

About electron transfer over long distances with tunable sub/supersonic velocities

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ABSTRACT

Provided in this paper is a theory of long-range electron transfer with near sound (supersonic or subsonic) velocity along one-dimensional crystal lattices. The theory represents the development of an earlier work by introducing Marcus formulation. To illustrate its application to a realistic case, the theory is used to offer an explanation of two puzzling observations made by Donovan and Wilson in transient photoconduction experiments with non-dopable perfectly crystalline polydiacetylene crystals in the presence of an electric field: transport velocity value close to sound velocity being independent of field for four orders of magnitude of field (10^2 V/m– 10^6 V/m) and, in the low field values, an ultra-high mobility greater than $20 \text{ m}^2/\text{V s}$. We also study factors eventually leading to lowering of the transport velocity.

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I. INTRODUCTION

One of the most elementary chemical steps consists in bringing an electron from a donor site to an acceptor site where some reaction may be initiated. In a path breaking series of papers, Marcus provided deep insight with an elegant and successful theory^{1–6} (see also the study of Hush⁷). Apparent limitations of the theory are travel distances only in the 20 Å range and the difficulty to take into account the detailed chemical structure of matter separating the donor and acceptor sites. In particular, it is not possible to define a velocity of the transferred electron under such conditions.

Recently, travel distances in the range of 20 nm and more and, on occasion, with supersonic velocity of the charge carrier have been observed.^{8–13} In the present paper, we propose a model theory approach to the electron transfer (ET) problem in one-dimensional (1D) crystal lattices (the theory also exists for two-dimensional crystal lattices, but we shall not consider this case here). The model is based on the use of nonlinear carriers that when binding an electron permit both the travel distance in the 20 nm range and beyond and traveling super- or subsonically. This depends on the values of parameters, such as the electron–lattice distortion interaction (akin to the electron–phonon interaction). We refer to wave-like excitations in arrays/chains/lattices of units such as atoms, molecules, and

the like (expecting no confusion; in the following, we shall be interchangeably using unit, site, or cell). The units can exhibit on-site vibrations and/or inter-site (otherwise said, bond) elongations due to potential functions such as harmonic or anharmonic (for instance, Morse potentials¹⁴).

With inter-site Morse potentials, there is the possibility of traveling nonlinear crystal lattice distortions in the form of soliton-like waves, i.e., waves that can propagate supersonically along the solid keeping their shape without change of form.^{15–21} Other possible traveling localized crystal lattice distortions are discrete breathers [DB, aka intrinsic localized modes (ILM)].^{22,23} Then, if one such soliton lattice distortion binds an electron (the argument applies *verbatim* to a positive hole), the soliton–electron compound would be the appropriate transport quasiparticle, like the polaron in the case of a harmonic crystal lattice.^{24–31}

Soliton-assisted transport, although starting with harmonic interactions, has also been advanced by Davydov and co-workers^{32–34} (see also Ref. 35–41), by Heeger, Schrieffer, and co-workers (SSH) with their so-called Hamiltonian for dopable and messy, poorly crystalline polymer crystal like *trans*-polyacetylene (tPA) and related so-called “synthetic metals,”^{42,43} and by Wilson for the non-dopable perfectly crystalline polydiacetylene (PDA) crystal.⁴⁴ Davydov started with a harmonic crystal lattice Hamiltonian with an added excess electron. Then, making use of the nonlinear electron–phonon interaction and an adequate passage from the discrete lattice to the continuum approximation, he was able to reformulate the problem as one of a soliton-bearing dynamic evolution equation. Unfortunately, Davydov’s predictions—at that level—were not supported by experiment nor did they survive going to temperatures beyond a few K,³⁶ although this result was not without criticism.⁴¹ The instability at a few K is a property of the CO vibration localized in an acoustic lattice distortion. There is much greater stability for an electron localized in an acoustic instability.⁴⁴ In the decades 1980–1990, Davydov and co-workers (Chap. 6 of Refs. 34 and 40) extended the original theory by using Hamiltonians with cubic and quartic anharmonic interactions, thus allowing for supersonic soliton-assisted charge transport with, once more, all results studied only at 0 K. The SSH Hamiltonian builds on the degeneracy of the ground state and the tight binding approximation (TBA, in short) to account for band formation as a means of electron transport. Still today, there is no unifying theory accounting for conduction in the whole range of doping fraction of such dopable polymers.

It seems worth emphasizing that PDA is a perfect crystal and it is non-dopable. The latter constitutes an advantage because there is no disorder introduced by counterions. Furthermore, PDA is composed of parallel long π conjugated carbon chains spaced apart by inert side groups such that their interchain distance is sufficiently large and the π -electron transfer between chains is not possible. Thus, they appear as perfect 1D transport lines. Donovan and Wilson measured the time dependent photocurrent created by a single light pulse of typically 5 ns duration. Such a current created at the end of the pulse is due to the product of the charge created and the velocity of the charge. These authors were able to establish the amount of charge created by means of experiments unique to the high one dimensionality of the crystal (which they called “cuts”⁴⁵ and “walls”⁴⁶ experiments). In this way, the velocity of the charge carriers was measured. The great surprise was the

constancy of this velocity close to the sound velocity over four decades of electric field (10^2 V/m– 10^6 V/m) and an ultra-high mobility, greater than $20 \text{ m}^2/\text{V s}$ in the presence of an electric field. This is the opposite of the almost universal existence of a charge velocity linearly dependent on field in metals, semiconductors, and ions in solution. However, these striking findings for a non-dopable, perfect polymer crystal passed unnoticed in the literature, most surely because of the great success achieved with the dopable conducting polymers. It is this extraordinary experimental establishment of such features that is given an explanation in the present paper.

The theory developed by Wilson⁴⁴ aimed at explaining charge transport features of the PDA crystal.^{45–50} Building upon the SSH approach—with, however, no degeneracy of the ground state in PDA—and following Davydov’s approach (distortion-dependent electron transfer), he advanced the concept of solitary wave acoustic polaron (SWAP) as the charge carrier, whose stability was also studied,⁴⁴ clearly extending the original polaron realm into the soliton-like assisted transport, and quite a different mechanism for transport relative to the dopable PA family. As in the cases of Davydov and the SSH theory, although the lattice dynamics enters well beyond the simplest induced lattice distortion, we still have, as in the standard polaron case, a genuine electronic excitation, since without the added excess electron, there is no evidence for the crystal excitation.

Extending historical works on the polaron,^{51,52} one expects that when the lattice inter-unit distance is modified during the wave passage, this, in turn, modifies the rate of energy or charge transfer between two adjacent sites. In the case of an electron transfer, we can thus imagine a situation where the electron would “surf” on the wave as the soliton–electron compound forms a kind of bound state (denoted as solelectron). The latter is thus different from the polaron and the transport quasiparticles introduced to account for electron transport in tPA and the other so-called synthetic metals, as well as different from Wilson’s SWAP concept. In the solelectron case, there is already a crystal lattice carrier, the soliton, capable of traveling and transport at supersonic velocities. Once this is identified, we can add an excess electron or other, thus leading to the mentioned compound/bound state. Note that when adding an excess electron, there is indeed a polaron effect that can be considered as a weak, negligible disturbance upon the stronger one leading to the solelectron.⁵³ If so, we can safely speak of mechanical control of electron transfer at the nanolevel. The solelectron velocity is going to depend on the strength of the electron–lattice distortion interaction, hence offering the possibility of super- or subsonic transport.^{54–61} Note-worthy is that in a crystal lattice with Morse interactions, solitons are expected to be significant lattice disturbances at temperatures above the Dulong–Petit plateau in the specific heat, which is past the Debye temperature. It has been shown that in such a crystal lattice, solitons survive when heating the system to, say, physiological temperatures (~ 300 K). The same has also been shown for solelectrons formed in such a crystal lattice model.^{62–65} In view of the above, we shall not dwell on the temperature influence in our problem here.

It seems also pertinent to insist in that in the polaron realm or in Davydov’s theory or in the SSH theory for dopable conducting polymers or in Wilson’s theory for PDA, the charge transport is ensured by an applied electric field. In the case of soliton-assisted/solelectron

transport, i.e., with an electron surfing on a soliton wave crystal lattice distortion, the motion of the charge follows that of the soliton wave, as the former is slaved by the latter, thus offering the possibility of transport in the absence of an applied electric field. Let us also insist that at variance with the polaron, as we here have the traveling soliton before any excess charge is added to the crystal lattice, there is indeed a clear case of mechanical control of the electron/charge at the nanolevel. For the related problem of electron surfing on (however, high amplitude is always linear) surface acoustic waves, see Ref. 59. For real cases where soliton-assisted transport would be possible, it seems clear that long distance transport (surely in the 20 nm range and beyond) and tunable sub/supersonic velocities are to be expected. In view of the above, we see a connection between the idea of going beyond Marcus theory and presenting a theory that tries to account, the proper way, for the features observed in PDA.

On-site motions changing the vibrational and electronic energy of a given unit (independent of the inter-site distance) have a long story. They are encountered in solid state physics in small-polaron theory, for instance, in the work of Holstein starting in 1959.²⁸ In solution chemistry, there is an analogous effect (complicated by the fact that the units are randomly distributed) leading to the theory of electron transfer developed by Marcus^{1–6} and also by Hush.⁷ In molecular mixed-valence compounds, there are typically two possible localization sites for one electron, and the intramolecular electron transfer rate depends on the competition between an electronic interaction factor and a site-localized distortion analogous to the polaron distortion.^{66–69} Worth also being recalled is that intramolecular electron transfer between a donor and an acceptor site can be monitored over long distances,^{70–73} and its distance dependence is frequently assigned to the decay of the (indirect) electronic coupling between donor and acceptor, the process being one-step. Another mechanism is the multiple hopping mechanism with charge localization on intermediate bridging sites,^{8–12} but the hops are uncorrelated (drunken sailor walk). By contrast, the system studied in the present paper will present soliton-like coherent motion.

Of course, the on-site motion introduces the possibility of the trapping of the electron in a potential well created by its own presence. Extracting from the well then requires a thermal activation, which is a slow and random process, incompatible with the coherent character of the soliton propagation. Thus, the main question addressed in the present paper is as follows: How far can we go without destroying the appealing soliton process? Note that in a similar preoccupation, Mozafari and Stafström have elaborated a model with an on-site degree of freedom, but since, like Davydov, SSH, and Wilson, their used potentials are harmonic,^{74–76} the model cannot describe non-linear effects of the soliton type in the absence of an added excess charge.

The paper is thus organized as follows: In Sec. II, inspired by Marcus seminal concepts on electron transfer (ET) and by Fröhlich emphasis about the significant role to be played by the dynamics of the crystal lattice on the electron–lattice cooperative behavior, albeit with consideration of only harmonic interactions, we present the basic features of the model bridge between donor and acceptor, identifying its Hamiltonian with Morse interactions and also introducing, in a simplifying approach, an “effective” on-site degree

of freedom. In Sec. III, we discuss the parameters and their realistic values, which could be convenient for the emblematic PDA and related sulfonate derivatives. Section IV is devoted to the results of computer simulations of the dynamical evolution (soliton-like wave and electron probability densities). In Sec. V, we illustrate the role of an external electric field and its interplay with the soliton dynamics, thus allowing estimating the range of values where there is possible field-independent electron transfer and, consequently, the ultra-high mobility. Finally, in Sec. VI, we summarize the major results found and a few concluding remarks targeting experiments.

II. DESCRIPTION OF THE MODEL

Taking into account the large disparity between the large mass of the lattice units relative to the much smaller of the electron, we shall be considering a mixed classical–quantum model. The classical part will be accounting for the Newtonian dynamics and evolution of the crystal lattice units in their allowed on-site vibrations and in their relative motions (inter-site elongation/bond changes). As usual with this commonly used type of Molecular Dynamics, the classical motion is based on the Ehrenfest approximation allowing defining the force acting on nuclei from the derivative of the energy. However, this approach could be questioned as it can lead to an underestimation of the polaron extension, or a bad description of excited electronic states.^{77,78} However, in the present case, we still believe that the Ehrenfest approach could capture the essential features of the process because we are concerned with low-energy excitations without an electronic component. We estimate the soliton energy, coming essentially from the soliton part, at about 1.3 eV, which is much lower than typical energies for excited electronic states such as Frenkel excitons.⁷⁸ In addition, due to the complexity of the molecule, there would be too many vibrational modes to combine in order to get a full quantum description. By contrast with nuclei, the excess electron dynamics follows Schrödinger evolution on the discrete crystal lattice support using the Hückel approximation (TBA in solid state physics). Thus, the principle is to describe units classically by their potential and kinetic energy, but electrons quantum mechanically, i.e., they are characterized by their total energy without decomposition into potential and kinetic energy. For illustration and in view of the comments made in the introduction, we shall focus attention to PDA having in mind the Marcus approach. Starting from its known structure illustrated in Fig. 1, we define a site (or unit cell) as a C₄R₂ group (C₄, in short). An excess electron is added to generate the charge carrier.

Working one step at a time, in the first step, we start neglecting the internal structure of the unit cell and model the crystal lattice units as point particles (solid spheres) as shown in Fig. 2. Schematically, each sphere represents a C₄R₂ block, the quantity $V_{n,n-1}$ accounts for the electronic coupling between the blocks, and ϵ_n is the electronic energy of a block (in chemical terms, the energy of the Lowest Unoccupied Molecular Orbital—LUMO).

The Hamiltonian is decomposed as H_{lattice} (a scalar) and $\widehat{H}_{\text{elec}}$ (an operator acting only on the added excess electron wavefunction). The latter contains the electron–phonon (more precisely here the lattice deformation) coupling term. It is of the Peierls type because

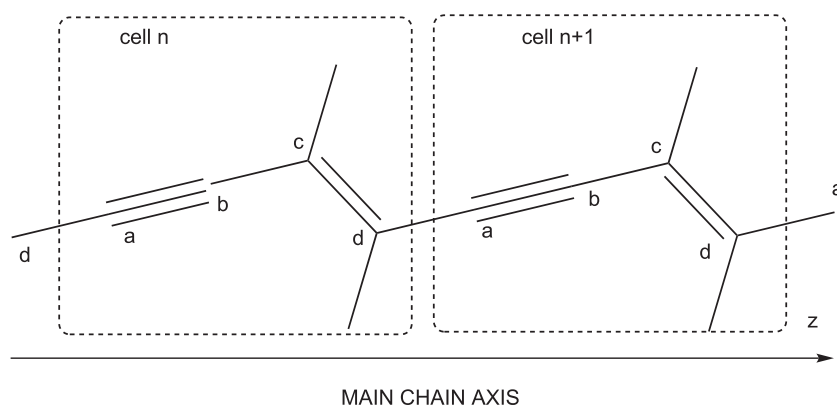


FIG. 1. PDA structure. The unit cell is a block with carbon atoms with an alternation of single and multiple (double or triple) bonds. Carbon atoms labeled (c) and (d) bear bulky substituents R.

the electron motion is assumed to modify only the inter-site distance and thus only the $V_{n,n-1}$ term.⁵¹ We have

$$H_{\text{latt}} = \sum_n \left(\frac{p_n^2}{2M} + U_{(n,n+1)}^M \right), \quad (1)$$

where $U_{(n,n+1)}^M$, with $r = x_{n+1} - x_n$, is Morse's potential function $U_{(r)}^M = D(e^{-2br} - 2e^{-br})$ ensuring anharmonicity of the inter-site bonds. The quantity x_n is the displacement of the n th unit (of mass M as all units are assumed to have equal mass) with respect to its initial equilibrium position, p_n is its corresponding momentum, b accounts for the stiffness of the Morse potential (at vanishing b , we recover the harmonic potential, and at very large values of b , we tend to the hard-sphere model), and D is the potential well depth or dissociation energy parameter of the Morse potential.

In second-quantization formalism, we set

$$\widehat{H}_{\text{elec}} = \sum_n \varepsilon_n \widehat{c}_n^\dagger \widehat{c}_n - \sum_n V_{n,n-1} (\widehat{c}_n^\dagger \widehat{c}_{n-1} + \widehat{c}_{n-1}^\dagger \widehat{c}_n), \quad (2)$$

with $\widehat{c}_n$ and $\widehat{c}_n^\dagger$ denoting annihilation and creation operators of an electron at site " n ." The one-electron wave function is decomposed into localized functions $|\Psi(t)\rangle = \sum_n c_n(t) |\varphi_n\rangle$, where $|\varphi_n\rangle$ is a wave function localized at site " n " and the time dependence is carried exclusively by the $c_n(t)$ coefficient. $V_{n,n-1}$ is the absolute value of the electronic coupling, which is strictly speaking negative and hence the $-$ sign in (2). Expecting no confusion, we shall be using the same letter " c " for the operators and for the numbers/probabilities. Then, noting that $\sum_n |c_n|^2 = 1$, it follows in numbers (TBA),

$$H_{\text{elec}} = \sum_n \varepsilon_n c_n c_n^* - \sum_n V_{n,n-1} (c_n^* c_{n-1} + c_n c_{n-1}^*). \quad (2')$$



FIG. 2. Crystal lattice model of the periodic 1D structure. The unit cells are symbolized by spheres. Each unit cell is characterized by an electronic energy, ε_n . The electronic interaction between units is denoted as $V_{n,n-1}$ and depends on their relative distance.

Following the study of Slater,⁷⁹ the inter-site dependence of the overlapping/hopping/transfer integrals between nearest-neighbors (Fig. 2), $V_{n,n-1}$, is taken in exponential form

$$V_{n,n-1} = V_0 \exp[-\alpha_{\text{SL}}(x_n - x_{n-1})], \quad (3)$$

where V_0 is the value of the electronic coupling for the initial equilibrium crystal lattice inter-site distance. Note that in the so-called SSH Hamiltonian used to describe the dynamics of tPA and the like, expression (3) is given in its linear approximation. Accordingly, our α_{SL} has dimension of length^{-1} , whereas the corresponding α_{SSH} parameter has dimensions of $\text{energy} \cdot \text{length}^{-1}$. Clearly, this parameter regulates how much the $V_{n,n-1}$ are influenced by the relative inter-site elongations along the lattice bridge.

For universality in the argument, we make use of the natural scales in the problem to appropriately make all quantities dimensionless. Thus, we take $1/b$ as the length unit and $1/\omega_M$ as the time unit with the angular frequency unit $\omega_M = (K/M)^{1/2} = (2Db^2/M)^{1/2}$. This angular frequency corresponds to the oscillatory motion associated with the harmonic approximation to the Morse potential using K as spring constant. Then, for energy, the unit is $2D$, and for space displacements, $1/b$; hence, $q_n = bx_n$ and $\alpha_{\text{SL}} = ba$. Note that it is not necessary to define a mass unit, the role of mass being introduced in ω_M , which in turn defines the time unit. The dimensionless electronic coupling is taken as $V = V_0/2D$.

In view of the above, the dynamics and evolution of our classical-quantum system are given by two sets of coupled differential equations: one is Newton's equations where the acceleration of a given unit is computed from its mass and the force acting on it, which is itself obtained from the derivative of

potential energy with respect to its corresponding atomic coordinate, and the other is a set of discrete Schrödinger equations, coming from the Time Dependent Schrödinger Equation (TDSE), $i\hbar \frac{d}{dt}|\Psi\rangle = \hat{H}|\Psi\rangle$ projected on each basis state [recall expression (2') given above]. Thus, assuming for simplicity $\varepsilon_n = 0$ (this corresponds to all ε_n being equal and hence shifting adequately the energy origin), we have

$$\frac{d^2 q_n}{dt^2} = \left[1 - e^{(q_n - q_{n+1})}\right] e^{(q_n - q_{n+1})} - \left[1 - e^{(q_{n-1} - q_n)}\right] e^{(q_{n-1} - q_n)} + 2\alpha V \left[\text{Re}(c_{n+1} c_n^*) e^{\alpha(q_n - q_{n+1})} - \text{Re}(c_n c_{n-1}^*) e^{\alpha(q_{n-1} - q_n)} \right], \quad (4)$$

$$\frac{dc_n}{dt} = i\tau \left[c_{n+1} e^{\alpha(q_n - q_{n+1})} + c_{n-1} e^{\alpha(q_{n-1} - q_n)} \right], \quad (5)$$

where τ , defined by the ratio $V_0/\hbar\omega_M$, allows the comparison of the time scales associated with the electron dynamics and crystal lattice unit motions, respectively (which in frequency terms refer to ultraviolet/electronic vs infrared/acoustic). These equations can be solved by alternate iteration using the Runge–Kutta method. This corresponds qualitatively to the following sequence of events: (a) units move, (b) then electron transfer occurs preferentially between units that are nearest at this moment, (c) units move again as a consequence of the previous motion (continuity of their kinetic energy) and the newly created electronic interaction, and so on. Results from computer simulations of the dynamics defined by Eqs. (4) and (5) can be found in Ref. 58.

Now, we proceed to a second step in our description of the system by focusing on the internal structure and corresponding degrees of freedom of the units/cells. Describing explicitly the complete deformation of the C_4R_2 block would need several parameters.⁸⁰ Hence, although the change in geometry of the unit cell upon addition or removal of an electron involves several bond length and angle changes inside the C_4R_2 block, for sake of simplicity, we introduce a single on-site fictitious, “effective” intra-site bond length and its corresponding energy. This is the “Holstein coupling.”²⁸ For molecular chemistry in solution, a similar process was identified in the 1955–1965 period by Marcus.^{1,2,5} Mathematically, we simply add a linear term Aw_n (A for the electron–phonon constant and w_n a quantity linked to intra-site bond lengths) in the diagonal term ε_n of the electronic Hamiltonian.⁶⁹ Holstein models are common, but until now, no examples have been published with the association of Holstein coupling, Peierls coupling, and anharmonicity. Treatments combining the Peierls and Holstein couplings (but not anharmonicity) appeared recently. One can quote the study of Girlando *et al.*⁸¹ on molecular organic semiconductors with the role of high-frequency or low frequency phonons, that of Shuai *et al.*⁸² on the charge mobility in organic materials starting with the identification of several regimes (self-trapping with hopping, scattering by Holstein–Peierls mechanism, and interaction with acoustic phonons), and the work of Mozafari and Stafström,^{74–76} studying the behavior of two-dimensional molecular crystal systems from the point of view of the competition between electron–phonon coupling and transfer integral.

Introducing such an additional “effective” single degree of freedom, the modification bears on the diagonal term of the electronic Hamiltonian,

$$\varepsilon_n = \varepsilon_0 + Aw_n \quad (6)$$

and also on the lattice Hamiltonian, which becomes

$$H_{latt} = \sum_n \left[\left(\frac{p_n^2}{2M} + U^M_{n,n+1} \right) + \left(\frac{p_{f,n}^2}{2M_f} + \frac{1}{2} k_f w_n^2 \right) \right], \quad (7)$$

where the contribution of the additional degree of freedom is represented by the term in the second parenthesis. The spring constant, k_f , is an “effective” spring force constant and m_f is its corresponding “effective” mass associated with the “off-bridge” on-site motion in our simplifying fictitious albeit representative form of the cells (hence the index “f”). This simplification with a parabolic potential energy is well in the spirit of Marcus approach.^{74–76,83} Then, the effect of the coupling is to replace the potential energy $1/2 k_f w_n^2$ by $1/2 k_f w_n^2 + Aw_n$. It is still a parabolic potential, but the location of its minimum has been shifted and occurs at a lower energy, as illustrated in Fig. 3.

Figure 4 schematically illustrates the structure of the crystal lattice bridge with units having internal structure, denoted by cells. This permits the depiction of the evolution in the system as a sequence of the following steps:

- Step 1: the cell $n - 1$ containing the extra electron has moved to the right by the quantity q_{n-1} .
- Step 2: since $V_{n-1,n}$ has been strongly increased, the electron transfer to site n is possible.
- Step 3: as a result of the presence of the electron at site n , the bond lengths change inside this site and also inside cell $n - 1$ (changes in w_n and w_{n-1}). This modifies the electron energy and could hinder the subsequent electron transfer (this is the usual effect of polaron formation).
- Step 3': at the same time, unit at site n is pushed to the right because of the strong repulsive interaction between $n - 1$ and n .
- Step 4: electron transfer to $n + 1$.

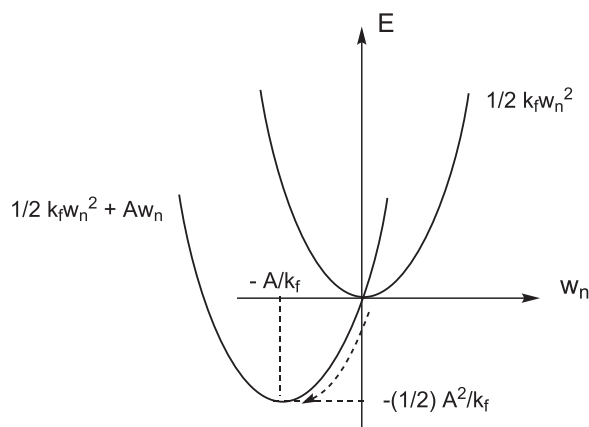


FIG. 3. Effect of the addition of the linear term Aw_n on the parabolic potential energy curve. The addition of an excess electron has two consequences: a change in equilibrium geometry and a relaxation process with stabilization of the system.

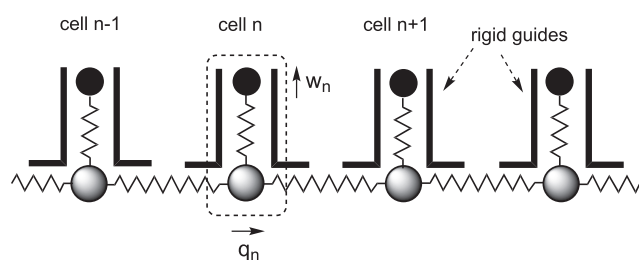


FIG. 4. Schematic mechanical analogue of the crystal lattice bridge model with both inter-site elongations and on-site vibrations. Exaggerated to emphasize the significant role played by on-site vibrations. Upon the passage of a soliton along the main (horizontal) axis, the n th cell moves as a whole. The on-site w_n motion is here taken independent of the q_n motion.

As in the earlier presented model without on-site motion, we now express internal on-site accelerations using Newton dynamics, and for the time evolution of the added excess electron wave function, we continue using the discretized Schrödinger equations on the crystal lattice. Then, as both dynamics are coupled together, the more complete problem dynamics and evolution have an additional Newton equation describing the motion of the w_n coordinate at each site. In dimensionless form, the latter is bw_n , but to simplify notation, we shall use w_n in the following. We have

$$\frac{d^2 w_n}{dt^2} = -\omega_f^2 w_n - A_1 |c_n|^2, \quad (8)$$

where ω_f the angular frequency of on-site vibration is given by

$$\omega_f = (k_f/m_f)^{1/2}/\omega_M \quad (9)$$

and A_1 is a quantity estimating the influence of the added excess electron upon the off-bridge motions as we shall see below.

In addition, a new term ($-iA_2 w_n c_n$) appears in the discretized Schrödinger equation,

$$\frac{dc_n}{dt} = i\tau \left[c_{n+1} e^{\alpha(q_n - q_{n+1})} + c_{n-1} e^{\alpha(q_{n-1} - q_n)} \right] - iA_2 w_n c_n. \quad (10)$$

Indeed, for electron transfer to occur (c_n changes with time), an additional condition must be fulfilled: the on-site w_n coordinate must be “adapted,” as done in the Marcus approach.

In Eqs. (8) and (10), two new dimensionless parameters, A_1 and A_2 , appear, which derive from the electron–phonon coupling constant A . They are given by

$$A_1 = A \frac{b}{m_f \omega_M^2} = A \frac{M}{m_f 2Db} \quad \text{and} \quad A_2 = \frac{A}{\hbar \omega_M b}. \quad (11)$$

It clearly appears that Eqs. (8) and (10) are coupled together. On the one hand, A_1 accounts for the c_n dependence of the on-site motion, i.e., dependence on the electronic population at site n . On the other hand, the role of A_2 is to take care of the influence of w_n , i.e., the specific state (geometry) of site n , on the rate of variation of c_n with time (electron leaving or departing site n). As Eq. (8) describes a harmonic oscillator with frequency ω_f under the action of an external force proportional to $|c_n|^2$, this implies that the interaction of the added excess electron with the blocks is of a resonance kind. This is most effective when its frequency, ω_f , is close to the harmonics of the oscillation frequency associated with the crystal lattice. The latter is indeed assumed to be lower (see the details below in Sec. III). For illustration, we shall consider the cases $\omega_f = 3$ and $\omega_f = 2$ (in dimensionless terms, the angular frequency ω_f is two or three times higher than the ω_M of the crystal lattice bridge).

Before proceeding further, it seems convenient to introduce the following change of variable:

$$g_n = \left(\frac{dw_n}{dt} + i\omega_f w_n \right) e^{-i\omega_f t}, \quad (12)$$

TABLE I. Values of the used parameters. Parameters in italics are not independent, but computed from others.

Parameters group	Parameter	Symbol	Value or range
Bond between C4 units	Equilibrium distance		1.4 Å
	Dissociation energy	D	3.65 eV
	Force constant	K	13 eV Å ⁻² –20 eV Å ⁻²
	<i>Stiffness Morse potential</i>	<i>b</i>	1.33 Å ⁻¹
Mass of the moving unit and associated angular frequency	Mass of the moving unit	M	8 × 10 ⁻²⁶ kg–24 × 10 ⁻²⁶ kg
	<i>Angular frequency</i>	<i>ω_M</i>	4 × 10 ¹³ rad/s–5 × 10 ¹³ rad/s
Intersite electronic interaction	Electronic interaction	V ₀	0.78 eV
	Rate of decay with distance	α _{SL}	2.6 Å ⁻¹
Effective on-site motion	Mass	m _f	2 × 10 ⁻²⁶ kg–4 × 10 ⁻²⁶ kg
	Force constant	k _f	60 eV Å ⁻²
	<i>Angular frequency</i>	<i>ω_f</i>	1.55 × 10 ¹⁴ rad/s
	El–ph coupling	A	5.1 eV Å ⁻¹
Electron–phonon coupling with the on-site motion	<i>Derived parameter</i>	A ₁	1–6
	<i>Derived parameter</i>	A ₂	90–200

which, taking into account (8), yields

$$\frac{dg_n}{dt} = -A_1 |c_n|^2 e^{-i\omega_f t}. \quad (13)$$

From (12), we get

$$w_n = \frac{1}{\omega_f} \text{Im}(g_n e^{i\omega_f t}) \quad (14)$$

that when inserted in the discretized Schrödinger equation (10) gives

$$\frac{dc_n}{dt} = i\tau \left[c_{n+1} e^{a(q_n - q_{n+1})} + c_{n-1} e^{a(q_{n-1} - q_n)} \right] - i \frac{A_2 c_n}{\omega_f} \text{Im}(g_n e^{i\omega_f t}). \quad (15)$$

The modulus of g_n determines the vibrational energy of n th oscillator,

$$E_n = \frac{1}{2} \left(\frac{dw_n}{dt} \right)^2 + \frac{1}{2} \omega_f^2 w_n^2 = \frac{1}{2} |g_n|^2. \quad (16)$$

Now we have the complete set of equations to be integrated: (4), (13), and (15), but before doing this, we have to specify realistic values of the parameters involved in the evolution equations.

III. PARAMETERS AND THEIR REALISTIC VALUES

We have tried to estimate realistic values of the parameters, adapted to the PDA case. They are listed in Table I. Some of them are common literature values. For the other, in particular those corresponding to an effective motion, there is an uncertainty so that we give a plausible range of values. Lines in italics in Table I correspond to parameters that are not independent, but computed from others. The details of this estimation and corresponding references are given in the Appendix.

IV. RESULTS OF COMPUTER SIMULATIONS FOR ELECTRON TRANSFER IN THE ABSENCE OF EXTERNAL ELECTRIC FIELD (MECHANICAL CONTROL OF ELECTRONS AT THE NANOLEVEL)

As described in Sec. II, we have the interaction of an added excess electron with two “sub-lattices.” One is the basic crystal lattice, otherwise denoted as the “bridge” with a 100 units ($N = 100$, $n = 1$ to $n = 100$), and the other accounts for the additional on-site motions of the N units. Since the electron is represented by a wave function, we deal with a three-variable interaction process. As expected, in such a Hamiltonian conservative system, the evolution of the system depends on various features such as initial conditions, including energy localization at the initial time, and parameter values for both the crystal lattice (bridge and on-site units) and the electron. It also depends on the position of the soliton excitation and the relative localization (TBA) to that of the electron at the initial time. The case of an electron localized in the bridge at a site different from that of the soliton has been thoroughly studied elsewhere.^{55,56} Furthermore, it has also been shown that if an electron is allowed to completely delocalize by Schrödinger evolution, the latter leads to uniform probability density along the lattice; generally, a soliton in a Morse crystal lattice is able to trap the electron by reconstructing its localization in a kind of “vacuum cleaner effect.”^{55,56} Thus here, for simplicity, we shall concentrate on the case where both soliton excitation and electron are initially localized at the same site in the bridge. For the w -vibration of the on-site units, we assume equilibrium, and hence, they start being at rest in the absence of interaction with the electron. Finally, we shall consider periodic boundary conditions in the $N = 100$ lattice units bridge. That is, periodic boundary conditions are used for all variables (q , v , w , c), meaning that when a representative point reaches one of the diagram boundaries, say the right one, it is transferred to the other opposite boundary of the panel.

Thus, we take the following initial conditions for the bridge units, positions q_n and velocities v_n , and the known analytical results for a Toda lattice adapted to the Morse case:^{15–21}

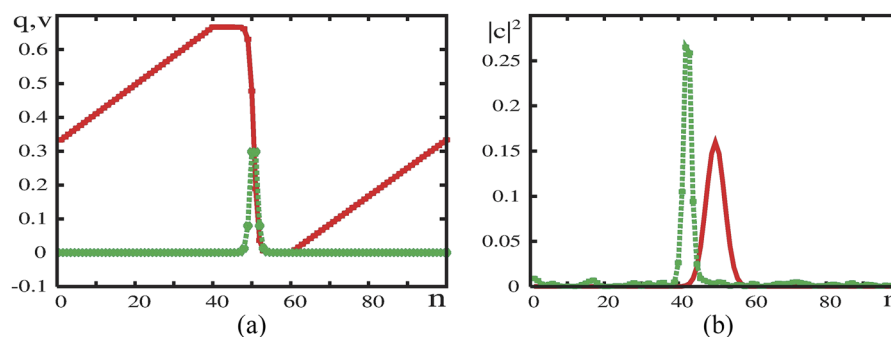


FIG. 5. Crystal lattice bridge ($N = 100$) location of soliton and electron. (a) Initial coordinates, q_n (red, kink-like; its derivative is the hyperbolic secant square with $\kappa = 1$) and velocities v_n (green) of units at $t = 0$ in the bridge with the soliton centered at site $N = 50$. (b) Initial electron distribution probability density, $|c_n|^2$ (red with $\sigma_{el} = 5$), at $t = 0$ and subsequent state at $t = 100$ (green) after having returned from passage through the right boundary as we have periodic boundary conditions. For illustration, $E_{\text{electron}} = -1.75$ eV (electron-bridge interaction energy), $E_w = 8.4 \times 10^{-4}$ eV (excitation energy of the second sublattice averaged over $t = 100$ indicating that the electron perturbation of this lattice is negligible), and $E_{\text{electron-w}} = 2.9 \times 10^{-3}$ eV (electron-sublattice interaction, which is also quite small). Such values indicate that the electron interaction with the sublattice is negligible, and hence, the bound state electron-bridge soliton (solelectron) is not significantly altered for such a long time.

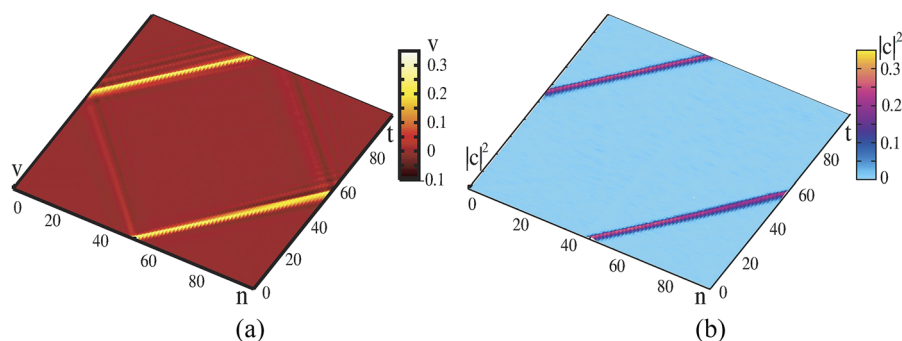


FIG. 6. Electron transfer along the crystal lattice bridge. Case $|g_n| = 0$. (a) Evolution of the velocities, $v_n(t) = dq_n/dt$. (b) Evolution of the electron probability densities, $|c_n|^2(t)$. Parameter values: $V = 0.1$, $\alpha = 2$, and $\tau = 23$.

$$q_n = q_{n+1} + \frac{1}{3} \ln \left[1 + \frac{\beta^2}{ch^2(\kappa(n - n_{sol}) - \beta t)} \right], \quad (17a)$$

$$\beta = sh\kappa, \quad (17b)$$

$$v_n = \dot{q}_n, \quad (17c)$$

where $1/\kappa$ defines the width of the soliton with an initial energy $\epsilon_{sol} \sim (\sinh \kappa \cosh \kappa - \kappa)$.^{15,16} For the electron wave function, we

assume, for simplicity, a Gaussian profile,

$$|c_n|^2 = \frac{2}{\sqrt{2\pi}\sigma_{el}} e^{-\frac{2(n-n_{el})^2}{\sigma_{el}^2}}, \quad (18)$$

where σ_{el} characterizes the width of the distribution $|c_n|^2$ of the probability density to find an electron at n th site and n_{el} indicates the site number with maximal value of such probability.

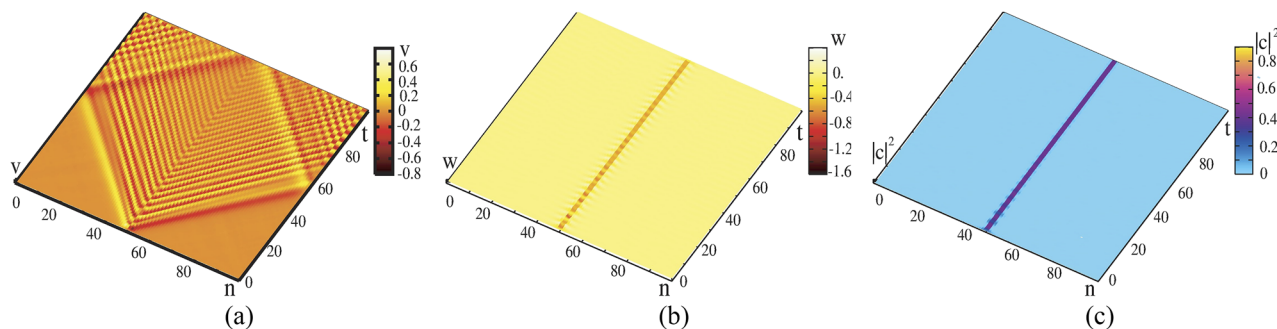


FIG. 7. Pinned polaron. Initial conditions at $t = 0$: $q_n = w_n = dw_n/dt = 0$ for all n . (a) Evolution of the velocities, $v_n(t)$, of units of the crystal lattice bridge without any initial excitation; (b) "local" coordinates, $w_n(t)$, corresponding to on-site motions in the additional off-bridge sublattice; and (c) probability densities, $|c_n|^2(t)$. Note that once the excess electron is added, it binds to both the on-site vibration and the bridge excitation of neighboring units. The former process binding creates the pinned w -polaron, whereas the latter process produces weak motions (kind of phonons) moving forward and backward along the bridge. Parameter values: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 5$, $A_2 = 120$, and $\omega_f = 2$.

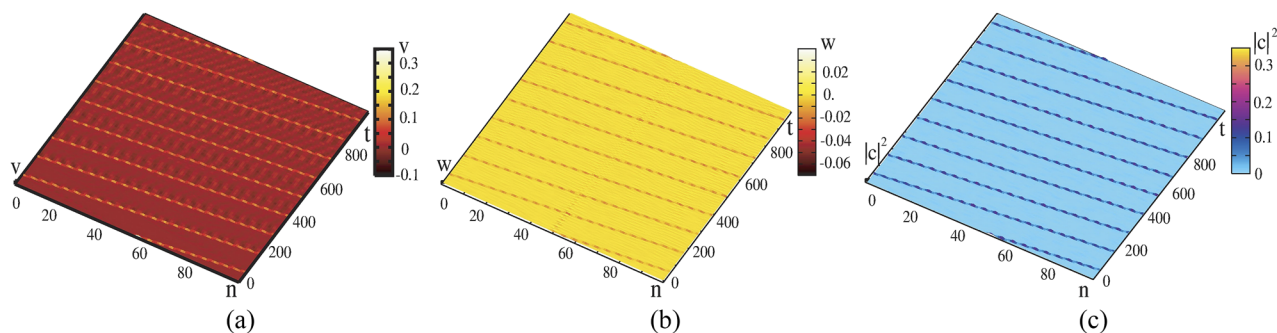


FIG. 8. Solitron. (a) Evolution of the velocities, $v_n(t)$, of units of the crystal lattice bridge; (b) "local" coordinates, $w_n(t)$, corresponding to on-site motions in the off-bridge sublattice; and (c) probability densities, $|c_n|^2(t)$. Parameter values: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 1$, $A_2 = 110$, and $\omega_f = 3$.

Accordingly, in particular, we assume that at $t = 0$, in the crystal lattice bridge, a soliton (17a)–(17c) is created and centered at site $n_{\text{sol}} = N/2 = 50$ with velocity $v_{\text{sol}} = 1.16$ (in units of the sound velocity) and $\kappa = 1$ [Fig. 5(a)]. At the same time, an electron is created with a wave function localized on a narrow cluster of sites symmetrically disposed around also $n_{\text{sol}} = N/2$ with the Gaussian profile (18) [Fig. 5(b)].

The system of Eqs. (4), (13), and (15) presents two extreme opposite particular cases: (i) if all $w_n = 0$, the on-site motions are suppressed. It corresponds to the Morse crystal lattice with an added excess electron, which may be trapped by the soliton and then transported along the bridge with formation of the solelectron quasiparticle with sub- or supersonic velocity. For example, if $v_{\text{sol}} \sim 1.16v_{\text{sound}}$ (v_{sound} is the sound velocity along the crystal lattice bridge), we can consider it as a rather low-energetic excitation offering the possibility of subsonic solelectron transport; hence, the electron transfers via surfing on the soliton with velocity $v_{\text{slctr}} = 0.94v_{\text{sound}}$ (Fig. 6), a result already known.⁵⁸ (ii) If A is large and, at the same time, V_0 is small, there is a strong tendency for the electron to self-trap at a given site, thus giving rise to a pinned polaron [Figs. 7(b) and 7(c)]. If excited, the soliton passage along the bridge does not bind the electron, which is no longer sensitive to the inter-site elongations (through the q_n coordinates), rather couples to the w_n motions (Fig. 4). In this case, there is preponderance of the Holstein–Marcus type of coupling. Then, it makes sense to call the corresponding quasi-particle a w -polaron. Such a localized pinned polaron excites only weakly phonons in the basic lattice bridge [Fig. 7(a)] if the latter is initially unperturbed.

If now $A_1 = 1$ and $A_2 = 110$, one can observe a very stable solelectron propagating for at least a time interval up to $\Delta t = 1000$ and attaining very long distances $\Delta n = 900$ with subsonic velocity, $v_{\text{slctr}} = 0.9$ (Fig. 8) exhibiting only small perturbations (Fig. 9). (Recall that sound velocity corresponds to 1 site/time unit in the dimensionless scale.) It appears that the on-site w_n motions just follow the perturbations of components of the wave function [Fig. 8(b)], but have practically no influence on the dynamics of the solelectron whose velocity is only slightly subsonic. Later on we shall consider the range of parameter values $1 < A_1 < 6$ and $90 < A_2 < 200$.

Further increasing values, when $A_1 = 6$ and $A_2 = 160$, a pinned w -polaron is formed (Fig. 10) at the initial site where the electron is

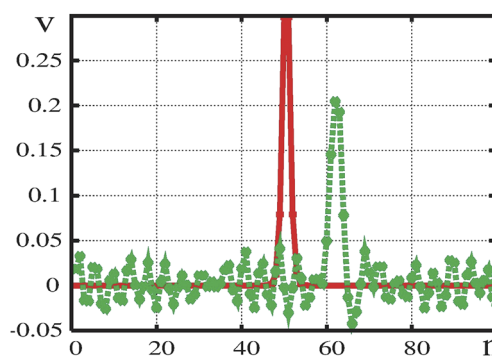


FIG. 9. Solelectron. Velocities, $v_n(t)$, of units of the crystal lattice bridge at the initial time ($t = 0$, red curve) and at time $t = 1000$ (green locus) corresponding to the panels in Fig. 8. One can observe that the soliton keeps its shape for quite a long time as the related disturbances of the lattice outside the main component of the soliton are small. Parameter values as in Fig. 8: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 1$, $A_2 = 110$, and $\omega_f = 3$.

placed, although an initially (moving) soliton has been created in the crystal lattice bridge like in the preceding Fig. 8. The soliton seems to travel “free” as apparently no electron has been trapped. However, a detailed analysis shows that the initial soliton having a velocity about $1.1v_{\text{sound}}$ splits in two solitonic components both being slightly supersonic, but with velocities lower than that of the initial soliton ($v_{\text{sol1}} \approx 1.05$ and $v_{\text{sol2}} \approx 1.005$).

Suppose we maintain constant $A_2 = 120$ and increase A_1 in the range $1 < A_1 < 6$, for how long the results depicted in Fig. 6 could survive? It appears that when $A_1 \leq 2$, a solelectron forms and travels for a long distance practically keeping its shape and velocity. Then, as A_1 reaches the value 2 and proceeds to higher values, one may note a difference in the evolution from the one illustrated in Fig. 8. First of all, of the two solitons created from the initial one (like in Fig. 8), one of them becomes a subsonic solelectron after binding an electron. Then, the velocity of that slow solelectron decreases while travelling [Figs. 11(a) and 11(b)], and the larger the A_1 parameter value, the faster the velocity decreases, as observed

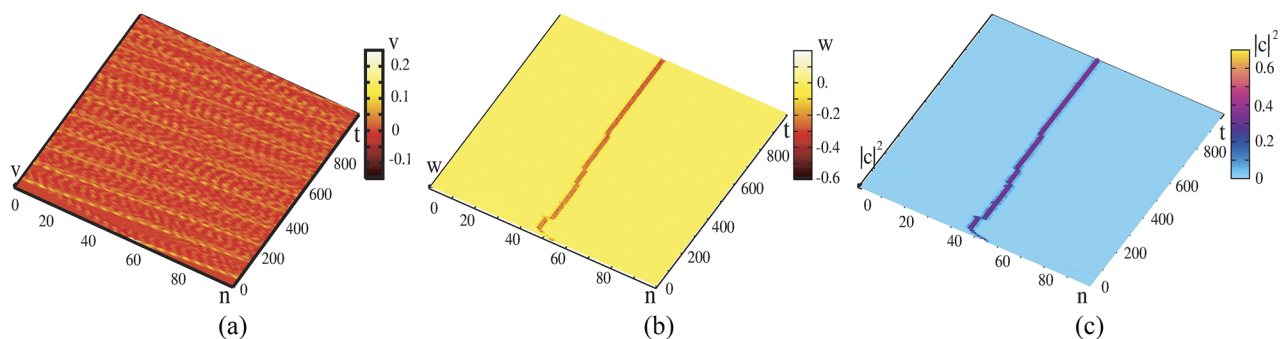


FIG. 10. Pinned w -polaron. (a) Evolution of the velocities, $v_n(t)$, of units of the crystal lattice bridge; (b) “local” coordinates, $w_n(t)$, corresponding to on-site motions in the additional out-of-bridge sublattice; and (c) probability densities, $|c_n|^2(t)$. Parameter values: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 6$, $A_2 = 160$, and $\omega_f = 3$.

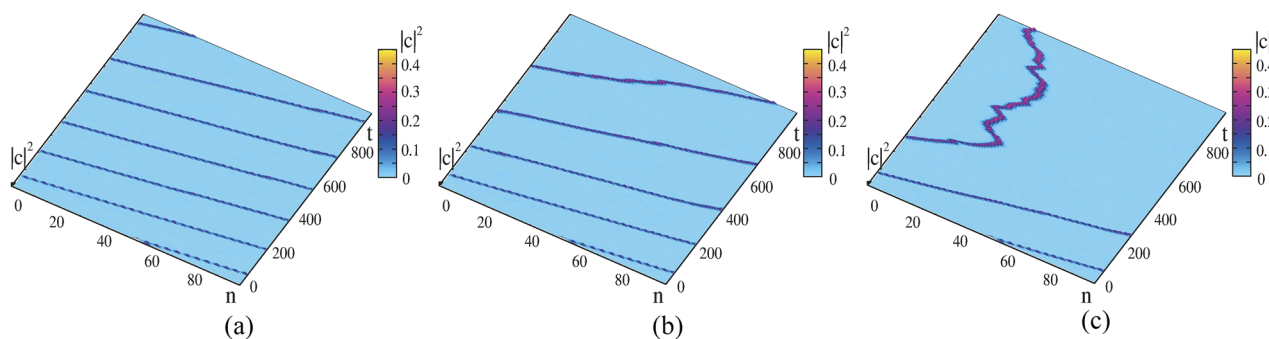


FIG. 11. Evolution of the electron probability densities, $|c_n|^2(t)$, for varying values of A_1 : (a) $A_1 = 4$, (b) $A_1 = 4.5$, and (c) $A_1 = 5$. The corresponding mean soliton velocities are (a) 0.58, (b) 0.45, and (c) 0.35. Parameter values: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_2 = 120$, and $\omega_f = 3$.

when comparing Figs. 11(a) and 11(b). In particular, at time $t = 1000$, the mean velocity is $v_{av} = 0.58$ for $A_1 = 4$ and $v_{av} = 0.45$ for $A_1 = 4.5$, respectively. Finally, sooner or later, the solectron transforms into a w-polaron [Fig. 11(c), for $A_1 = 5$]. (The irregular shape of the time evolution of the w-polaron, not straight trajectory as illustrated in Fig. 10, is of no significance because the polaron now evolves in a perturbed lattice due to the periodic boundary conditions.)

The results so far described seem to indicate that there is a kind of bifurcation from solectron behavior to polaron behavior. We may convene that a traveling lattice soliton deformation binding an added excess electron ought to be considered as a solectron if its trajectory is longer than half the bridge length, $N/2$. Then, we expect a “bifurcation” value $A_{1bif}(A_2)$ for each parameter value A_2 . In particular, $A_{1bif} \approx 5.5$ for $A_2 = 120$. For illustration, we plot in Fig. 12 the loci of A_{1bif} in the A_1 against A_2 plane for the values $\omega_f = 3$ and $\omega_f = 2$.

In view of the results found, we can safely say that the existence domain of solectrons, with different subsonic velocities, is quite wide for $\omega_f = 3$ and rather narrow for $\omega_f = 2$ because the interaction of the added excess electron with the out-of-bridge units is

strengthened due to resonance in the second case. Despite the possibility of the electron to “surf” on a moving soliton, thanks to the tendency of the latter to bind/slave the earlier at the beginning of the transient process, the electron rather tends to (polaronically) interact with the off-bridge vibrating units thus leading to losing energy.

V. TRANSPORT BEHAVIOR IN THE PRESENCE OF AN EXTERNAL ELECTRIC FIELD

Let us now consider the action of an externally imposed electric field. This is achieved by adding a corresponding term to Eq. (15). Then, we have

$$\frac{dc_n}{dt} = i\tau \left[c_{n+1} e^{i\alpha(q_n - q_{n+1})} + c_{n-1} e^{i\alpha(q_{n-1} - q_n)} \right] - i \frac{A_2 c_n}{\omega_f} \text{Im}(g_n e^{i\omega_f t}) + i n E c_n, \quad (19)$$

where $E = E'/(h/2\pi)\omega_M/\sigma e$ with E' being the dimensional field in V m^{-1} and e denotes the electron charge. The evolutionary problem is now composed of Eqs. (4), (13), and (19). Results of simulations are provided in Fig. 13.

A. Results

- (a) Figure 13 depicts the results obtained for the case presented in Fig. 8 but for a shorter time lapse in the evolution, $t = 50$, for the parameter values corresponding to the red star depicted in Fig. 12: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 1$, $A_2 = 110$, and $\omega_f = 3$. It appears that the evolution of the (solectron) quasi particle is not significantly affected by the presence of the external electric field as the latter is not able to accelerate it. Furthermore, the field is not able to extract the electron from its bound state with the soliton. One expects, however, that such an extraction would be possible for higher enough electric field strengths, but they are supposed to be experimentally unachievable. Accordingly, we can conclude that v_{slctr} is independent on E in this case (Fig. 14). The first set of two panels in Fig. 13 corresponds to $E = 0$ and the second set to $E = 0.1$ (note that the dimensionless value $E = 0.1$ corresponds to the dimensional value $E' = 10^6 \text{ V/m}$).

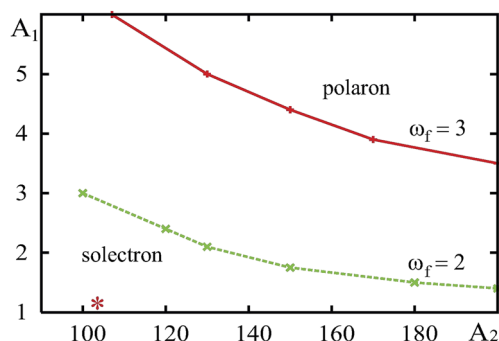
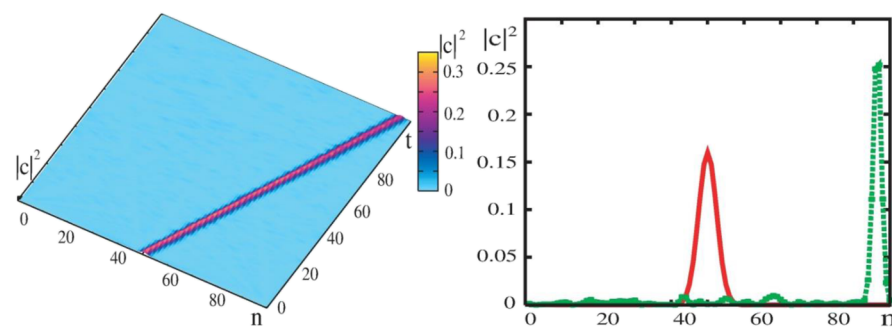


FIG. 12. Loci $A_{1bif}(A_2)$ in the (A_1, A_2) plane delineating the existence domains of solectron (below each curve) and pinned w-polaron (above each curve) for $\omega_f = 3$ (red curve) and $\omega_f = 2$ (green curve). Other parameter values: $V = 0.1$, $\alpha = 2$, and $\tau = 23$.



E=0

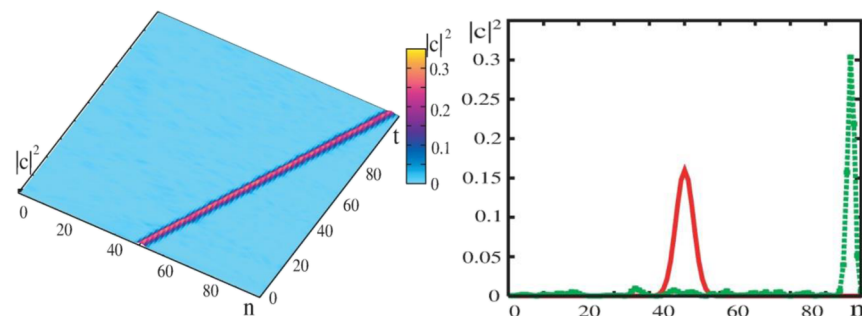
E=0.1 (corresponding to 10^6 V/m in dimensional units)

FIG. 13. Evolution of the probability density, $|c_n|^2(t)$ (left) and $|c_n|^2$ at $t = 0$ (red) and $t = 50$ (green) (right). Parameter values: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 1$, $A_2 = 110$, and $\omega_f = 3$.

- (b) For the case of Fig. 7, with parameter values $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 5$, $A_2 = 120$, and $\omega_f = 2$, we have observed that the electric field, in the strength range $0 < E < 0.1$, does not appreciably alter the evolution of $v_n(t)$, $w_n(t)$, and $|c_n|^2(t)$, which justifies that we do not present new figures here.
- (c) To complete the case analyzed above, let us consider now the following sequence of excited crystal lattice soliton cases: $\kappa = 1.35$ with $v_{\text{sol}} = 1.3$, $\kappa = 1$ with $v_{\text{sol}} = 1.16$, and $\kappa = 0.5$ with

$v_{\text{sol}} = 1.04$, recalling that $1/\kappa$ characterizes the width of the soliton. To the above, we once more consider Eqs. (4), (13), and (19), thus offering the possibility of forming a diversity of soliton–electron bound states.

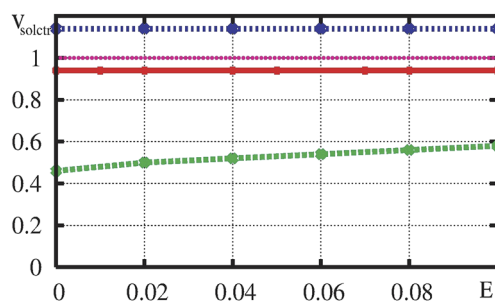


FIG. 14. Electron transfer by solitons illustrating the role of the electric field strength over a wide range of electric field strength values: dotted blue, red, and green lines correspond to v_{solctr} against E for $\kappa = 1.35$ [$v_{\text{sol}} = 1.3$ ($E_{\text{soliton}} = 3.8$ eV in dimensional units)] to $\kappa = 1$ [$v_{\text{sol}} = 1.16$ ($E_{\text{soliton}} = 1.3$ eV in dimensional units)] and to $\kappa = 0.5$ [$v_{\text{sol}} = 1.04$ ($E_{\text{soliton}} = 0.15$ eV in dimensional units)], respectively. For reference, the pink line delineates $v_{\text{sound}} = 1$ the linear sound velocity along the crystal lattice. Parameter values: $V = 0.1$, $\alpha = 2$, $\tau = 23$, $A_1 = 1$, $A_2 = 110$, and $\omega_f = 3$.

Figure 14 illustrates the results found. Focus on the dotted blue line. It appears that a “highly energetic” soliton ($v_{\text{sol}} = 1.3$; recall that solitons are always supersonic) is able to bind an electron, thus leading to a soliton with velocity $v_{\text{solctr}} = 1.14$. We have supersonic electron transfer with the additional feature that electron transfer is field independent up to a field strength value 0.1 corresponding to the dimensional value 10^6 V/m. As earlier noted, in experiments with PDA, Donovan and Wilson observed, on the one hand, transport velocity value close to sound velocity being independent of field for four orders of magnitude of field (10^2 V/m– 10^6 V/m) and, on the other hand, ultra-high mobility greater than $20 \text{ m}^2/\text{V s}$.^{45–51} Focus attention now on the red line. It corresponds to launching a “moderately energetic” soliton ($v_{\text{sol}} = 1.16$). Once more, there is a formation of a soliton, but this time with velocity $v_{\text{solctr}} = 0.94$, which is subsonic. Yet, the outstanding feature remains that electron transfer is field independent up to the field strength value 0.1. Finally, focus on the dotted green line corresponding to a “low energetic” soliton launched, supersonic indeed, $v_{\text{sol}} = 1.04$. Once more the soliton is able to bind the electron forming a soliton with velocity $v_{\text{solctr}} = 0.46$ at $E = 0$. Clearly, the electron transfer velocity is subsonic, yet its value is growing as the field strength increases but never reaching the sound velocity in the range of values studied up to $E = 0.1$.

VI. CONCLUDING REMARKS

When an excess electron is added to a crystal lattice, it creates a mechanical disturbance that provides a polarization field able to trap the electron. This classical self-trapping process was Landau's seminal idea (originally proposed for ionic crystals),²⁴ which later got completed by Pekar²⁵ and appropriately framed in the electron (Schrödinger) quantum mechanics description by Fröhlich *et al.*,^{26–31,51,52} and led to the polaron concept so useful for the development of the quantum transport theory in solid state physics. Let us emphasize that such a polaron concept builds upon the addition of linear elasticity in the crystal (on-site vibrations and inter-site elongations both governed by harmonic potentials) to the (Schrödinger) quantum description of the electron. It is known that the limitation to harmonic potentials does not permit explaining all features of a crystalline solid and may not be valid to account for certain cases of charge transport in a crystal lattice. The approach explored in this paper is based upon the idea that adding nonlinear elasticity to quantum mechanics may provide a useful generalization of the polaron concept.⁵⁶ Thus, in the simplest possible approach, we have introduced anharmonic (Morse) interactions to describe inter-site elongations while maintaining harmonic potentials to describe on-site vibrations in a crystal lattice. We have recalled that the Morse anharmonicity allows the creation of lattice disturbances in the form of solitons, which are nonlinear waves capable of supersonically traveling undeformed along the crystal. Furthermore, we have argued that such waves are capable of trapping added excess charges and hence allowing fast charge transfer over long distances. The addition of an excess electron does indeed lead to a polaron effect.⁵³ Yet the fact that before adding the excess charge, we have a robust wave carrier that can bind the charge, in a form of mechanical control of the charge, is the dominant ingredient of the theory applied in this paper. As an illustration of this concept, we have considered a model for non-dopable perfectly crystalline PDA crystals in order to offer an explanation of two puzzling observations made by Donovan and Wilson in transient photoconduction experiments in the presence of an electric field:^{44–48} transport velocity value close to sound velocity, being independent of the field for four orders of magnitude of the field (10^2 V/m– 10^6 V/m), and, in the low field values, an ultra-high mobility, greater than $20 \text{ m}^2/\text{V s}$. The model is a significant improvement upon an earlier attempt⁵⁸ by introducing Marcus formulation, as we have considered here on-site vibrations in an adequate description of the PDA structure, as schematically illustrated in Fig. 4.

With respect to the earlier work,⁵⁸ the question was as follows: “Will the introduction of the on-site motion destroy the coherent motion characteristic of soliton propagation?” We found that, for realistic values of the parameters adapted to the case of PDA, the charge transport is still possible, giving support to this hypothesis. Note that a key ingredient is the non-linearity of the main lattice, which allows a coherent motion with a definite directionality. Such a supersonic lattice soliton is different from the subsonic one of the SSH theory^{42,43} as the latter originates in the degeneracy of the ground state of their Hamiltonian for the dopable tPA and related other messy, poorly crystalline materials, which is not the case for the undopable perfectly crystalline PDA. Finally, the possibility of “mechanical control of electrons at the

nano-scale,” which is the consequence of the soliton-assisted (solutelectron) transport theory here used, offers universality. Indeed, besides the application here described to PDA, it is expected to be applicable for other materials whose stiffness and crystal vibrations permit strong enough compressions capable of exhibiting nonlinear soliton excitations.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to this work.

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APPENDIX: PARAMETERS IN THE DYNAMICS

Parameters for the PDA polymer crystal are obtained from a microscopic approach, and most of them are known from previous studies. For those whose estimation is difficult, rather than a single value, we shall consider a kind of mean/intermediate values in a reasonable parameter range.

1. Parameters defining the basic crystal lattice dynamics and the soliton propagation along it

a. Bond between C4 units

It is a Morse function with equilibrium distance 1.4 Å , $D = 3.65 \text{ eV}$, $K = 13 \text{ eV Å}^{-2}$, and $b = 1.33 \text{ Å}^{-1}$, the latter being obtained from K and D by the relation $K = 2Db^2$ (recall the note earlier given about the linear force spring constant). These values come from standard references for a single C–C bond⁸⁴ and from Refs. 80 and 85 for the force constant. However, to cope with various uncertainties and the mixed single–double character of the bonds, we shall take the force constant in the range $K = 13 \text{ eV Å}^{-2}$ – 20 eV Å^{-2} .

b. Mass of the moving unit

If we restrict it to the C4 group, assuming that the off-bridge units are intermingled and cannot follow the basic crystal lattice bridge motion, $M = 8 \times 10^{-26} \text{ kg}$. However, the off-bridge groups could partially move, so we extend the range to a threefold value, that is, $M = 8 \times 10^{-26}$ to $24 \times 10^{-26} \text{ kg}$. With $K = 13 \text{ eV Å}^{-2}$ and $M = 8 \times 10^{-26} \text{ kg}$, the angular frequency ω_M would be $5.09 \times 10^{13} \text{ rad/s}$. If rather we take a value in the estimated interval, such as $K = 16 \text{ eV Å}^{-2}$ and $M = 16 \times 10^{-26} \text{ kg}$, then $\omega_M = 4.0 \times 10^{13} \text{ rad/s}$.

2. Parameters describing electron motion along the lattice

a. Electronic interaction between C4 units (denoted V_0 or frequently t_0)

It is obtained from a model calculation of two C4 units in interaction using standard quantum chemical programs.⁸⁶ It gives V_0 (or t_0) = 0.78 eV .

b. Rate of decay of the electronic interaction with distance α_{SL}

This parameter is the Peierls electron–phonon coupling. As mentioned above, the dependence of the electronic interaction on elongations is defined by a Slater exponential (3). From literature values,⁸⁷ we take $\alpha_{SL} = 2.6 \text{ \AA}^{-1}$.

3. Parameters describing the “effective” on-site motion

a. The moving mass m_f

Since this an “effective” mode, it is impossible to assign with certainty a value. Considering that this describes internal motions of the C4 unit, we take a range of values from C to C2 and then $m_f = 2 \times 10^{-26}$ to 4×10^{-26} kg.

b. The harmonic force constant

It is taken as $60 \text{ eV \AA}^{-2}$, considering that $20 \text{ eV \AA}^{-2}$ is a standard value for such bonds with a mixed double-single character⁸⁵ and that three of them are modified by the addition/removal of an electron.

c. The associated angular frequency

Using the values $m_f = 4 \times 10^{-26}$ kg and $k_f = 60 \text{ eV \AA}^{-2}$, the angular frequency for the harmonic oscillator motion is $\omega_f = (k_f/m_f)^{1/2} = 1.55 \times 10^{14} \text{ rad/s}$, i.e., about three times ω_M . Note that with a mean/intermediate estimate 3×10^{-26} , one gets 1.79×10^{14} . Then, the ratio $\omega_f/\omega_M = 4.5$. In such a case with all other parameter values maintained as above, solitons can be excited and survive in the whole range of values of A_1 and A_2 . If, however, ω_f/ω_M is about unity, only pinned polarons are to be seen (see the discussion in Sec. IV).

d. The Holstein-type electron–phonon coupling constant

We take $A = 5.1 \text{ eV \AA}^{-1}$ or 51 eV/nm . This value is estimated from quantum chemical calculations⁸⁶ giving a relaxation energy of 0.22 eV upon addition or removal of an electron on the C4 structure and considering that this energy is equal to $(A^2/2k_f)$ (see Fig. 3). From this value of A and the definitions of A_1 and A_2 , the following ranges are obtained: $1 < A_1 < 6$ with a mean/intermediate value around 3 and $90 < A_2 < 200$ with a mean/intermediate value around 145.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

- ¹R. A. Marcus, *J. Chem. Phys.* **24**, 966 (1956).
- ²R. A. Marcus, *Annu. Rev. Phys. Chem.* **15**, 155 (1964).
- ³R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta, Rev. Bioenerg.* **811**, 265 (1985).
- ⁴R. A. Marcus and N. Sutin, *Comments Inorg. Chem.* **5**, 119 (1986).
- ⁵R. A. Marcus, “Electron transfer reactions in chemistry: Theory and experiments,” in *Nobel Lectures, Chemistry 1991–1995*, edited by B. G. Malmström (World Scientific, Singapore, 1997).
- ⁶R. A. Marcus, *Adv. Chem. Phys.* **106**, 1 (1999).
- ⁷N. S. Hush, *Trans. Faraday Soc.* **57**, 557 (1961).
- ⁸B. Giese, S. Wessely, M. Spormann, U. Lindemann, E. Meggers, and M. E. Michel-Beyerle, *Angew. Chem., Int. Ed.* **38**, 996 (1999).
- ⁹M. Bixon, B. Giese, S. Wessely, T. Langenbacher, M. E. Michel-Beyerle, and J. Jortner, *Proc. Natl. Acad. Sci. U. S. A.* **96**, 11713 (1999).
- ¹⁰C. Wan, T. Fiebig, S. O. Kelley, C. R. Treadway, J. K. Barton, and A. H. Zewail, *Proc. Natl. Acad. Sci. U. S. A.* **96**, 6014 (1999).
- ¹¹C. Wan, T. Fiebig, O. Schiemann, J. K. Barton, and A. H. Zewail, *Proc. Natl. Acad. Sci. U. S. A.* **97**, 14052 (2000).
- ¹²T. Renger and R. A. Marcus, *J. Phys. Chem. A* **107**, 8404 (2004).
- ¹³J.-P. Launay, *Chem. Soc. Rev.* **30**, 386 (2001).
- ¹⁴P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
- ¹⁵M. Toda, *Theory of Nonlinear Lattices*, 2nd ed. (Springer, Berlin, 1989).
- ¹⁶M. Toda, *Nonlinear Waves and Solitons* (KTK Scientific Publishers, Tokyo, 1989).
- ¹⁷J. Dancz and S. A. Rice, *J. Chem. Phys.* **67**, 1418 (1977).
- ¹⁸T. J. Rolfe, S. A. Rice, and J. Dancz, *J. Chem. Phys.* **70**, 26 (1979).
- ¹⁹M. G. Velarde, W. Ebeling, and A. P. Chetverikov, *Int. J. Bifurcation Chaos* **15**, 245 (2005).
- ²⁰A. P. Chetverikov, W. Ebeling, and M. G. Velarde, *Int. J. Bifurcation Chaos* **16**, 1613 (2006).
- ²¹A. P. Chetverikov, W. Ebeling, and M. G. Velarde, *Eur. Phys. J. B* **51**, 87 (2006).
- ²²S. V. Dmitriev, E. A. Korznikova, Yu. A. Baimova, and M. G. Velarde, *Phys. - Usp.* **59**, 446 (2016) and references therein.
- ²³M. G. Velarde, A. P. Chetverikov, W. Ebeling, S. V. Dmitriev, and V. D. Lakhno, *Eur. Phys. J. B* **89**, 233 (2016).
- ²⁴L. D. Landau, *Phys. Z. Sowjetunion* **3**, 664 (1933).
- ²⁵S. I. Pekar, *Sov. Phys. JETP* **16**, 335 (1946).
- ²⁶H. Fröhlich, H. Pelzer, and S. Zienau, *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **41**, 221 (1950).
- ²⁷H. Fröhlich, *Adv. Phys.* **3**, 325 (1954).
- ²⁸T. Holstein, *Ann. Phys.* **8**, 325 (1959); **8**, 343 (1959); reprinted: **281**, 706 (2000); **281**, 725 (2000).
- ²⁹*Polarons in Advanced Materials*, edited by A. S. Alexandrov (Springer, Dordrecht, 2007).
- ³⁰D. Emin, *Polarons* (Cambridge University Press, Cambridge, 2013).
- ³¹*Polarons: Recent Progress and Perspectives*, edited by A. Laref (Nova Science, New York, 2018).
- ³²A. S. Davydov, *J. Theor. Biol.* **38**, 559 (1973).
- ³³L. S. Brizhik and A. S. Davydov, *Phys. Status Solidi B* **115**, 615 (1983).
- ³⁴A. S. Davydov, *Solitons in Molecular Systems*, 2nd ed. (Reidel, Dordrecht, 1991) and references therein.
- ³⁵*Davydov’s Solitons Revisited. Self-Trapping of Vibrational Energy in Protein*, edited by A. L. Christiansen and A. C. Scott (Plenum Press, New York, 1983).
- ³⁶P. S. Lomdahl and W. C. Kerr, *Phys. Rev. Lett.* **55**, 1235 (1985).
- ³⁷J. P. Cottingham and J. W. Schweitzer, *Phys. Rev. Lett.* **62**, 1792 (1989).
- ³⁸J. W. Schweitzer, *Phys. Rev. A* **45**, 8914 (1992).
- ³⁹A. Scott, *Phys. Rep.* **217**, 1 (1992) and references therein.
- ⁴⁰A. V. Zolotareyuk, K. H. Spatschek, and A. V. Savin, *Phys. Rev. B* **54**, 266 (1996).
- ⁴¹L. Cruzeiro-Hansson and S. Takeno, *Phys. Rev. E* **56**, 894 (1997) and references therein.
- ⁴²A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, *Rev. Mod. Phys.* **60**, 781 (1988) and references therein.
- ⁴³S. Roth and H. Bleier, *Adv. Phys.* **36**, 385 (1987).
- ⁴⁴E. G. Wilson, *J. Phys. C: Solid State Phys.* **16**, 6739 (1983); see also *Synth. Met.* **28**, D551 (1989).
- ⁴⁵K. J. Donovan and E. G. Wilson, *Philos. Mag. B* **44**, 9 (1981); **44**, 31 (1981).

- ⁴⁶K. J. Donovan, P. D. Freeman, and E. G. Wilson, *J. Phys. C: Solid State Phys.* **18**, L275 (1985).
- ⁴⁷K. J. Donovan and E. G. Wilson, *J. Phys. C: Solid State Phys.* **18**, L51 (1985).
- ⁴⁸K. J. Donovan, J. W. P. Elkins, and E. G. Wilson, *J. Phys.: Condens. Matter* **3**, 2075 (1991).
- ⁴⁹E. G. Wilson, *J. Phys. C: Solid State Phys.* **15**, 3733 (1982).
- ⁵⁰R. T. Read and R. J. Young, *J. Mater. Sci.* **19**, 327 (1984).
- ⁵¹R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1965).
- ⁵²M. I. Kaganov and I. M. Lifshitz, *Quasiparticles. Ideas and Principles of Solid Quantum Physics* (Mir, Moscow, 1979).
- ⁵³O. G. Cantu Ros, L. Cruzeiro, M. G. Velarde, and W. Ebeling, *Eur. Phys. J. B* **80**, 545 (2011).
- ⁵⁴M. G. Velarde, W. Ebeling, D. Hennig, and C. Neissner, *Int. J. Bifurcation Chaos* **16**, 1035 (2006).
- ⁵⁵D. Hennig, A. P. Chetverikov, M. G. Velarde, and W. Ebeling, *Phys. Rev. E* **76**, 046602 (2007).
- ⁵⁶M. G. Velarde, *J. Comput. Appl. Math.* **233**, 1432 (2010).
- ⁵⁷A. P. Chetverikov, W. Ebeling, and M. G. Velarde, *Eur. Phys. J. B* **85**, 291 (2012).
- ⁵⁸M. G. Velarde, A. P. Chetverikov, W. Ebeling, E. G. Wilson, and K. J. Donovan, *Eur. Phys. Lett.* **106**, 27004 (2014).
- ⁵⁹M. G. Velarde, *Eur. Phys. J.: Spec. Top.* **225**, 921 (2016).
- ⁶⁰M. G. Velarde and E. G. Wilson, in *Polarons: Recent Progress and Perspectives*, edited by A. Laref (Nova Science, New York, 2018), Chap. V.
- ⁶¹M. G. Velarde and E. G. Wilson, "Solelectron field effect transistor and inverter," UK patent serial number GB 2533105 (20 May 2020).
- ⁶²D. Hennig, C. Neissner, M. G. Velarde, and W. Ebeling, *Phys. Rev. B* **73**, 024306 (2006).
- ⁶³M. G. Velarde, W. Ebeling, and A. P. Chetverikov, *Int. J. Bifurcation Chaos* **18**, 3815 (2008).
- ⁶⁴A. P. Chetverikov, W. Ebeling, and M. G. Velarde, *Eur. Phys. J. B* **70**, 217 (2009).
- ⁶⁵A. P. Chetverikov, W. Ebeling, and M. G. Velarde, *Int. J. Quantum Chem.* **110**, 46 (2010).
- ⁶⁶S. B. Piepho, E. R. Krausz, and P. N. Schatz, *J. Am. Chem. Soc.* **100**, 2996 (1978).
- ⁶⁷D. M. D'Alessandro and F. R. Keene, *Chem. Soc. Rev.* **35**, 424 (2006).
- ⁶⁸P. Day, N. S. Hush, and R. J. H. Clark, *Philos. Trans. R. Soc., A* **366**, 5 (2008).
- ⁶⁹J.-P. Launay and M. Verdaguer, in *Electrons in Molecules*, 2nd ed. (Oxford University Press, Oxford, 2018), Chap. III.
- ⁷⁰H. B. Gray and J. R. Winkler, *Annu. Rev. Biochem.* **65**, 537 (1996).
- ⁷¹J. Winkler, *Curr. Opin. Chem. Biol.* **4**, 192 (2000).
- ⁷²H. B. Gray and J. R. Winkler, *Q. Rev. Biophys.* **36**, 341 (2003).
- ⁷³H. B. Gray and J. R. Winkler, *Proc. Natl. Acad. Sci. U. S. A.* **102**, 3534 (2005).
- ⁷⁴E. Mozafari and S. Stafström, *Phys. Lett. A* **376**, 1807 (2012).
- ⁷⁵E. Mozafari and S. Stafström, *J. Chem. Phys.* **138**, 184104 (2013).
- ⁷⁶S. Stafström, *Chem. Soc. Rev.* **39**, 2484 (2010).
- ⁷⁷W. Barford, M. Marcus, and O. R. Tozer, *J. Phys. Chem. A* **120**, 615 (2016).
- ⁷⁸J. R. Mannouch, W. Barford, and S. Al-Assam, *J. Chem. Phys.* **148**, 034901 (2018).
- ⁷⁹J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.
- ⁸⁰Y. Li, G. Hu, C. Xia, D. Liu, and S. Xie, *Sci. China, Ser. G: Phys., Mech. Astron.* **49**, 430 (2006).
- ⁸¹A. Girlando, L. Grisanti, M. Masino, I. Bilotti, A. Brillante, R. G. Della Valle, and E. Venuti, *Phys. Rev. B* **82**, 035208 (2010).
- ⁸²Z. Shuai, L. Wang, and Q. Li, *Adv. Mater.* **23**, 1145 (2011).
- ⁸³D. Baeriswyl and A. R. Bishop, *J. Phys. C: Solid State Phys.* **21**, 339 (1989).
- ⁸⁴A. J. Gordon and R. A. Ford, *The Chemist's Companion* (John Wiley, NY, 1972), p. 113, see also www.kentchemistry.com/links/bonding/bondenergy.htm.
- ⁸⁵W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. B* **22**, 2099 (1980).
- ⁸⁶Computations realized with Materials Studio with semi-empirical PM6 method.
- ⁸⁷R. R. Chance, M. L. Shand, C. Hogg, and R. Silbey, *Phys. Rev. B* **22**, 3540 (1980).