Electron motion in a Holstein molecular chain in an electric field

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Presently, there are a lot of papers devoted to modeling the motion of a charged particle in various-type molecular chains (see books and reviews \textsuperscript{11}-\textsuperscript{15} and references therein). Interest in the problem is associated with possible practical applications of such chains in nanoelectronics \textsuperscript{6},\textsuperscript{7}. Functioning of nanoelectronic devices is based on the motion of charges along molecular chains placed in an external electric field. Notwithstanding the great number of publications on the problem of charge motion in a molecular chain, it would be an exaggeration to say that the problem is conclusively solved.

It is well known that an electron in an ideal non-deformable molecular chain placed in an electric field demonstrates Bloch oscillations \textsuperscript{8}-\textsuperscript{11}. In a deformable molecular chain an electron turns into a polaron state. In the simplest case of a Holstein molecular chain in the absence of Peierls-Nabarro potential there. The critical value of the electric field intensity at which the moving polaron starts oscillating at Bloch frequency is found. It is shown that the polaron can demonstrate Bloch oscillations retaining its shape. It is also shown that a breathing mode of Bloch oscillations can arise. In all cases the polaron motion along the chain is infinite.

The aim of this paper is to model numerically the motion of charges along molecular chains placed in an external electric field. Notwithstanding the great number of publications on the problem of charge motion in a molecular chain, it would be an exaggeration to say that the problem is conclusively solved.

To study the dynamics of the charge motion in the chain use is usually made of a semiclassical description based on the fact that the site's mass exceeds greatly the electron mass. In order to pass on to semiclassical description we will seek the wave function of the system \(|\Psi\rangle\) in the form of its expansion in terms of coherent states:

\[
|\Psi(t)\rangle = \sum_n b_n(t) a_n^\dagger |0\rangle \exp\left\{ -i \frac{\hbar}{\nu} \sum_j \left[ \beta_j(t) \hat{P}_j - \pi(t) q_j \right] \right\},
\]

where \(|0\rangle\) is the vacuum wave function, while the quantities \(\beta_j(t)\) and \(\pi(t)\) satisfy the relations:

\[
|\Psi(t)\rangle q_n |\Psi(t)\rangle = \beta_n(t), \quad (\Psi(t)|\hat{P}_n|\Psi(t)) = \pi_n(t).
\]

Dynamical equations for the quantities \(b_n(t)\) and \(\beta_n(t)\) obtained from \textsuperscript{11}-\textsuperscript{13} have the form:

\[
\begin{align*}
\hbar \dot{b}_n &= \nu (b_{n+1} + b_{n-1}) + \alpha' \beta_n b_n + e \mathcal{E} a_n b_n, \\
M \ddot{\beta}_n &= -K \beta_n - \alpha' |b_n|^2.
\end{align*}
\]
Equations (4) are Schrödinger equations where the $\kappa$ are displacements $\beta$ of the amplitudes of the probabilities of the charge localization at $\kappa$. The Herewith the quantities correspond to the idea of the strong coupling polaron.

Turning to coherent states using transformation (2) corresponds to the idea of the strong coupling polaron. Herewith the quantities $\beta_n$ determine the phonon "environment" surrounding the particle. Notice that in the absence of an electric field, the steady motion of the polaron along the chain is impossible. The reason is that the group velocity of phonons $v_g = \partial \Omega / \partial k$ is equal to zero since the quantity $\Omega$, according to (5), does not depend on the wave vector $k$: $\Omega = \sqrt{K/M}$. In other words, in the absence of dispersion in the chain, the polaron "environment" cannot follow the particle’s motion along the chain.

For numerical modeling of the polaron motion, we used dimensionless variables in which system (4), (5) has the form:

$$\frac{d b_n}{dt} = \eta (b_{n+1} + b_{n-1}) + \kappa \omega^2 u_n b_n + E n b_n,$$

$$\frac{d^2 u_n}{dt^2} = -\omega^2 u_n - |b_n|^2,$$

where dimensional quantities involved in (4), (5) are related to dimensionless quantities involved in (6), (7) as:

$$\eta = \nu \hbar / \omega, \quad \kappa^2 = \nu^2 K / M, \quad \kappa = \beta u_n, \quad t = \tau \tilde{t},$$

$$\omega^2 = \kappa^3 (\kappa' / M h), \quad \beta = \sqrt{\kappa' / M}, \quad E = e \nu \tau / \hbar,$$

where $\tau$ is an arbitrary time scale. In view of arbitrariness of $\tau$ any set of dimensionless parameters $\eta, \omega, \kappa, E$ correspond to a continuum of possible dimensional parameters of the molecular chain: $\nu, K, \alpha', E$.

In the continuum limit, solution of (6), (7) yields the following relation between the polaron equilibrium velocity $V = \nu a/\tau$ and the electric field intensity $E$ [12]:

$$E = 2 \nu^2 \omega^4 \eta^2 \frac{1}{\kappa} \frac{V^4}{\kappa^2 \sin^2(2\pi \eta \omega / \kappa V)}.$$  

According to [12], the steady motion of a polaron in the conservative system under consideration in an electric field appears possible due to the fact that while the polaron moves along the chain it leaves behind a "tail" of excited oscillators. In this process the work done by the electric field is expended for excitation of these oscillators.

Figure 1 shows the polaron motion in an electric field $E = 0.01$ at $\omega = 1, \eta = 1.276$ for various values of the parameter $\kappa$: (a) $\kappa = 2$, (b) $\kappa = 3$. Oscillations of the polaron shape whose amplitude depends on the values of $\kappa$ are conspicuous (here and elsewhere $\tau = 10^{-14}$ sec.)

![Figure 1](image1.png)

**Fig. 1.** Motion of the polaron at a constant velocity in an electric field of intensity $E = 0.01$ at $\omega = 1, \eta = 1.276$ for various values of the parameter $\kappa$: (a) $\kappa = 2$, (b) $\kappa = 3$. Oscillations of the polaron shape whose amplitude depends on the values of $\kappa$ are conspicuous (here and elsewhere $\tau = 10^{-14}$ sec.)

The right top point $(\bullet)$ on the graph corresponds to the value $E = 0.0001$. The straight line corresponds to the graph $T_{PN} = 1/V$.

![Figure 2](image2.png)

**Fig. 2.** Numerical $(\bullet)$ comparison of the oscillation period $T_{PN}$ with the quantity $1/V$ for $E = 0.02, 0.015, 0.01, 0.005, 0.003, 0.001, 0.0007, 0.0005, 0.0003, 0.0002, 0.0001$ at the following parameter values: $\kappa = 2, \omega = 1, \eta = 1.276$. The right top point $(\bullet)$ on the graph corresponds to the value $E = 0.0001$. The straight line corresponds to the graph $T_{PN} = 1/V$. The chains length was varied in the form of an inverse hyperbolic cosine:

$$|b_n(0)| = \left| b_n(0) \right| (n-1) / \sqrt{2}, \quad y_n = \left| b_n(0) \right| (n-1) / \sqrt{2},$$

$$u_n = \left| b_n(0) \right|^2 / \omega_n^2, \quad du_n^2 / dt = 0.$$

The parameter values were taken to be: $\omega = 1, \eta = 1.276$. The chains length was varied in the form of an inverse hyperbolic cosine:

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$$u_n = \left| b_n(0) \right|^2 / \omega_n^2, \quad du_n^2 / dt = 0.$$
fitted to suit the calculations duration with the proviso that the polaron should not come too close to the end of a chain when calculations are over. To calculate the numerical dependence of the polaron velocity $V$ on the electric field intensity $E$ the sequence length was taken in the range from $N = 5000$ to $N = 30000$ depending on $E$. The value of $n_0$ (the center of an initial inverse hyperbolic cosine) in (10) was fitted so that at the beginning of the calculations the polaron be far away from the end of the chain. For the parameter values chosen in this work it was appropriate to take $n_0$ from $n_0 = 300$ to $n_0 = 700$. 

To calculate numerically the polaron velocity $V$ we used the relations:

$$V = dX/dt, \quad X(t) = \sum_n n|b_n(t)|^2. \quad (11)$$

Figure 1 suggests that while moving steadily, the polaron shape oscillates periodically every $T_{PN} = 1/V$ due to the presence of Peierls-Nabarro potential in a discrete chain. The amplitude of these oscillations turns to zero in the continuum approximation when the polaron size exceeds considerably the distance between neighboring sites. Numerical comparison of the oscillation period $T_{PN}(E)$ with the quantity $1/V(E)$ for various values of the electric field intensity $E$ is given in Figure 2.

Figure 3 demonstrates the dependencies of the polaron velocity $V$ on the field intensity $E$ determined by relation (9) for various values of the parameter $\kappa$. All the $V(E)$ curves have an infinite derivative at zero point: $V'(0) = \infty$, which corresponds to infinite mobility of the polaron in the conservative system under consideration determined by Hamiltonian (1). Figure 3 compares the average velocity of the polaron steady motion obtained by numerical integration of system (6), (7) with the theoretical curve determined by (9) for the following parameter values: $\kappa = 1, \eta = 1.276, \omega = 1$. For these values of the parameters $\kappa$ and $\eta$, continuum approximation is fulfilled to a high accuracy since the polaron state radius: $\bar{r} = \tau/a = 4\eta/\kappa \approx 5.1 \gg 1$. It is seen from Figure 3 that the difference between the theoretical and experimental values increases as $V$ grows. This difference is likely to be due to the fact that in deriving the theoretical dependence (9) we did not take into account that the polaron shape changes as velocity $V$ increases.

At small values of the electric field intensity, when the polaron velocity is small, its motion is not accompanied by Bloch oscillations Figure 4. The reason is that the energy of excited oscillators in the "tail" of the moving polaron increases during the period of Bloch oscillations and exceeds greatly their energy. It can be said that while moving along the chain a polaron emits phonons. In a conservative system, such emission plays the role of friction, prohibiting the polaron from accelerating in an electric field. This makes possible polaron's motion at a constant velocity in a weak electric field.

As the electric field intensity increases, the situation changes: the energy of Bloch oscillations grows, while the length of the "tail" which has grown in the course of oscillations, decreases. When the energy of Bloch oscillations exceeds the "tail's" energy, they become visible Figure 4.

Depending on the values of the system's parameters Bloch oscillations can look like oscillations of a polaron as a whole, or may take the form of a breathing mode of Bloch oscillations.

The period of Bloch oscillations in dimensionless variables is $T_{BO} = 2\pi/E (T_{BO} = 2\pi \hbar/\tau E a, E = \epsilon / e a / \hbar)$. If the electric field intensity $E = 0.05$ the period of Bloch oscillations is $T_{BO} \approx 125.66$. Figure 4, demonstrates some periods of Bloch oscillations at the onset of the polaron motion in the electric field of intensity $E = 0.05$. The graph of the function $|b_n(t)|^2$ on Figure 4 demonstrates a small segment of the polaron motion at a constant speed in the electric field of intensity $E = 0.0005$. Figure 4 also represents the graph of the function $X(t)$ (11) for the time $t = 34400$. The length of a chain for this case was chosen to be $N = 32000$. The period of Bloch oscillations for the electric field intensity $E = 0.0005$ is $T_{BO} \approx 125.66$. Hence we observe a stationary motion of a polaron (without any oscillations) for the time corresponding to almost three periods of Bloch oscillations for $E = 0.0005$. At the end of calculations ($t = 34400$) we observe the same graph of the function $|b_n(t)|^2$, as presented.
in the chain while the polaron moves along it) during the period of Bloch oscillations: $\bar{t}$ = 1000. These results are in a good agreement with theoretical conclusions \[12\], Figure 3b).

In order to estimate numerically the critical value of the electric field $E_{cr}$ at which Bloch oscillations (BO) arise let us set the energy of oscillators on the interval which the polaron runs during the period of Bloch oscillations: $W_{osc} = \hbar \omega n_{osc}$ (where $n_{osc} = vT_{BO}/a$ is the number of oscillating sites on the interval $vT_{BO}$, $T_{BO}$ is the period of Bloch oscillations) equal to the energy of Bloch oscillations $W_{BO} = \hbar \omega_{BO}, \hbar \omega_{BO} = eE_0$. As a result, the field’s critical value will be $E_{cr} = \sqrt{2\pi\omega V}$. The electric field is weak: $E < E_{cr}$, if the energy of Bloch oscillations is less than the loss of energy by polaron (caused by excitation of oscillations in the chain while the polaron moves along it) during the period of the polaron’s BO. Accordingly, the field is strong if $E > E_{cr}$.

The upper branch of the curve for the $V(E)$ dependence in Figure 5b is unstable and is not reproduced in experiments. When $E > E_{max}$, where $E_{max}$ is the maximum electric field at which the steady motion of the polaron is possible, (in numerical experiments this happens well before $E = E_{max}$ is achieved) Bloch oscillations become dominating. In this case the energy which the electron gets from the electric field goes into Bloch oscillations which, in turn, transfer it to the oscillators of the chain.

The velocity at which the mass center of a Bloch oscillator moves in the electric field is also limited and reaches its maximum at $E \leq E_{max}$. In the limit $E \to \infty$ this velocity vanishes, since the BO amplitude turns into zero and the polaron localizes at one site.

The results obtained testify to the complicated character of the charge motion in a molecular chain.

The statement that a Holstein polaron cannot move in a molecular chain with dispersion-free oscillations of sites was first made by Davydov and Enol’skii in \[19\]. In their subsequent works this statement was generalized to the case of polar crystals with optical phonons \[20\], \[21\]. Some erroneous works devoted to this problem were analyzed in \[12\].

In conclusion it may be said that in this work we have carried out a direct numerical modeling of the Holstein polaron motion in a dispersion-free chain. The modeling demonstrated that in an electric field $E < E_{cr}$ the polaron moves along the chain at a constant velocity. In the range of parameter values at which the polaron size becomes comparable with the lattice constant, its motion is accompanied by oscillations of its shape (height and width of distribution $|b_n|^2$). In the course of oscillations the polaron velocity $V$ remains invariant. In the conservative system under consideration this invariance is caused by the fact that while traveling along the chain, the polaron excites oscillations of sites.

When $E > E_{cr}$, the steady motion of the polaron becomes impossible: the energy obtained by the polaron from the field per unit time becomes greater than that lost to the excitation of oscillations in the chain. The steady motion in this case "falls" and turns to Bloch oscillations. As distinct from Bloch oscillations in a non-deformable chain when the oscillation center is left in place (finite motion), in a deformable chain the polaron’s mass center demonstrates translational movement accompanied by Bloch oscillations (infinite motion). In a strong field the polaron motion becomes similar to the breathing mode of Bloch oscillations.

Though in this work we have considered the case of a one-dimensional Holstein chain, the results obtained are rather general and can be applied to any media with dispersion-free phonons in which formation of a localized polaron state is possible. In particular, these results are valid for a strong coupling polaron in ionic crystals.

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