



## ON THE MATHEMATICAL MODELING OF SOLITON-MEDIATED LONG-RANGE ELECTRON TRANSFER

MANUEL G. VELARDE\*, ALEXANDER P. CHETVERIKOV†

and WERNER EBELING‡

*Instituto Pluridisciplinar-UCM,  
Paseo Juan XXIII, 1, Madrid-28040, Spain*

\**mgvelarde@pluri.ucm.es*

†*chetverikovAP@info.sgu.ru*

‡*ebeling@physik.hu-berlin.de*

DIRK HENNIG

*Institut für Physik, Humboldt-Universität,  
Newtonstrasse 15, Berlin-12489, Germany*

*hennigd@physik.hu-berlin.de*

JOHN J. KOZAK

*DePaul University, 243 South Wabush Avenue,  
Chicago, IL60604-2301, USA*

*KOZAK@depaul.edu*

Received June 8, 2009; Revised June 29, 2009

We discuss here possible models for long-range electron transfer (ET) between a donor (D) and an acceptor (A) along an anharmonic (Morse–Toda) one-dimensional (1d)-lattice. First, it is shown that the electron may form bound states (solelectrons) with externally, mechanically excited solitons in the lattice thus leading to one form of soliton-mediated transport. These solelectrons generally move with supersonic velocity. Then, in a thermally excited lattice, it is shown that solitons can also trap electrons, forming similar solelectron bound states; here, we find that ET based on hopping can be modeled as a diffusion-like process involving not just one but several solitons. It is shown that either of these two soliton-assisted modes of transport can facilitate ET over quite long distances.

*Keywords:* Morse interaction; anharmonicity; lattice solitons; solelectrons; electron transfer; biomolecules.

Long-range electron tunneling through biomolecules like azurin and DNA has been studied intensively both experimentally and theoretically over the last three decades [Marcus, 1956, 1999; Hopfield, 1974; Potasek & Hopfield, 1977; Marcus & Sutin, 1985; Wan *et al.*, 1999, 2000; Winkler, 2000; Gray & Winkler, 2003, 2005; Bollinger, 2008; Shih *et al.*,

2008]. However, if one focuses on long-range tunneling (beyond 20 Å) and on the transport velocities measured (near or even at supersonic levels) not everything has been explained theoretically. To develop this point, we refer to recent work on the influence of nonlinear lattice excitations on electron transfer [Velarde *et al.*, 2005, 2006, 2008a, 2008b;



parameters need to be assigned to specify the governing Hamiltonian and implement the model: these parameters can be extracted from the literature. First, from the crystal structure of azurin [Crane *et al.*, 2001], one can calculate the N to N distance between each of the residues from THR 126 to MET 121. Although the N–N distances change a bit, the average distance is  $\sim 3.5 \text{ \AA}$ . Second, the mass of each residue from THR 126 to MET 121 is known, and an average mass per residue,  $\sim 100 \text{ amu/residue}$  can be established. Third, the bond dissociation energy  $D$  and the bond stiffness  $B$  for the peptide bonds must be assigned, as we shall do it below by adopting the Morse potential.

The electron will be considered within the tight binding approximation [Ashcroft & Mermin, 1976] while the lattice dynamics will be treated classically. The lattice interactions are assumed to be of Morse type (or adapted Toda–Morse, akin to the Lennard–Jones interaction) [Toda, 1989], hence allowing for phonon — and soliton — longitudinal vibrations with compressions governed by the repulsive part of the potential [Chetverikov *et al.*, 2006a, 2006b]. Thus, we consider a 1d anharmonic lattice with dynamics described by the Hamiltonian  $H = H_{\text{lattice}} + H_{\text{electron}}$ , with

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

Here  $M$  denotes the mass of a lattice particle, the coordinates and momenta are  $q_n, p_n$ ; ( $n = 1, \dots, N$ ) and describe their respective displacements from equilibrium positions and momenta,  $B$  characterizes the stiffness of the spring-like constant in the Morse potential,  $D$  is the depth of the potential well, and  $\sigma$  defines the equilibrium lattice spacing. Keeping in mind that the experimental system we wish to model is azurin, the Morse frequency can be taken to be of order of a vibration frequency, viz.  $\Omega_{\text{Morse}} = (2DB^2/M)^{1/2} \approx 10^{13} \text{ s}^{-1}$ . Once the value of the dissociation energy  $D$  of the peptide bond has been set, the value of the bond stiffness  $B$  can be estimated from the harmonic approximation to the potential in Eq. (1). To get a more global sense of the interplay between  $D$  and  $B$ , we list in Table 1 complementary values of these two parameters assuming that the Morse frequency,  $\Omega_{\text{Morse}}$ , and the mass  $M$  per residue have been set as stated above.

Table 1. Relation between the dissociation energy  $D$  and the lattice stiffness  $B$  with the fixed oscillation frequency  $\Omega_{\text{Morse}} = 10^{13} \text{ s}^{-1}$  and the molecular mass  $M = 100 \text{ amu}$ .

$D$ [eV]	$B$ [ $\text{\AA}^{-1}$ ]
0.1	2.28
0.3	1.31
0.5	1.02
1.0	0.72

For the electron contribution to the Hamiltonian we take

$$H_{\text{electron}} = E_n(q_k) c_n^* c_n - \sum_n V_{nn-1}(q_k) (c_n^* c_{n-1} + c_n c_{n-1}^*), \quad (2)$$

with  $n$  denoting the lattice site where the electron is “placed”; the complex quantities  $c_n$  give the  $n$ th component of the wave function, and  $p_n = |c_n|^2$  gives the probability of finding the electron residing at site  $n$ . The bound state energy at site  $n$  may depend on the particle shifts of the neighbors. We shall use the ansatz

$$E_n = E_n^0 + \chi_0(q_{n+1} - q_{n-1}). \quad (3)$$

This is a translation-invariant modification of the linear shift used by Holstein [1959, 1981] and Kalosakas *et al.* [1998, 2003]. The parameter  $\chi_0$  always has a relatively low value. In fact, in our computations we shall set it to zero to simplify; the reason is that we want to suppress effects owing to energy shifts and concentrate more on the influence on the transfer elements. The quantity  $V_{nn-1}$  defines the transfer matrix element responsible for the transport (hopping) of the electron along the chain (considering only nearest neighbors). This element 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

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

where the parameter  $\alpha$  accounts for the strength of the coupling. Since we shall measure all energies in units  $\hbar\Omega_{\text{Morse}}$  it is convenient to scale the energy levels in  $V_0$  which gives

$$E_n = \hbar\Omega_{\text{Morse}}[\varepsilon_n + \chi(q_{n+1} - q_{n-1})], \quad (5)$$

with  $\varepsilon_n = E_n^0/\hbar\Omega_{\text{Morse}}$  and  $\chi = \chi_0/\hbar\Omega_{\text{Morse}}$  (recall that to simplify we set  $\chi = 0$ ). Further we consider

the system in a “thermal bath” characterized by a Gaussian white noise,  $\xi_j$ , of zero mean and time delta correlated. For the sake of universality, it is best to rescale quantities and consider a dimensionless problem. We take as unit of time  $\Omega_{\text{Morse}}^{-1}$ . For displacements we take  $B^{-1}$  as the unit, for momenta we take  $(2MD)^{-1/2}$ , for the interaction force we have  $\alpha V_0/2BD$ , and hence  $\alpha$  is measured in  $(B^{-1})$  units. To avoid introducing a new set of variables to denote dimensionless quantities, we simplify our discussion by retaining the same symbols for the dimensional variables as used above. Then, the dynamics of the Hamiltonian system yields the following equations for the components of the electron wave function  $c_n$ , and the lattice vibrations,  $q_n$ ,

$$i \frac{dc_n}{dt} = [\varepsilon_n + \chi(q_{n+1} - q_{n-1})]c_n - \tau \{ \exp[-\alpha(q_{n+1} - q_n)]c_{n+1} + \exp[-\alpha(q_n - q_{n-1})]c_{n-1} \}, \quad (6)$$

$$\begin{aligned} \frac{d^2 q_n}{dt^2} = & \{ 1 - \exp[-(q_{n+1} - q_n)] \} \exp[-(q_{n+1} - q_n)] \\ & - \{ 1 - \exp[-(q_n - q_{n-1})] \} \\ & \times \exp[-(q_n - q_{n-1})] + \chi [c_{n+1}^* c_n - c_{n-1}^* c_n] \\ & - \alpha V \{ (c_{n+1}^* c_n + c_{n+1} c_n^*) \\ & \times \exp[-\alpha(q_{n+1} - q_n)] - (c_n^* c_{n-1} + c_n c_{n-1}^*) \\ & \times \exp[-\alpha(q_n - q_{n-1})] \}, \quad (7) \end{aligned}$$

where the new dimensionless parameters are  $V = V_0/2D$ ,  $\alpha = \alpha_0/B$ , and  $\tau = V_0/\hbar\Omega_{\text{Morse}}$ . Note that  $\tau$  gives the ratio of the two time scales involved in the dynamics which, in frequency terms, refer to ultraviolet/electronic *versus* infrared/acoustic processes for electrons and phonons. For purposes of illustration we shall use the following parameter values:  $\sigma = 4.0 \text{ \AA}$ ,  $B = 4.45 \text{ \AA}^{-1}$ ,  $\alpha = 1.75B$ ,  $D = 0.1 \text{ eV}$ ,  $V_0 = 0.05 \text{ eV}$ ,  $\Omega_{\text{Morse}} = 3.04 \cdot 10^{12} \text{ s}^{-1}$ ,  $v_{\text{sound}} = \sigma\Omega_{\text{Morse}} = 12.1 \text{ \AA/ps}$ ,  $\Omega_{\text{electron}} = V_0/\hbar = 0.608 \cdot 10^{14} \text{ s}^{-1}$ ,  $\tau = 10\text{--}20$ . Muto *et al.* [1989] provided the DNA values, just for comparison, we give here for our Morse potential:  $\sigma = 3.4 \text{ \AA}$ ,  $B = 2.1 \text{ \AA}^{-1}$ ,  $D = 0.23 \text{ eV}$ ,  $\Omega_{\text{Morse}} = 5.0 \cdot 10^{12} \text{ s}^{-1}$ ,  $v_{\text{sound}} = 17 \text{ \AA/ps}$ . All these values are comparable with those used earlier in modeling azurin, as well as for some other biosystems such as the  $\alpha$ -helix [Davydov, 1991; Christiansen & Scott, 1990; Scott, 1992].

The existence of bound states between electrons and lattice deformations in 1d-lattices was studied

in the *continuum* case by Davydov and collaborators ([Brizhik & Davydov, 1983] see also [Cruzeiro-Hansson & Takeno, 1997]) and was studied in a discrete (Morse) lattice model in our previous work [Velarde *et al.*, 2006, 2008a, 2008b; Hennig *et al.*, 2006, 2007]. In principle, this effect may be used as a way to manipulate the transport of electrons between donor and acceptor. Clearly, in our case, we can have a polaron-like effect due to a electron-phonon (or soliton) interaction coupled to lattice solitons, the latter owing to the *anharmonicity* of the lattice vibrations. This permits soliton rather than phonon assisted hopping.

Let us begin with the first model of ET. We can estimate how the path of an electron may be influenced by a soliton generated by an external, mechanical perturbation of the lattice near a localized electron.

The added, excess electron is placed at  $t = 0$  at the donor,  $D$ , located at site  $n = 100$  [Fig. 2(a)]. Due to the electron-lattice interaction ( $\alpha = 1.75$ ) we observe soliton-mediated ET. We see in Fig. 2(a) that the electron moves with the soliton with a slightly *supersonic* velocity  $v_{\text{soliton}} \sim (120/100)v_{\text{sound}}$ , and runs to the right border of the square plot, where we assume that there is the acceptor. This means that the electron is guided by the soliton from D to A. In reality, the electron cannot ride on just a single soliton from donor to acceptor; several solitons must be involved in transport. Therefore, the above given soliton velocity is an upper bound for ET in the lattice. In order to study the superposition and cooperation of several solitons acting on one electron we studied in another computer experiment the evolution of an electron in the field of two solitons. We have observed that as time proceeds there is a splitting of the electron probability density [Fig. 2(b)].

Note that the solitons which we have considered are externally excited. The solitons were launched at some site of the lattice at  $t = 0$  as an initial condition and simultaneously we place the electron at a different site. Note also that temperature plays no role. However, we know that for solitons to be sustained moving unaltered along the lattice, the temperature must be high. Indeed according to the specific heat characteristics of the lattice, the solitons are expected beyond the Dulong–Petit plateau before the melting point of the lattice [Chetverikov *et al.*, 2006a].

Let us consider now a lattice heated to some temperature  $T$ . Then solitons may be excited due

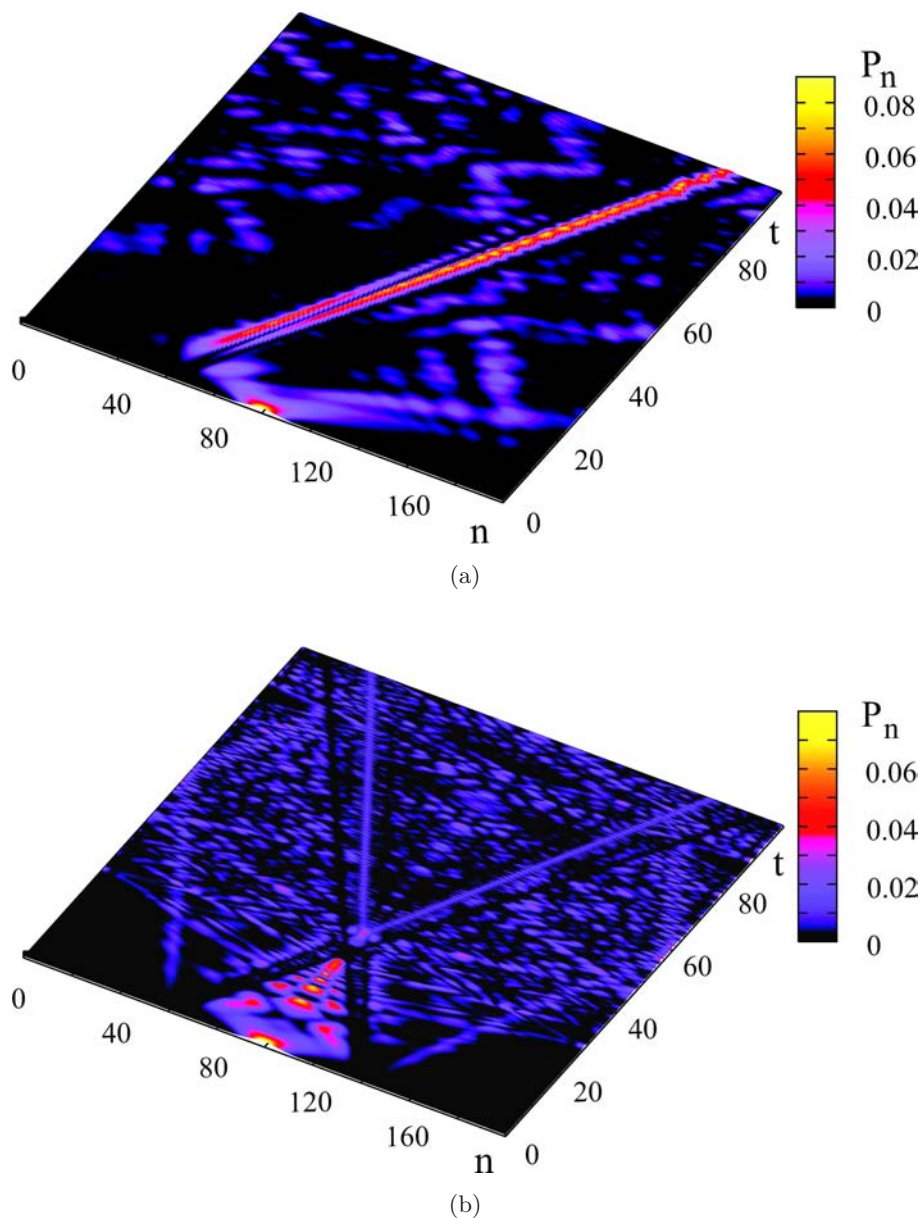


Fig. 2. Morse lattice. (a) Evolution of one electron (in terms of its probability density) starting at lattice site 100 and a soliton starting at lattice site 50. After 10–20 time units of the initial situation the soliton catches the electron and forms a bound state (soliton) which moves with slightly *supersonic* velocity. Parameter  $\alpha = 1.75$ . (b) The motion of an electron starting at position 100 between two solitons emitted at positions 60 and 140. The electron probability density splits between the two solitons, moving away from each other. Parameter  $\alpha = 1.75$ .

to the influence of the thermal imbedding. However we do not have just one or two solitons, but many of them, as well as many phonons, generated by the heat bath. We see up to the range of physiological temperatures many small local solitons in the system which have a finite life-time up to a few picoseconds. The general picture is such that the electron probability 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 another series of computer experiments.

In this series of experiments, we released an electron into a lattice thermally excited by the heat from friction and noise sources. These sources are switched-off at  $t = 0$ . Then the electron is placed at a lattice site. The result is shown in Fig. 3. In Fig. 3(a) we demonstrate the electron density developing in a lattice heated up to  $T = 0.05$ . We see that

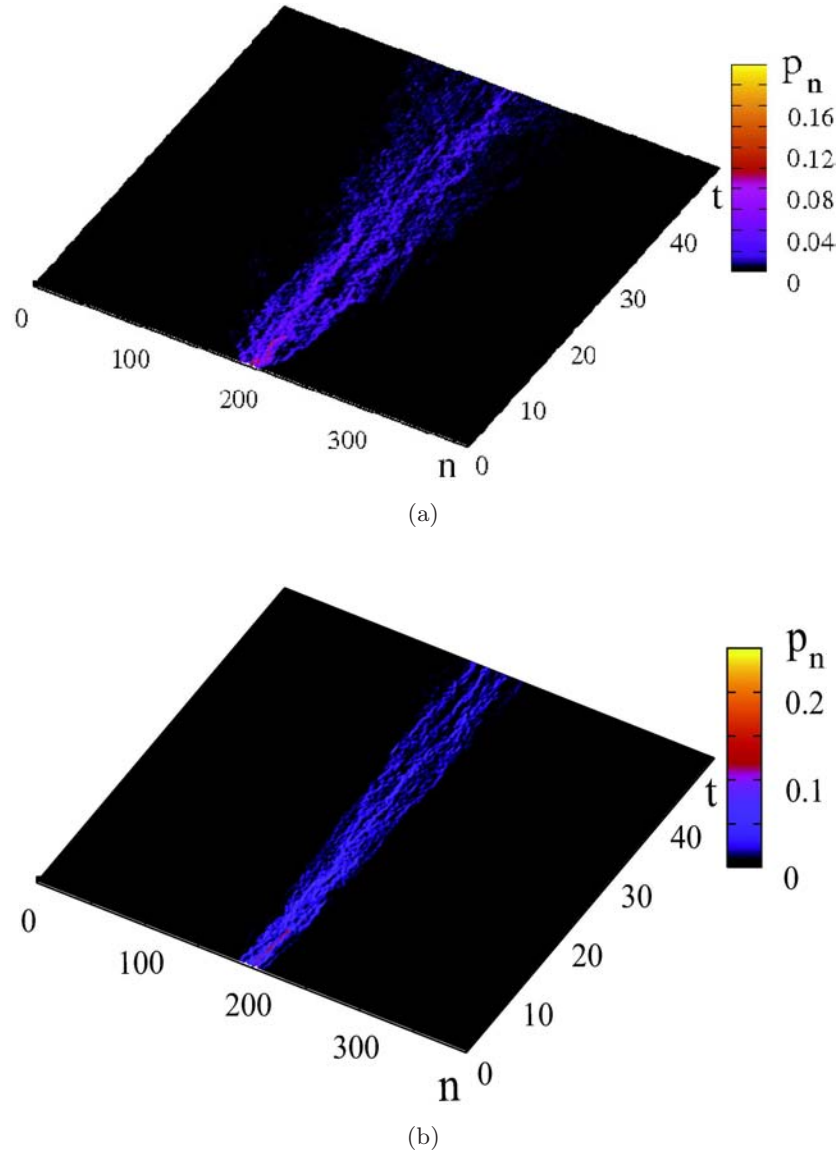


Fig. 3. Heated Morse lattice. (a) An electron is placed at site 200 of a heated lattice ( $T = 0.05$ ,  $\tau = 10$ ,  $\alpha = 1.75$ ). The probability density gets concentrated at places of local soliton excitations (with a size up to 10 lattice sites) and survives there a finite time (may be a few picoseconds). Subsequently, it moves to another “hot spot”. (b) The density of an electron released into a thermal lattice at a higher temperature than in (a) ( $T = 0.5$ ,  $\tau = 10$ ,  $\alpha = 1.75$ ). Again the density is concentrated at places of local soliton excitations and now the cone significantly narrows. Note that the widening of the cone determines the *effective* diffusion constant.

the electron probability density is confined more or less in a cone.

What we see in Figs. 3(a) and 3(b) is that the electron probability density splits into many small spots which are localized at thermally excited solitons. These “hot spots” may comprise up to ten lattice sites each having a short lifetime which is in the range of a few picoseconds [Velarde *et al.*, 2008b]. The little maximum of the electron density “dies” with the soliton and eventually moves to the next local soliton. The overall process is

time-dependent as the “hot spots” are created and annihilated in the thermal process. Note that the spots denote only probabilities. In Fig. 3(b) we see the evolution of the electron density in a lattice heated up to temperature  $T = 0.5$  higher than in Fig. 3(a) ( $T = 0.05$ ). Again the electron density is confined to a cone but the cone occupied by the electron probability density is significantly narrower.

Modeling the net-transfer of the electrons is rather difficult due to the complexity of the life of an electron after injection. At a first glance it

looks like a diffusion-like process. Let us study the question whether ET is indeed a diffusion process. Given the linearity of the Schrödinger equation, the electron probability density spreads analogous to a diffusion process, meaning that the mean square displacement grows linearly in time. On the other hand, as shown by Brizhik and Davydov [1983] the nonlinear Schrödinger equation corresponds to processes which are much more complicated, e.g. the spreading of the probability density may be fractal-like and may even depend on the initial conditions. Thus we cannot assume that ET at  $T = 0$  may be modeled as a diffusion-like process. Given this, we consider a diffusion approach here at temperatures  $T > 0.1$ , since we expect that the thermal motion regularizes the spreading process. We have to study in detail the mean square displacement on the thermally excited lattice. For simplicity, we place the injected electron initially at  $t = 0$  and  $n = n_0$ . The mean square displacement is given by

$$\langle n(t)^2 \rangle = \sum n^2 c_n(t) c_n^*(t), \quad (8)$$

where  $n$  is now defined relatively to  $n_0$  (i.e.  $n - n_0$ ) and  $c_n(t)$  have to be calculated according to the discrete Schrödinger Eq. (7). This procedure gives, however, only the quantum-mechanical mean. We still need here a second average with respect to the stochastic trajectories of the lattice due to Eq. (6). Accordingly, we define diffusion as a function of time

$$d(t) = \langle \langle n(t)^2 \rangle \rangle = \left\langle \sum n^2 c_n(t) c_n^*(t) \right\rangle. \quad (9)$$

The outer bracket means that we have to take the average over many realizations of the lattice dynamics. The result has to be drawn as a function of time. We expect that this function is linear in time at least in certain temperature range. This is what our computer simulations confirm (see Fig. 4).

It is instructive to compare the results found (Figs. 4 and 5) with the results of an earlier stochastic computer simulation using Pauli's master equation shown by the dashed curve in Fig. 5 [Chetverikov *et al.*, 2010]. We see that both approaches disagree at low temperatures. In order to avoid discussing the origin of such discrepancy which may be due to more than one cause not yet very clear to us, we concentrate here in the range  $T > 0.1$ . The diffusion theory tells us that an electron initially placed at position  $n_0$  has a

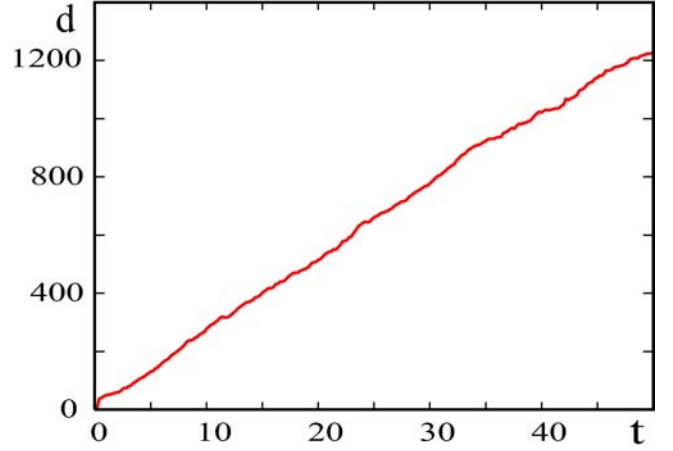


Fig. 4. Heated Morse lattice. The diffusion function  $d$  versus time  $t$  for temperature  $T = 0.5$ .

time-dependent probability density described by

$$\rho(n, t) = \frac{1}{\sqrt{4\pi D_{\text{eff}} t}} C \exp \left[ -\frac{(n - n_0)^2}{4D_{\text{eff}} t} \right]. \quad (10)$$

If we identify  $n_0$  with the donor, this formula shows how the electron density appears at some distance, in particular, at the site where the absorber or acceptor is. The mean square displacement is given by

$$\langle n(t)^2 \rangle = 2D_{\text{eff}} t, \quad (11)$$

thus showing that the distance traveled by the electron goes as the square root of time  $t$ , a relatively

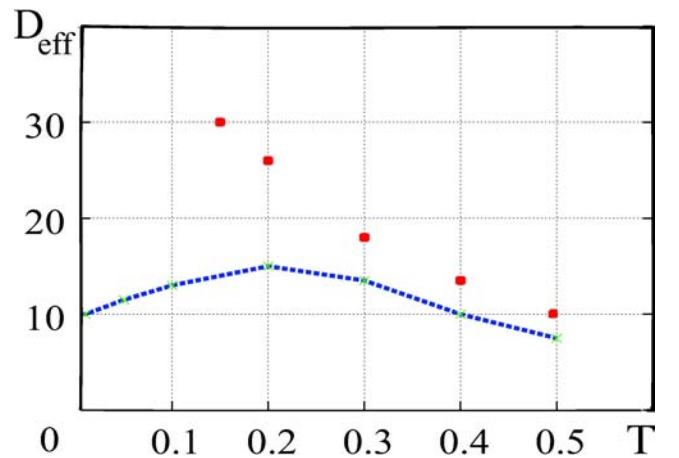


Fig. 5. Heated Morse lattice. The effective diffusion coefficient,  $D_{\text{eff}}$ , of the thermal electron hopping between soliton spots including quantum-mechanical and thermal hopping effects. The points correspond to neglecting the thermal influence and using only quantum-mechanical hopping, whereas the dashed line is based on a stochastic calculation. Values are expected to be significant only for  $T > 0.1$ .

fast mechanism. On the other hand, the probability density decays exponentially with the distance, and hence the *log* of the density decays with the square of the distance from the source. We note that the charge trapping in vibrational hot spots was observed also in a recent work of Kalosakas *et al.* [2003]. On the other hand, most authors report a linear decay of the *log* with the density. This remains still an open problem. Evidently only some ET processes are diffusion-controlled while some others are genuine tunneling processes not considered here.

In the framework of our diffusion model, the process is considered as a diffusion-controlled reaction. Following Smoluchowski theory [Ebeling & Sokolov, 2005], the reaction rate of an electron with probability density  $n_e$  and one absorber with radius  $r_A$  at a fixed position is given by

$$r = n_e r_A D_e. \quad (12)$$

Hence, the rate is proportional to the diffusion coefficient of the electron. The electronic density decreases with the distance and develops in time according to the diffusion law (10). According to our estimate of the diffusion constant, reaction rates based on diffusion would first increase with temperature, then reach a maximum and then decay. The optimal temperature is somewhere around  $T \sim 0.2$  in units of 2D (Fig. 5).

Let us particularize estimates for the two mechanisms studied here. For diffusion transport, the mean square displacement is given by Eq. (11). By returning to quantities with dimensions as Å and picoseconds, the mean square displacement is

$$\langle \Delta x^2 \rangle = 2D_{\text{eff}} t = 2\sigma^2 D'_{\text{eff}} \frac{t}{t_0}, \quad D_{\text{eff}} = \frac{\sigma^2}{t_0} D'_{\text{eff}}. \quad (13)$$

For the dimensionless effective diffusion coefficient  $D'$  we estimate a value around 15 near to the maximum with respect to the temperature. This is about 80 Å/ps in dimensional units which is a value around the maximum and accordingly the mean square displacement is

$$\langle \Delta x(\text{Å})^2 \rangle = 160 \left( \frac{\text{Å}^2}{\text{ps}} \right) t(\text{ps}). \quad (14)$$

Following Chandrasekhar [1943] we may estimate on the basis of the mean square displacement Eq. (14) the time  $t$  which is required to bring the largest part of the probability through an absorbing barrier (the acceptor) at a distance  $l(t)$  from

the start (the donor). Giving the result as *log* of the reciprocal time over the distance  $l(t)$  (in Å), we find

$$\log \left[ \frac{1}{t(s)} \right] = 14.2 - 2 \log \left[ \frac{l(t)}{\text{Å}} \right]. \quad (15)$$

If the electron has the chance to ride on an external mechanically excited soliton from donor to acceptor, it will travel approximately with sound velocity, an estimated distance  $l(t) = ct$ . A sound velocity of 16.9 Å/ps was measured for DNA [Hakim *et al.*, 1984; Wan *et al.*, 1999, 2000]. By using our estimated sound velocity of 10–20 Å/ps we find

$$\log \left[ \frac{1}{t(s)} \right] = 12 + \frac{20}{l(\text{Å})}. \quad (16)$$

Thus the straight ride on external mechanically excited solitons is the most effective transport mechanism, since it yields the shortest time interval for a given distance.

Riding of the electrons on thermal solitons shows the transport mechanism, due to the quick change of thermal soliton directions. However, if one accounts for bond anharmonicity this ride is for free since thermal solitons are always present in biomolecules, at physiological temperature. One cannot exclude that in reality the action of thermal solitons might be complemented by external mechanically excited solitons [Chetverikov *et al.*, 2009a, 2009b, 2010]. A possible candidate of the source for exciting solitons is Volkenstein's "conformon", whereby the displacement of an electron probability density in a biomolecule may cause a significant conformational rearrangement [Volkenstein, 1970]. A similar conclusion has been made recently based on a completely different method [Balabin *et al.*, 2008]. These authors conclude, that "electronic coupling is most likely determined by nonequilibrium geometries beyond a critical distance (6–7 Å in proteins and 2–3 Å in water)". In our work, some kind of "nonequilibrium geometries" are identified as local deformations due to thermal soliton excitations.

## Acknowledgments

The authors wish to express their gratitude to Professors A. S. Alexandrov, E. Brandas, L. Brizhik, L. Cruzeiro-Hansson, P. G. de Gennes (deceased), G. Nicolis and G. Tsironis, for enlightening suggestions. This research has been sponsored by the



European Union under the Grant SPARK-II-FP-7-ICT-216227.

## References

- Ashcroft, N. W. & Mermin, N. D. [1976] *Solid State Physics* (Thomson Learning, Philadelphia).
- Balabin, I. A., Beratan, D. N. & Skoutis, S. S. [2008] “Persistence of structure over fluctuations in biological electron-transfer reactions,” *Phys. Rev. Lett.* **101**, 158102-1-4.
- Bollinger, J. M. [2008] “Electron relay in proteins,” *Science* **320**, 1730-1731.
- Brizhik, L. S. & Davydov, A. S. [1983] “Soliton excitations in one-dimensional molecular systems,” *Phys. Status Sol.* **115**, 615-630.
- Chandrasekhar, S. [1943] “Stochastic problems in physics and astronomy,” *Rev. Mod. Phys.* **15**, 1-89.
- Chetverikov, A. P., Ebeling, W. & Velarde, M. G. [2006a] “Dissipative solitons and complex currents in active lattices,” *Int. J. Bifurcation and Chaos* **16**, 1613-1632.
- Chetverikov, A. P., Ebeling, W. & Velarde, M. G. [2006b] “Non-linear excitations and electric transport in dissipative Morsa-Toda lattices,” *Eur. Phys. J. B* **51**, 87-99.
- Chetverikov, A. P., Ebeling, W. & Velarde, M. G. [2009a] “Electron dynamics in tight-binding approximation – the influence of thermal lattice excitations,” *Contr. Plasma Phys.* **49**, 529-537.
- Chetverikov, A. P., Ebeling, W. & Velarde, M. G. [2009b] “Local electron distributions and diffusion in anharmonic lattices mediated by thermally excited solitons,” *Eur. Phys. J. B* **70**, 217-227.
- Chetverikov, A. P., Ebeling, W. & Velarde, M. G. [2010] “Thermal solitons and solectrons in nonlinear conducting chains,” *Int. J. Quant. Chem.* **110**, 46-61.
- Christiansen, P. L. & Scott, A. C. (eds.) [1990] *Davydov’s Soliton Revisited. Self-Trapping of Vibrational Energy in Proteins* (Plenum Press, NY).
- Crane, B. R., DiBilio, A. J., Winkler, J. R. & Gray, H. B. [2001] “Electron tunneling in single crystals of *pseudomonas aeruginosa* azurins,” *J. Am. Chem. Soc.* **123**, 11623-11631.
- Cruzeiro-Hansson, L. & Takeno, S. [1997] “Davydov model: The quantum, mixed quantum-classical, and full classical systems,” *Phys. Rev. E* **56**, 894-906; and references therein.
- Davydov, A. S. [1991] *Solitons in Molecular Systems*, 2nd edition (Reidel, Dordrecht).
- Ebeling, W. & Sokolov, I. [2005] *Statistical Thermodynamics and Stochastic Theory of Nonequilibrium Systems* (World Scientific, Singapore).
- Gray, H. B. & Winkler, J. R. [2003] “Electron tunneling through proteins,” *Quart. Rev. Biophys.* **36**, 341-372.
- Gray, H. B. & Winkler, J. R. [2005] “Long-range electron transfer,” *Proc. Natl. Acad. Sci. (USA)* **102**, 3534-3539.
- Hakim, M. B., Lindsay, S. M. & Powell, J. [1984] “The speed of sound in DNA,” *Biopolymers* **23**, 1185-1192.
- Hennig, D., Neissner, C., Velarde, M. G. & Ebeling, W. [2006] “Effect of anharmonicity on charge transport in hydrogen-bonded systems,” *Phys. Rev. B* **73**, 024306-1-10.
- Hennig, D., Chetverikov, A. P., Velarde, M. G. & Ebeling, W. [2007] “Electron capture and transport mediated by lattice solitons,” *Phys. Rev. E* **76**, 046602-1-9.
- Holstein, T. [1959] “Studies of polaron motion. I. The molecular-crystal model,” *Ann. Phys. NY* **8**, 325-342.
- Holstein, T. [1981] “Higher-order effects in hopping-type transport of small polarons. II. Quantal occurrence-probability treatment,” *Ann. Phys. NY* **132**, 212-234.
- Hopfield, J. J. [1974] “Electron transfer between biological molecules by thermally activated tunneling,” *Proc. Nat. Acad. Sci. USA* **71**, 3640-3644.
- Kalosakas, G., Aubry, S. & Tsironis, G. P. [1998] “Polaron solutions and normal-mode analysis in the semiclassical Holstein model,” *Phys. Rev. B* **58**, 3094-3104.
- Kalosakas, G., Rasmussen, K. O. & Bishop, A. R. [2003] “Charge trapping in DNA due to intrinsic vibrational hot spots,” *J. Chem. Phys.* **118**, 3731-3735.
- Marcus, R. A. [1956] “On the theory of oxidation-reduction reactions involving electron transfer. I,” *J. Chem. Phys.* **24**, 966-978.
- Marcus, R. A. & Sutin, N. [1985] “Electron transfer in chemistry and biology,” *Biochim. Biophys. Acta* **811**, 265-322.
- Marcus, R. A. [1999] “Electron transfer, past and future,” *Adv. Chem. Phys.* **106**, 1-6.
- Muto, V., Scott, A. C. & Christiansen, P. L. [1989] “Thermally generated solitons in a Toda lattice model of DNA,” *Phys. Lett. A* **136**, 33-36.
- Potasek, M. J., Hopfield, J. J. [1977] “Experimental test of the vibronically coupled tunneling description of biological electron transfer,” *Proc. Natl. Acad. Sci. USA* **74**, 229-233.
- Scott, A. C. [1992] “Davydov’s soliton,” *Phys. Rep.* **217**, 1-67.
- Shih, C., Museth, A. K., Abrahamsson, M., Blanco-Rodriguez, A. M., Di Bilio, A. J., Sudhamsu, J., Crane, B. R., Ronayne, K. L., Towrie, M., Vleck, A., Richards, J. H., Winkler, J. R. & Gray, H. B. [2008] “Tryptophan-accelerated electron flow through proteins,” *Science* **320**, 1760-1762.
- Toda, M. [1989] *Theory of Nonlinear Lattices*, 2nd edition (Springer-Verlag, Berlin).
- Velarde, M. G., Ebeling, W. & Chetverikov, A. P. [2005] “On the possibility of electric conduction mediated by dissipative solitons,” *Int. J. Bifurcation and Chaos* **15**, 245-251.

- Velarde, M. G., Ebeling, W., Hennig, D. & Neissner, C. [2006] "On soliton-mediated fast electric conduction in a nonlinear lattice with Morse interactions," *Int. J. Bifurcation and Chaos* **16**, 1035–1039.
- Velarde, M. G., Ebeling, W., Chetverikov, A. P. & Hennig, D. [2008a] "Electron trapping by solitons classical versus quantum mechanical approaches," *Int. J. Bifurcation and Chaos* **18**, 521–526.
- Velarde, M. G., Ebeling, W. & Chetverikov, A. P. [2008b] "Thermal solitons and solitons in 1D anharmonic lattices up to physiological temperatures," *Int. J. Bifurcation and Chaos* **18**, 3815–3823.
- Volkenstein, M. V. [1983] *Biophysics* (Mir, Moscow) Sections 6.6. and 13.4 and references therein.
- Wan, C., Fiebig, T., Kelley, S. O., Treadway, C. R., Barton, J. K. & Zewail, A. H. [1999] "Femtosecond dynamics of DNA-mediated electron transfer," *Proc. Natl. Acad. Sci. USA* **96**, 6014–6019.
- Wan, C., Fiebig, T., Schiemann, O., Barton, J. K. & Zewail, A. H. [2000] "Femtosecond direct observation of charge transfer between bases in DNA," *Proc. Natl. Acad. Sci. USA* **97**, 14052–14055.
- Winkler, J. R., Nocera, D. G., Yocom, K. M., Bordignon, E. & Gray, H. B. [1982] "Electron-transfer kinetics of pentaammineruthenium (III) (histidine-33)-ferricytochrome c. Measurement of the rate of intramolecular electron transfer between redox centers separated by 15.Å in a protein," *J. Amer. Chem. Soc.* **104**, 5798–5800.
- Winkler, J. R. [2000] "Electron tunneling pathways in proteins," *Curr. Opin. Chem. Biol.* **4**, 192–198.