

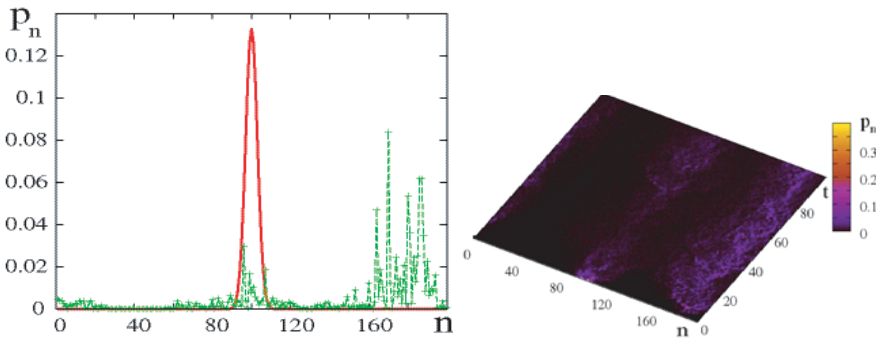


Fig. 9 Evolution of the electron density of a tunneling electron at a higher temperature $T = 0.5$. Left: Distribution at the initial and the final time. Right: Representation in time and space. The interaction between the electron and the thermal excitations leads to a thermally stimulated transition to the second lower minimum. (Online colour: www.cpp-journal.org)

6 Conclusions

In summary, the findings (and conjectures) on ET obtained in this work are: In most cases we considered here a free electron was injected with a maximum of its probability density distribution in the center of the lattice. We have shown that the creation of a soliton at the same time and place may give rise to a very stable bound state -the solectron- which moves with supersonic velocity along the lattice and may transfer the electron over hundreds of lattice sites. Further we have shown that even the injection at different places but small distance may also give rise to an electron-soliton bound state. To say it in simple terms: Free electrons and solitonic excitations may support each other in traveling through the lattice. On the other hand we have shown that the electron tunneling between energetic minima in the lattice is also influenced by solitons in the medium, however this is a more complex process. All the mentioned effects could help to understand the observed electron transfer (ET) over long distances with only small loss of energy [14–18].

As open problems remain, at first to explore all details of the interaction between solitons and tunneling processes from well to well We have shown that there is a whole spectrum of possibilities between tunneling-dominated well-to-well-transitions at low temperatures, over a combination between tunneling and thermal activations, to the case of high-temperature transitions dominated by thermal activation. All the finer details of the combination of tunneling and thermal activation are still to be explored. In any case our model may contribute to the understanding of the observed electron transfer (ET) in biomolecules [14–18]. A second question which remains partially open is, how energy-rich solitons may be excited in the lattice. In principle, any fast mechanical

deformation or structural reconformation could be responsible for the excitation of solitons running along the lattice. As we have shown here, it seems to be most natural to assume that the thermal solitons, which are always present in the medium, play the role of carriers of the electron, as a kind of surfing of the latter on the solitonic excitations.

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