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Ratchet behaviour of polarons in molecular chains

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Abstract

We study the ratchet behaviour of polarons in diatomic molecular chains under the influence of an external electromagnetic field which is periodic in time. We show that in asymmetric chains a harmonic unbiased field causes a drift of polarons. This phenomenon has a threshold with respect to the intensity and the frequency of the field. In spatially symmetric chains a harmonic periodic electric field generates oscillations of polarons but does not result in their movement. The polaron drift current can be induced in symmetric chains by a time periodic asymmetric external field. This complex dynamics of polarons is generated by the interplay between the Peierls–Nabarro barrier and dissipative effects in the chains.

(Some figures in this article are in colour only in the electronic version)

The ratchet phenomenon has recently been attracting a great deal of attention due to its importance both for the understanding of the functioning of biological motors and for promising technical applications, including in molecular motors and in nanoscale technologies. The phenomenon involves the appearance of a directed current (drift) under the action of stochastic or deterministic unbiased (zero-mean) ac forces [1]. Many interesting theoretical models of ratchets have been proposed and a large variety of experimental realizations have become available (see, e.g., review [1] and references therein). In particular, semiconducting heterostructures, such as diode (n, p) junctions, semiconductor superlattices, Josephson junction arrays, SQUID ratchets, and quantum dot arrays with broken spatial symmetry, have been engineered and shown to possess ratchet properties. Here we show that the ratchet phenomenon can be realized in (quasi-)one-dimensional molecular chains which support the existence of self-trapped electron states. Such states, called polarons (or condensons) and in one-dimensional systems known as solitons, are formed as localized states of electrons due to the electron–lattice interaction [2–4]. Their properties have been studied in great detail both theoretically and experimentally. The class of low-dimensional molecular systems in which polarons exist or are predicted to exist is quite large. It includes quasi-1D organic and inorganic compounds (like conducting platinum chain compounds),

conducting polymers (e.g., polyacetylene [3], polypyrrole [5], polythiophene [6]), biological macromolecules (α -helical proteins [2], DNA [7]) etc.

Note that the necessary conditions for the ratchet effect, both in classical and quantum systems, involve the presence of a spatially periodic potential (ratchet potential) in the system with dissipation and an external unbiased force periodic in time. Some of the necessary requirements for this effect are naturally intrinsic to solitons in molecular systems. Energy dissipation in molecular systems is always present due to the interaction of atoms with the many degrees of freedom of the surrounding medium which can be considered as a thermal bath. This is especially true for biological macromolecules in the cellular cytoplasm. In a discrete system solitons move in the Peierls–Nabarro potential which is periodic, with a period equal to the lattice constant [8]. Therefore, one can expect the ratchet phenomenon to arise in systems involving polarons.

The origin of the net motion of polarons is associated with the breaking of the space–temporal symmetries of the system [1, 9]. In molecular chains with a reflection symmetry, like in a simple molecular chain [8], the Peierls–Nabarro potential is symmetrical. This symmetry can be broken in asymmetric chains with more complicated structure and one can expect that such molecular chains would exhibit the ratchet effect even under the influence of harmonic external forces. To demonstrate this, we have performed numerical simulations

of the polaron dynamics in asymmetric molecular chains in the presence of an external periodic unbiased electromagnetic field. We have considered a diatomic molecular chain that contains two different atoms, or groups of atoms, in a unit cell, periodically arranged along the chain axis at their equilibrium positions, $z_{n,1}^0 = na$, $z_{n,2}^0 = a(n + b)$, where a is the lattice constant and b is the relative distance between the two atoms in the unit cell.

The Hamiltonian which describes the states of extra electrons in such a system in an external field, taking into account the electron interaction with lattice vibrations, is represented by a sum of terms:

$$H = H_e + H_{\text{ph}} + H_{\text{e-ph}} + H_{\text{int}}. \quad (1)$$

We write H in the site representation and in the nearest-neighbour approximation and, as we consider only one extra electron in the chain, we can omit the electron spin index. If $a_{n,j}^\dagger$ ($a_{n,j}$) are creation (annihilation) operators of an electron on the site (n, j) , \mathcal{E}_j the on-site electron energy describing the influence of the neighbouring atoms,

$$H_e = \sum_n [\mathcal{E}_1 a_{n,1}^\dagger a_{n,1} + \mathcal{E}_2 a_{n,2}^\dagger a_{n,2} - J_s (a_{n,1}^\dagger a_{n,2} + a_{n,2}^\dagger a_{n,1}) - J_l (a_{n,1}^\dagger a_{n-1,2} + a_{n-1,2}^\dagger a_{n,1})], \quad (2)$$

where J_s and J_l are the energies of the hopping interactions with the nearest neighbours from the same unit cell and from the neighbouring cell, respectively. The harmonic lattice vibration Hamiltonian is

$$H_{\text{ph}} = \frac{1}{2} \sum_n \left[\frac{p_{n,1}^2}{M_1} + \frac{p_{n,2}^2}{M_2} + w_s (u_{n,1} - u_{n,2})^2 + w_l (u_{n,1} - u_{n-1,2})^2 \right], \quad (3)$$

where M_1 and M_2 are the masses of the atoms; $u_{n,j}$ are the longitudinal displacements of atoms from their equilibrium positions; $z_{n,j} = z_{n,j}^0 + u_{n,j}$; $p_{n,j}$ are the momenta, canonically conjugate to $u_{n,j}$; w_s and w_l are the elasticity constants for the interactions between, respectively, the nearest-neighbour atoms belonging to one unit cell and to the neighbouring cells. In the linear lattice displacement approximation the electron-phonon interaction Hamiltonian is

$$H_{\text{e-ph}} = \sum_n \left[[a_{n,1}^\dagger a_{n,1} [\chi_l (u_{n,1} - u_{n-1,2}) - \chi_s (u_{n,1} - u_{n,2})] + a_{n,2}^\dagger a_{n,2} [\chi_l (u_{n+1,1} - u_{n,2}) - \chi_s (u_{n,1} - u_{n,2})]] \right]. \quad (4)$$

Here χ_s and χ_l are the coefficients of the electron-phonon interaction between nearest neighbours. Finally, the Hamiltonian of the interaction with the external electric field $E(t)$ is given by

$$H_{\text{int}} = -eE(t) \sum_n ((na - n_0) a_{n,1}^\dagger a_{n,1} + (a(n + b) - n_0) a_{n,2}^\dagger a_{n,2}). \quad (5)$$

Next we define $M = M_1 + M_2$, $W = w_s + w_l$, $J = J_s + J_l$, $X = \chi_s + \chi_l$, and

$$m = \frac{M_1 - M_2}{M}, \quad w = \frac{w_s - w_l}{W}, \quad (6)$$

$$d = \frac{J_s - J_l}{J}, \quad x = \frac{\chi_s - \chi_l}{X}.$$

Self-trapped states of electrons in such systems are usually described in the adiabatic approximation in which the wavefunction of the system is represented in a multiplicative Born–Oppenheimer form, equivalent to the semiclassical consideration in which the vibrational subsystem is treated as a classical one. Considering one extra electron in the chain and using a well known approach, we obtain a system of dynamical equations for the quasi-particle and the phonons. For numerical simulations it is convenient to measure time, energies and displacements in units of \hbar/J , J and $l = \hbar\sqrt{2/JM}$, respectively. In the presence of an external electric field $E(t)$, we have

$$\begin{aligned} i \frac{d\Psi_{n,1}}{dt} &= \left[-1 + \frac{D}{2} + (n - n_0) E(t) \right] \Psi_{n,1} \\ &+ \frac{1}{2} (1 + d) \Psi_{n,2} + \frac{1}{2} (1 - d) \Psi_{n-1,2} \\ &+ G[(1 + x)(u_{n,1} - u_{n,2}) \\ &- (1 - x)(u_{n,1} - u_{n-1,2})] \Psi_{n,1}, \\ i \frac{d\Psi_{n,2}}{dt} &= \left[-1 - \frac{D}{2} + (n - n_0 + b) E(t) \right] \Psi_{n,2} \\ &+ \frac{1}{2} (1 + d) \Psi_{n,1} + \frac{1}{2} (1 - d) \Psi_{n+1,1} \\ &+ G[(1 + x)(u_{n,1} - u_{n,2}) \\ &- (1 - x)(u_{n+1,1} - u_{n,2})] \Psi_{n,2}, \\ \frac{d^2 u_{n,1}}{dt^2} &= -\frac{C}{1 - m} [(1 + w)(u_{n,1} - u_{n,2}) \\ &+ (1 - w)(u_{n,1} - u_{n-1,2})] \\ &+ \frac{G}{1 - m} [2x |\Psi_{n,1}|^2 - (1 - x) |\Psi_{n-1,2}|^2 \\ &+ (1 + x) |\Psi_{n,2}|^2] - \eta \frac{du_{n,1}}{dt}, \\ \frac{d^2 u_{n,2}}{dt^2} &= \frac{C}{1 + m} [(1 + w)(u_{n,1} - u_{n,2}) \\ &+ (1 - w)(u_{n+1,1} - u_{n,2})] \\ &+ \frac{G}{1 + m} [-2x |\Psi_{n,2}|^2 + (1 - x) |\Psi_{n+1,1}|^2 \\ &- (1 + x) |\Psi_{n,1}|^2] - \eta \frac{du_{n,2}}{dt}. \end{aligned} \quad (7)$$

Here the intensity of the electric field $E(t)$ is measured in units ea/J and we have defined

$$G = \frac{Xl}{2J}, \quad C = \frac{\hbar^2 W}{MJ^2}, \quad D = \frac{\mathcal{E}_2 - \mathcal{E}_1}{J}. \quad (8)$$

The terms proportional to η in (7) describe the damping force which models the interaction between the atoms and the thermal bath responsible for the dissipation of the energy. In all our simulations we have taken $\eta = 0.2$.

To study the polaron dynamics, we have calculated first some stationary solutions of equations (7) in the absence of an external field, i.e., by setting $E(t) = 0$, and then used them as the initial conditions in the presence of the field at $E(t) \neq 0$. We have chosen the numerical values of the parameters (8) so

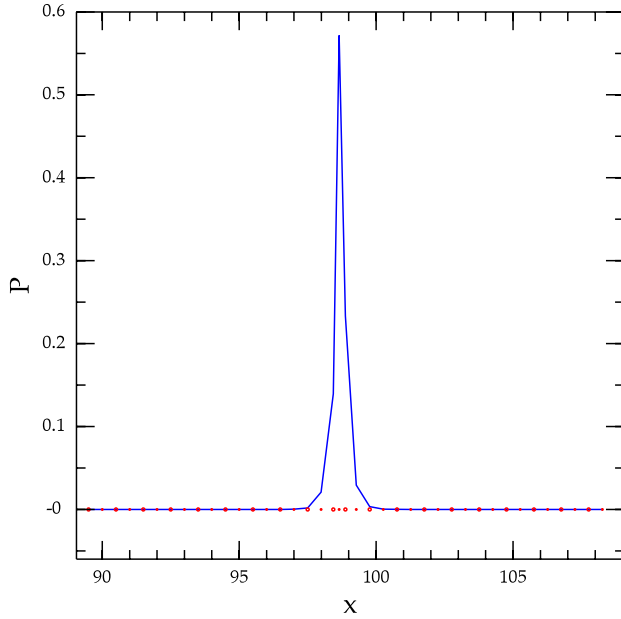


Figure 1. Stationary distribution of the electron probability $P = |\Psi|^2$ as a function of the lattice site for the parameter values $G = 0.4, C = 0.22, d = D = 0.1, x = 0.05, w = 0.15, m = 0.3$.

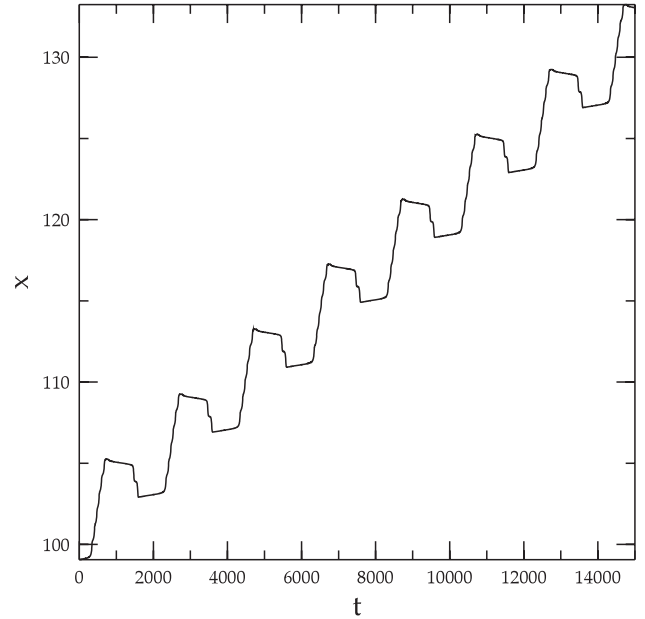


Figure 2. Position of the c.m. of the soliton as a function of time in an external harmonic field at $G = 0.4, C = 0.22, E_0 = 0.08, T = 2000$ d.u. in an asymmetric chain with $d = D = 0.1, x = 0.05, w = 0.15, m = 0.3$.

that the stationary solution is self-trapped within few lattice sites as is shown, for instance, in figure 1.

We have studied numerically the time evolution of such an excitation by calculating its profile, half-width and the position of the quasi-particle centre of mass (c.m.) for various forms of the external periodic unbiased electric field. The field itself does not significantly affect the profile of the soliton, though it causes oscillations of the c.m. of the soliton and of its width. In figure 2 we plot the c.m. coordinate as a function of time for an asymmetric chain with nonzero asymmetry parameters (6) in the presence of an unbiased harmonic field $E(t) = E_0 \sin(2\pi t/T)$ at $E_0 = 0.08, T = 2000$. The figure shows very clearly that the harmonic field causes a drift of the soliton, i.e., it generates a directed current in the chain. A directed current of polarons under harmonic perturbation in molecular systems is also present if there is an asymmetry in the electronic subsystem only, i.e., when only two parameters, d and D , are nonzero. In this case the plot of the c.m. coordinate as a function of time looks like the one shown in figure 2 but is not presented here for lack of space.

As can be seen from figure 2, in an asymmetric chain in the electric field periodic in time, the soliton trajectory is a sum of a drift and oscillations with a certain amplitude. This effect has a threshold with respect to the intensity of the field and its period, i.e., the effect takes place provided that $E > E_{0,cr}, T > T_{cr}$. The value of T_{cr} depends on the field intensity, for instance, for $E_0 = 0.08$ and for the given chain parameters $T_{cr} = 400$.

Note that chains with only one nonzero anisotropy parameter, d or D , possess a reflection symmetry. In such cases a harmonic electric field causes polaron oscillations around its initial position but does not generate a drift. Instead, one can expect the ratchet phenomenon to take place in a symmetric

chain in an external unbiased field, periodic in time, if this field breaks the time-reversal symmetry, namely, if there is no time τ such that $E(\tau + t) = E(\tau - t)$ for all t . For instance, this can be a non-harmonic, e.g., biharmonic or, more generally, multi-harmonic field at proper values of the harmonic phases.

Instead, the ratchet phenomenon takes place in an external unbiased periodic field asymmetric in time. This is shown in figure 3, which presents the trajectory of a soliton in the unbiased biharmonic periodic field, $E(t) = E_0(\sin(2\pi t/T) + \beta \sin(4\pi t/T - \varphi))$ at $E_0 = 0.08, \beta = 0.6, \varphi = \pi/2$.

Note that the case of $D = 0, d \neq 0$ applies to polyacetylene with alternating chemical bonds [3], while $d = D = 0$ corresponds to a simple chain with one atom in a unit cell with the lattice constant $a/2$. From figure 3(b) we see that, even in such simple systems, the ratchet effect takes place!

The ratchet phenomenon in molecular chains can be explained qualitatively. For properly chosen values of the system parameters, when the polaron size is not too small, equations (7) can be studied in the continuum approximation (see, e.g., [2]). As is well known, in this approximation, after elimination of the vibrational variables, equations (7) can be reduced to the nonlinear Schrödinger equation (NLSE), with a cubic nonlinearity, for the electron wavefunction. In general this equation contains also additional terms which describe corrections due to the external field, dissipation, and lattice discreteness. These additional terms can be treated as small perturbations provided the field and dissipation are sufficiently weak. In the leading order approximation the NLSE has the well known soliton solution. The perturbation theory [2, 8, 10] with respect to additional terms gives the dynamic equation for the c.m. coordinate of the soliton, $R(t)$:

$$M_s \ddot{R} + \gamma \dot{R} - f(R) - E(t) = 0, \quad (9)$$

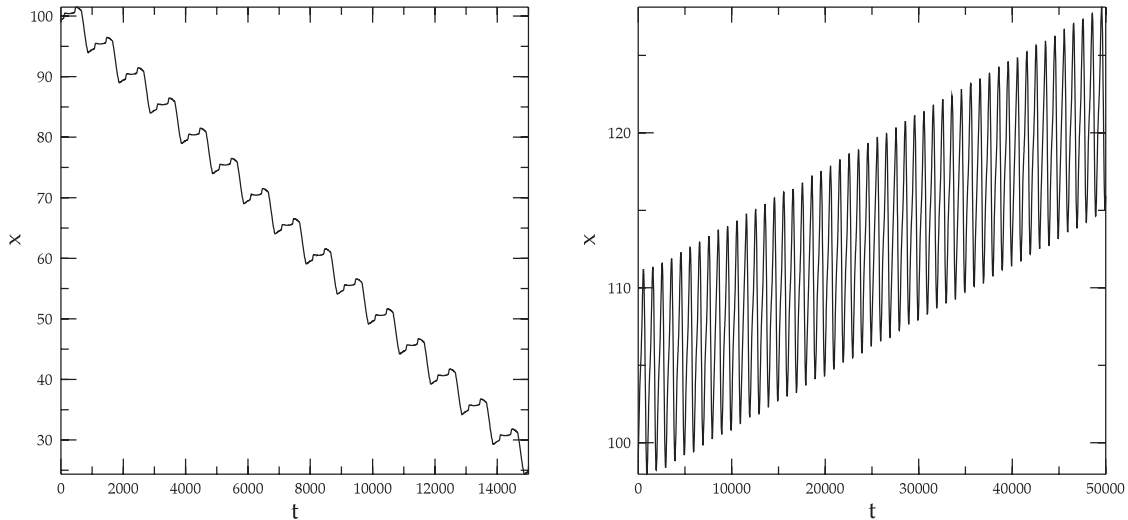


Figure 3. Position of the c.m. of the soliton as a function of time in an external biharmonic field at $G = 0.4$, $E_0 = 0.08$, $\beta = 0.6$, $\varphi = \pi/2$, $T = 1000$ in a symmetric chain at (a) $C = 0.22$, $d = 0.1$, $D = x = w = m = 0$; (b) $C = 0.25$, $d = D = x = w = m = 0$.

where M_s is the effective mass of the soliton, ‘dressed’ with phonons, $\gamma \propto \eta$ [10], and $f(R) = -dU_{PN}/dR$ with U_{PN} being the Peierls–Nabarro potential which is periodic with the same period as the lattice [8].

Equation (9) is of a type leading to the ratchet phenomenon and it is well known that the breaking of the symmetry of either the ratchet potential (in our case this is the periodic potential of the Peierls–Nabarro barrier) or the driving force is enough for this effect to take place [1, 9].

In a chain with one atom in a unit cell, the Peierls–Nabarro potential is given by the expression $U_{PN}(R) = U_0 \cos(2\pi R/b)$, where b is the lattice constant of the chain and the height of the barrier depends on the electron–phonon coupling [8]. A detailed study of the Peierls–Nabarro barrier in a diatomic chain will be reported elsewhere [11]. Here we point out that, in molecular chains with a reflection symmetry, the Peierls–Nabarro barrier is indeed symmetrical, while in molecular chains without a reflection symmetry, this barrier is asymmetrical. This fact explains our numerical results shown in figures 2 and 3, and can also be demonstrated by the motion of a polaron in a dc field. As is clear from equation (9), the presence of the Peierls–Nabarro potential results in the pinning of the soliton by the lattice and, in a static electric field, the soliton can move if the external field exceeds some threshold value. In a symmetric chain this threshold is symmetric for fields E and $-E$, and it is asymmetric for chains without reflection symmetry. We have studied the dynamics of the soliton governed by the discrete equations (7) in a constant field and have proved that $E_{th}(E) = E_{th}(-E)$ for symmetric chains, while $E_{th}(E) \neq E_{th}(-E)$ for asymmetric ones, as is shown in figure 4.

In conclusion, our study has shown that the ratchet effect can take place in one-dimensional molecular systems which admit large polarons (solitons). Such self-trapped electron states are formed at intermediate values of the electron interaction with lattice deformations. The coupling constant of this interaction has to be large enough, as the Peierls–Nabarro

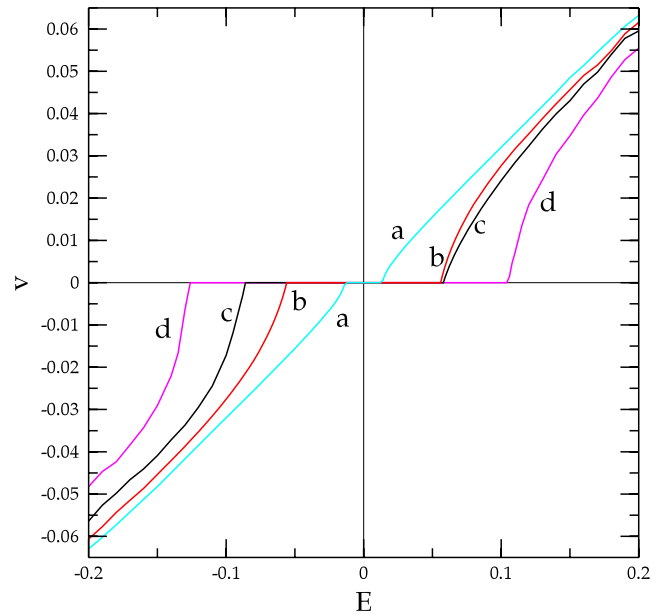


Figure 4. Dependence of the average soliton velocity on the constant electric E field for $G = 0.4$, $C = 0.22$, $b = 0.5$ and (a) $D = d = 0$; (b) $D = 0$, $d = 0.1$; (c) $D = 0.1$, $d = 0.1$; (d) $D = 0.2$, $d = 0.1$.

barrier is essential for the dynamics of the soliton; on the other hand, this coupling should not be very large, to prevent the formation of small polarons, whose transport properties are qualitatively different from those of the solitons.

Notice that, similarly to the deterministic fields considered here, a symmetric white noise [12] can also cause uni-directed current of solitons in low-dimensional molecular systems, though the dynamics of solitons in such cases is less symmetric and more complicated than in the harmonic fields discussed here (we plan to report on this in the near future).

Furthermore, there is a class of low-dimensional compounds, such as polyacetylene (PA), polythiophene (PT), etc, which provide experimental evidence for the existence

of large polarons and bipolarons [3, 5, 6]. On the basis of our results we expect that, in these compounds, the unbiased alternating electric field can induce a directed current. In the compounds with an asymmetric unit cell, such as polyphenylenevinylene or polythiénylenevinylene, this directed current can be induced by a harmonic periodic field, while in compounds with a symmetric unit cell, such as PA, PT, polyphenylene, polypyrrole, etc, this effect can be observed in biharmonic, or, generally, in asymmetric in time, periodic fields.

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