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Nucleation of optically excited solitons and breathers in *trans*-polyacetylene

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Abstract. Solitons and breathers are well known self-localized stable excitations in *trans*-polyacetylene. Here we discuss numerically the optical excitation of soliton pairs and breathers in *trans*-polyacetylene by short (30 fs) and resonant ($\hbar\omega = 2.0$ eV) laser pulses. In a perfect uniform chain the formation of self-localized excitations is suppressed by the decay into extended excitations like optical phonons even if the chain has absorbed sufficient energy. A small change of the Hamiltonian at one monomer and very small fluctuations of bond lengths may serve to create nucleation centres, which aid the formation of spatially localized excitations. We present soliton pairs and breathers directly created by the electric field of a laser pulse within the dipole approximation and mean-field theory for the electron–phonon coupling. The time development of the π-electron system is solved in the framework of the single-particle Schrödinger equation with the SSH Hamiltonian. We neglect the Coulomb interaction of the π-electrons.

1. Introduction

Even though the existence of charged solitons in doped *trans*-polyacetylene (TPA) is well accepted [1] there are still some open questions concerning the creation of solitons on optical excitation across the Peierls gap in undoped TPA. Experiments on photoinduced absorption [2, 3], conductivity [4], and electron-spin resonance [5] have been carried out to study the nature of elementary excitations in TPA at resonant absorption. From a theoretical point of view these excitations may be solitons [6], polarons [7] or breathers [8]. The dynamical processes in optical excitation are, however, not well understood either experimentally or theoretically, despite several fs time-resolved studies having been performed [3, 9, 10]. Our goal was therefore to investigate numerically the primary optical absorption process in TPA.

We use the well-known Su–Schrieffer–Heeger (SSH) model [6] for TPA, which assumes independent tight-binding p_z orbitals of the carbon forming a half-filled electronic band. The transfer integrals depend linearly on the displacements of the monomers (the CH units in TPA) from their equidistant positions, while the monomers form an elastic chain with spring constant K representing the σ-bonds. The displacements are assumed to obey equations of motion which contain forces from the instantaneous electron distribution.

We have studied the dynamics of a finite chain over a time span of 1500 fs under the influence of a strong electromagnetic light pulse of some fs duration numerically and have observed the excitation of soliton pairs and breathers by the electric field of the laser pulse starting from the ground state for the first time. The dynamics of the SSH model has been investigated since the early days of the model [11, 12]. In contrast to what is done in our present contribution, however, Su and Schrieffer [11] started from an excited electron–hole pair and applied adiabatic dynamics. In their investigation the electron–hole pair develops

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after some tens of fs into a separating soliton pair which eventually is reflected at the chain ends. Since the creation energy of a soliton pair is less than the energy of an electron–hole pair the excess energy excites oscillations of the monomers with a frequency somewhat lower than the optical phonon frequency—so-called breathers [8].

Because of the electron–phonon coupling in TPA the optically excited electrons strongly distort the bond-length alternation already, during the absorption process. An electron–hole pair on a dimerized chain, therefore, seems to be rather artificial and not an adequate initial condition. We, therefore, in contrast to most earlier investigators, start with the ground state for a uniform chain instead of an already somehow excited state and excite the chain with a short electromagnetic pump field with a Gaussian envelope which is coupled to the SSH model by a scalar potential in the dipole approximation. Apart from the pump pulse the electronic Hamiltonian depends on time through the monomer displacements.

In order to appropriately excite the chain with an optical pump pulse it is important to solve the time-dependent Schrödinger equation; this is done within the mean-field approximation. This means that we actually calculate the changes in the occupation numbers of the instantaneous eigenstates, in contrast to in the adiabatic dynamics of [11], where the occupation is held fixed and the electronic wave functions are replaced by the time-dependent instantaneous eigenfunctions. An approach similar to ours was used by Terai [13] to study the motion of solitons in an odd-membered ring.

We have investigated the properties of this coupled electron–phonon system for $N = 140$ electrons of a TPA chain with 140 monomers and choose fixed boundary conditions for the monomer positions. In particular we have calculated the time evolution of the staggered monomer displacements (the order parameter), the electric charge density distribution, and the instantaneous electronic eigenvalues, using an electromagnetic pulse of 30 fs length with a mean photon energy of 2 eV. In order to properly excite solitons and breathers optically, however, an important extension of the SSH model was effected. We have found that the excitation of solitons by a pump pulse is facilitated if there exists some local perturbation as a nucleation centre for the creation of a soliton pair somewhere at the chain. We have successfully used two possibilities. First we introduced a small (10^{-8} to 10^{-3} eV) diagonal element in the Hamiltonian simulating a slightly different monomer on-site energy at one site near the centre of the chain. Second we used small (5×10^{-17} m) random fluctuations of all monomer positions without change of the total energy of the chain.

To obtain these localized excitations one has to apply rather high electric fields of some 10^8 V m^{-1}. We have thus found three types of localized excitation of the chain which remain stable for some 100 fs until they locally interact with each other as detailed below.

(1) Bound soliton pairs, which are similar to polaronic lattice distortions [14], moving with velocities ranging from two to four times the velocity of sound. In contrast to polarons they have among other different features a dipole moment oscillating with the difference frequency of the corresponding pair of gap states. Charge separation in a substituted polyacetylene was also found experimentally [10].

(2) Charged unbound soliton pairs which may repel each other, similar to those found by Su and Schrieffer [11] who started from an excited electron–hole pair.

(3) Localized charge-neutral lattice oscillations which are moving with different velocities along the chain lower than those of the solitons. They will be related to the breathers discussed by Bishop *et al* [8].

Despite the fact that electron–electron interaction will play an important role we restrict ourselves in this paper to the simple SSH model as a first attempt to investigate soliton dynamics starting from the dimerized ground state. While taking electron–electron

interaction within the unrestricted Hartree–Fock approximation into account by using a Pariser–Parr–Pople model (see [15]) introduces no important difficulties [16], a treatment beyond the Hartree–Fock method still awaits further work.

This contribution is organized as follows. In section 2 we introduce the model we have used. Section 3 contains our results obtained using a fixed nucleation centre at some monomer near the centre of the chain. In section 4 we discuss the bound soliton pairs within the continuum model [17] for TPA. In section 5 small random fluctuations of the monomer positions are introduced which conserve the energy of the chain. Again localized distortions are excited after the pump pulse and are very similar to those discussed in section 3. We conclude in section 6.

2. The model

In our calculations we apply the SSH Hamiltonian [6]

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_p + \mathcal{H}_E(t)$$

where

$$\mathcal{H}_e = \sum_{nn's} \mathbf{c}^\dagger_{ns} \mathbf{h}_{nn'} \mathbf{c}_{n's} = \sum_{nn's} \mathbf{c}^\dagger_{ns} \left(t^0_{nn'} + \sum_l \beta^l_{nn'} \mathbf{u}_l \right) \mathbf{c}_{n's}$$

is the Hamiltonian of the independent π-electrons with the tight-binding hopping integrals

$$t^0_{nn'} = -t_0(\delta_{n,n'+1} + \delta_{n,n'-1})$$

and the linear electron–phonon coupling

$$\beta^l_{nn'} = \alpha(\delta_{l,n} - \delta_{l,n'})(\delta_{n,n'+1} - \delta_{n,n'-1}).$$

We describe the harmonic lattice by

$$\mathcal{H}_p = \sum_l \frac{\mathbf{p}^2_l}{2M_l} + \frac{1}{2} \sum_{ll'} \mathbf{u}_l D_{ll'} \mathbf{u}_{l'}$$

with $D_{ll'} = K\left(2\delta_{l,l'} - \delta_{l,l'+1} - \delta_{l,l'-1}\right)$ and the dipole interaction with the electric field $E(t)$ by

$$\mathcal{H}_E(t) = e \sum_{ns} \mathbf{x}_n (\mathbf{c}^\dagger_{ns} \mathbf{c}_{ns} - \tfrac{1}{2}) E(t).$$

Here $\mathbf{x}_n = na + \mathbf{u}_n$ are the monomer positions.

The displacements $u_l(t) = \langle \mathbf{u}_l \rangle$ are calculated from their equation of motion

$$M_l \ddot{u}_l(t) = -\sum_{nn'} \beta^l_{nn'} \rho_{n'n}(t) - \sum_{l'} D_{ll'} u_{l'}(t) - eE(t)(\rho_{ll}(t) - 1)$$

with initial values given by $\partial E_{\text{tot}}/\partial u_l = 0$ (the dimerized ground state). The density matrix

$$\rho_{nn'}(t) = \sum_s \langle \mathbf{c}^\dagger_{n's} \mathbf{c}_{ns} \rangle = 2 \sum_k \psi_{nk}(t)\, f_k\, \psi^*_{n'k}(t)$$

is determined by the occupation f_k of the wave functions $\psi_{nk}(t)$ given as solutions of the time-dependent Schrödinger equation

$$\mathrm{i}\hbar \dot{\psi}_{nk}(t) = \sum_{n'} h_{nn'}(t) \psi_{n'k}(t). \tag{1}$$

Here $\mathbf{u}_l$ in $\mathbf{h}_{nn'}$ was replaced by its expectation value $\langle \mathbf{u}_l \rangle$ which corresponds to the mean-field approximation

$$\sum_s \langle \mathbf{c}^\dagger_{n's} \mathbf{u}_l \mathbf{c}_{ns} \rangle \approx \rho_{nn'}(t) u_l(t).$$

The states $\psi_{nk}(t)$ may be written in terms of the instantaneous eigenfunctions $\varphi_{nk}(t)$ of $h_{nn'}(t)$:

$$\psi_{nk}(t) = \sum_{k'} \varphi_{nk'}(t) \alpha_{k'k}(t) \tag{2}$$

which are determined by

$$\sum_{n'} h_{nn'}(t) \varphi_{n'k}(t) = \varepsilon_k(t) \varphi_{nk}(t).$$

Therefore $\alpha_{k'k}(t)$ obeys

$$\mathrm{i}\hbar \dot{\alpha}_{k'k}(t) = \varepsilon_{k'}(t) \alpha_{k'k}(t) - \mathrm{i}\hbar \sum_{n\,k''} \varphi^*_{nk'}(t) \dot{\varphi}_{nk''}(t) \alpha_{k''k}(t). \tag{3}$$

If we start with the charge-neutral half-filled chain we choose $\alpha_{k'k}(0) = \delta_{kk'}$ and f_k as the Fermi distribution function at $T = 0$ K.

In the adiabatic dynamics [11] the $\alpha_{k'k}$ are approximated with constants $\delta_{kk'}$ and equation (1) need not be solved.

For TPA we adopt the parameters often used [6]: $\alpha = 4.1$ eV Å^{-1}, $K = 21$ eV Å^{-2}, $t_0 = 2.5$ eV, and $M = 3114\hbar^2$ eV^{-1} Å^{-2}, and hence the electron–phonon coupling constant $\lambda = 4\alpha^2/(\pi t_0 K) = 0.408$, the Peierls gap $2\Delta_0 = 1.35$ eV, and the bare and renormalized optical phonon frequencies are $\omega_0 = 2\pi/(25.2\ \mathrm{fs})$ and $\omega_r = 2\pi/(39.4\ \mathrm{fs})$, respectively.

3. The electronic on-site nucleation centre

In order to find spatially localized excitations like solitons and breathers within the dipole approximation for the electric field it is important to introduce nucleation centres. One possible way is to modify the Hamiltonian by introducing a small defect at some site. We have used a finite constant diagonal element $h_{70,70} = \sigma$ of the Hamiltonian at the 70th site of our 140-monomer chain. We start our simulation with the ground state of an electrically neutral half-filled TPA chain with an even number of monomers and $\alpha_{k'k}(0) = \delta_{kk'}$. It shows a Peierls gap [18] in the electronic energy spectrum and alternating bond lengths. At $t_E = 150$ fs we apply a strong resonant laser pulse:

$$E(t) = E_0 \exp\left(-\left(\frac{t - t_E}{T} \right)^2 \right) \cos(\omega t)$$

with $T = 30$ fs. We have varied σ, E_0 and ω and have found a strong dependence of the evolutionary details from the values of these parameters, i.e. our model shows deterministic chaos as may be expected. Nevertheless there are several features in common ('scenarios') which will be discussed now for one characteristic example. We choose a rather strong resonant laser pulse with $E_0 = 2.59 \times 10^8$ V m^{-1} and $\hbar\omega = 2.0$ eV and a diagonal disturbance of the Hamiltonian of $\sigma = 1$ meV.

We first discuss our results in terms of the evolution of the order parameter (figure 1)

$$r_n(t) = -\frac{1}{4}(-1)^n (2u_n(t) - u_{n-1}(t) - u_{n+1}(t))$$

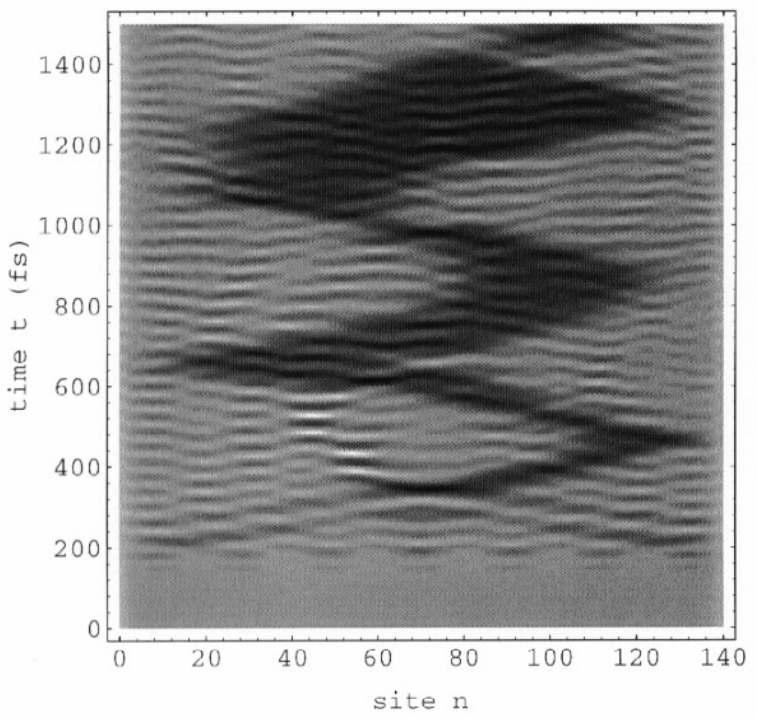

Figure 1. The order parameter $r_n(t)$ in the case of a diagonal disturbance $\sigma = -1$ meV of the Hamiltonian and a maximum electric field $E_0 = 2.59 \times 10^8$ V m^{-1} at $t_E = 150$ fs. The shading ranges from a maximum (8.6×10^{-10} m) to a minimum (-8.0×10^{-10} m).

and the smoothed total charge density (figure 2)

$$\varrho_n(t) = \frac{1}{4}\left(2\rho_n(t) + \rho_{n-1}(t) + \rho_{n+1}(t)\right)$$

with

$$\rho_n(t) = \frac{e}{a}\left(1 - 2\sum_{k=1}^{N/2} |\ \psi_{nk}(t)\ |^2\right).$$

High-frequency components of the charge density are suppressed by averaging over 1 fs.

In our numerical simulations we have found delocalized lattice vibrations, breathers and bound and free soliton pairs, which are discussed in detail below. Most interesting are bound soliton pairs found here for the first time. Soliton pairs show up in the plot of the order parameter (figure 1) as dark regions where the order parameter has changed sign. The bound soliton pairs apparently move with velocities ranging from two to four times the velocity of sound. The distance between the solitons of the bound pair may take different values.

Looking at the time evolution of the order parameter (figure 1) and the charge density (figure 2) of the chain we see that up to 120 fs (before the pump pulse) the chain remains in its dimerized ground state. In the range from 120 fs to 220 fs the vibrational pattern is due to electronic transitions from states near $-\hbar\omega/2$ to states near $\hbar\omega/2$ since despite the limited chain length of 140 monomers the k-selection rule is rather well satisfied. As is clearly seen from the density plot of the charge density (figure 2) at about 340 fs a bound soliton

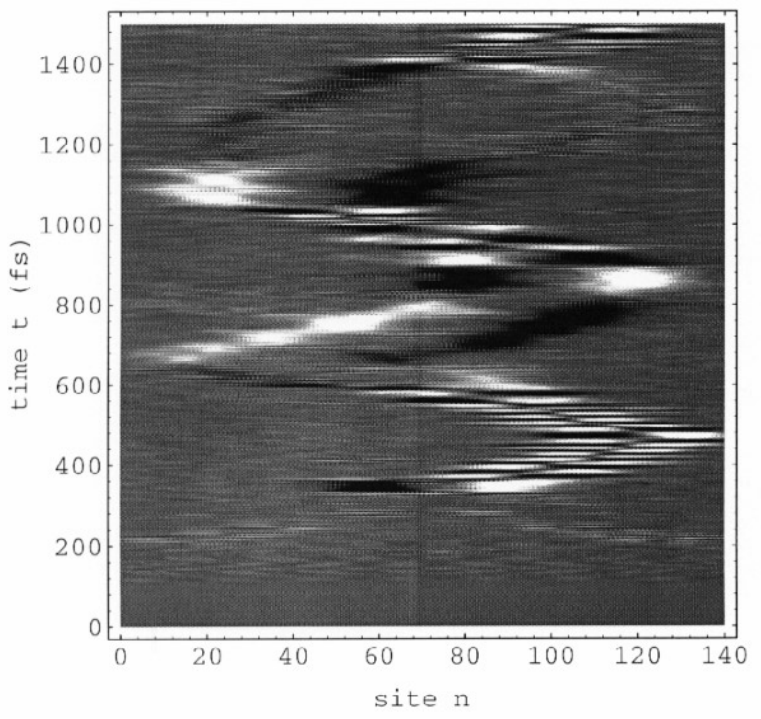

Figure 2. The charge density $\varrho_n(t)$ for the same diagonal disturbance of the Hamiltonian as in figure 1. The shading ranges from white ($0.073e/a$) to black ($-0.079e/a$).

pair develops. It is reflected at the right-hand boundary at 460 fs and exists up to 600 fs. It is remarkable that the bound soliton pair has an oscillating dipole moment which gives the largest contribution to the total dipole moment of the whole chain. We shall discuss these features in section 4 with the continuum model and its soliton pair solution. Furthermore figure 1 reveals a lot of localized lattice vibrations which are stable over some 100 fs, have a width of typically $9a$ and a frequency of $\omega_B \approx 0.94\omega_r \approx 2\pi/(45\text{ fs})$. We may call them breathers since they can be described by the analytic formula for breathers given by Horovitz (see [12]). They move with much lower velocities than the solitons. There is no appreciable charge found in the regions of localized or extended chain vibrations (cf. figure 2). The strong breather which develops at about 340 fs together with the bound soliton pair moves from the 54th to the 45th site and interacts at about 600 fs with the bound soliton pair where an unbound soliton pair emerges very quickly. In the time evolution of the instantaneous eigenvalues (figure 3) the soliton pair is represented by the highest eigenvalue ε_{70} and the strong breather by the oscillations of the eigenvalue ε_{69} (cf. the discussion by Bishop *et al* [8]). The scattering event at 600 fs clearly diminishes the oscillations of ε_{69} while the highest eigenvalue ε_{70} increases to form the unbound pair. Later on similar scattering events between solitons and breathers lead to changes in the velocity of solitons, to transformations between well separated soliton pairs and bound soliton pairs, and to changes in the velocity, strength, frequency, and width of the breathers. At about 1200 fs a diverging unbound soliton pair with a low polarization is formed.

The disturbance of the Hamiltonian can be chosen to be much smaller than 1 meV to obtain optically excited soliton pairs. We have calculated the optical excitation of the chain

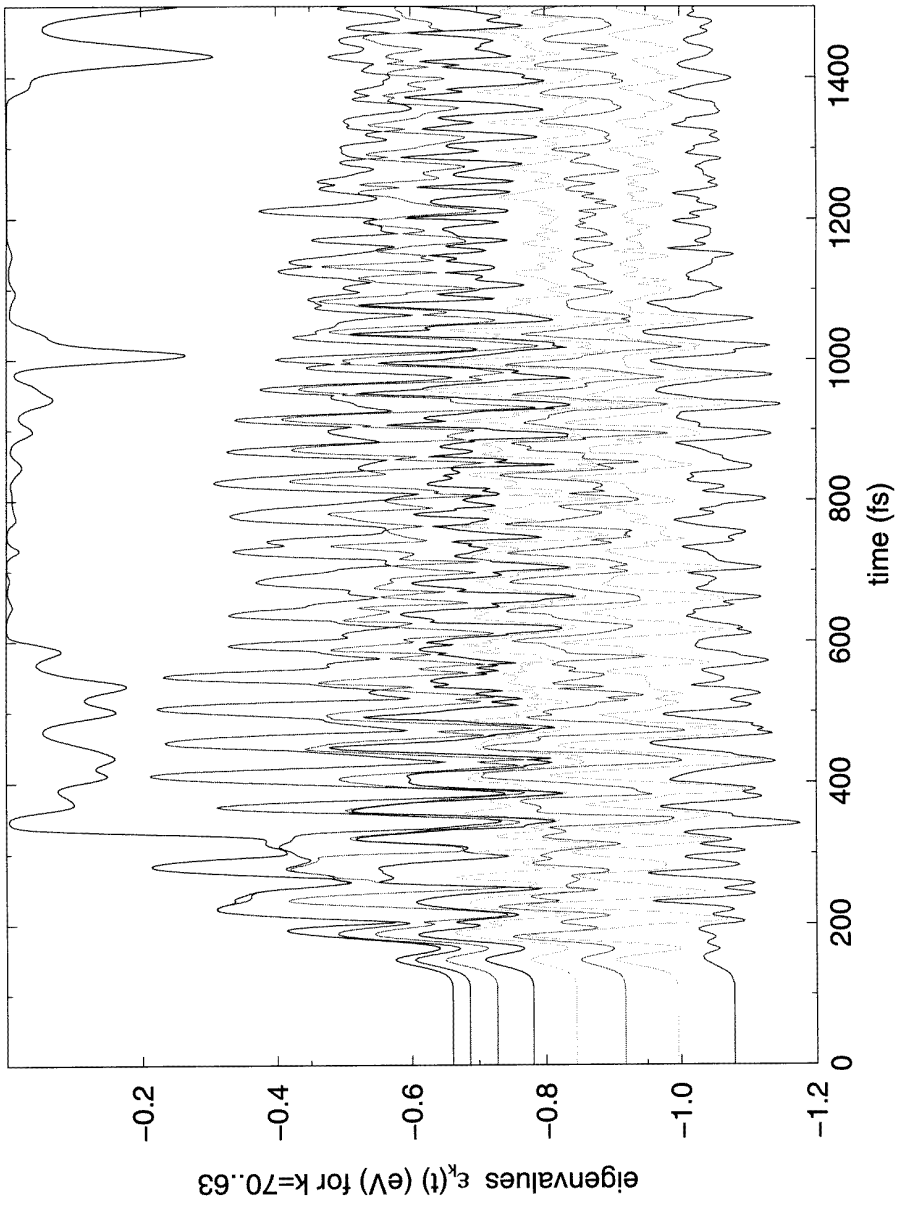

Figure 3. Instantaneous eigenvalues $\varepsilon_k(t)$ of the Hamiltonian for $k = 70$ to $k = 63$ (with parameters as in figure 1).

by the same electric field for disturbances of $\sigma = 10^{-8}$ eV, $\sigma = -10^{-7}$ eV, $\sigma = 10^{-6}$ eV, $\sigma = -10^{-5}$ eV, and $\sigma = 10^{-4}$ eV. In all cases we have found bound and well separated soliton pairs up to 1.5 ps. Although in each of these cases the order parameter and the local charge density have a different time evolution in detail, the general features discussed above are the same. Furthermore we have switched on the diagonal perturbation of the Hamiltonian at site 70 at different times after the pump pulse. In general localized excitations evolved only after the nucleation centre was introduced. If we switched off the disturbance some time after the pump pulse (e.g. at 400 fs) again a scenario of localized excitations was found.

4. The soliton pair in the continuum model

We now discuss the bound soliton pair in the continuum model for TPA. The electronic energy spectrum of the continuum Hamiltonian [17]

$$\mathcal{H} = 2at_0\left(-\mathrm{i}\frac{\partial}{\partial x}\right)\sigma_1 - \Delta(x)\sigma_2 \tag{4}$$

with the gap function

$$\Delta(x) = \Delta_0 - 2at_0\kappa[\tanh\kappa(x + x_0) - \tanh\kappa(x - x_0)] \tag{5}$$

for a soliton pair [7] consists of the valence and conduction bands and two gap states. The soliton distance $2x_0$ and the soliton width $1/\kappa$ obey $\Delta_0 \tanh 2\kappa x_0 = 2at_0\kappa$.

The total energy is minimized via the gap equation

$$\Delta(x) = 2\pi at_0\lambda\sum_k f_k\varphi_k^\dagger(x)\sigma_2\varphi_k(x) + 2\pi at_0\lambda(n_- - n_+)\varphi_-^\dagger(x)\sigma_2\varphi_-(x) \tag{6}$$

if the occupation numbers for one spin component are $f_k = 1, 0$ for the valence and conduction band states, respectively, and $n_\pm$ are arbitrary for the gap states, while the energies $\pm\hbar\omega_p$ of the gap states fulfil

$$\hbar\omega_p = \sqrt{\Delta_0^2 - (2at_0\kappa)^2} = \Delta_0 \sin\frac{\pi\nu}{2} \tag{7}$$

with $\nu = n_- - n_+$ the occupation difference of the lower and the upper gap states.

We stress that although 2ν is an integer in thermodynamic equilibrium at $T = 0$ K, equation (7) gives a stable, i.e. energy-minimizing, solution for any $0 < \nu < 1$. It describes a soliton pair whose distance $2x_0$ increases at $\nu \to 0$. The gap levels $\pm\hbar\omega_p$ therefore play the roles of anti-bonding and bonding states, respectively.

In the time-dependent continuum model the gap function $\Delta(x, t)$ obeys the equation of motion

$$\frac{\ddot{\Delta}(x,t)}{\omega_0^2} + \Delta(x,t) = 2\pi at_0\lambda\sum_k f_k\psi_k^\dagger(x,t)\sigma_2\psi_k(x,t) \tag{8}$$

while $\psi_k(x, t)$ is a solution of the time-dependent Schrödinger equation

$$\mathrm{i}\hbar\dot{\psi}_k(x,t) = \left[2at_0\left(-\mathrm{i}\frac{\partial}{\partial x}\right)\sigma_1 - \Delta(x,t)\sigma_2\right]\psi_k(x,t). \tag{9}$$

In order to describe a bound soliton pair with an oscillating dipole moment such as was found in our numerical simulations of the finite chain we derive an appropriate solution of the coupled equations (8) and (9). We accept the only time dependence of the wave functions to be given by the coefficients $\alpha_{k'k}(t)$ in equation (2). From equation (3) therefore $\alpha_{k'k}(t) = \alpha_{k'k}^0\exp(-(\mathrm{i}/\hbar)\varepsilon_k t)$, which solves equation (9).

Since our numerical calculations show that in the bound soliton pair regime the coefficients $\alpha^0_{k'k}$ are approximately diagonal for the band states, we assume $\alpha^0_{k'k} = \delta_{kk'}$ for $k \neq \pm$. Now the lower and upper gap states ($k = \pm$) are of the forms

$$\psi_-(x,t) = \beta_- e^{i\omega_p t}\varphi_-(x) - \beta_+ e^{-i\omega_p t}\varphi_+(x)$$
$$\psi_+(x,t) = \beta_+ e^{i\omega_p t}\varphi_-(x) + \beta_- e^{-i\omega_p t}\varphi_+(x)$$

with $\beta_-^2+\beta_+^2 = 1$ if we assume $\psi_{nk}(0)$ (and hence at any time t) to be a unitary wave function matrix which according to the Pauli principle forms a Slater determinant as the many-particle wave function of the independent electrons. Numerically the 'occupation numbers' $\beta_\pm^2$ turn out to be noninteger. They specify the contribution of the electrons to the lower- and upper-gap eigenstates, respectively. With $n_\pm = \beta_\pm^2$ the right-hand sides of equation (8) and equation (6) are now equal and the time-independent gap function equation (5) solves equation (8). Note that $\varphi_+^\dagger(x)\sigma_2\varphi_+(x) = -\varphi_-^\dagger(x)\sigma_2\varphi_-(x)$ and $\varphi_+^\dagger(x)\sigma_2\varphi_-(x) \equiv 0$. $n_+ + n_- = 1$ guarantees charge neutrality with an integer number of electrons despite the noninteger 'occupations' $n_\pm$.

The electronic dipole moment for this solution is

$$d_e(t) = 2e\sum_k f_k \int \mathrm{d}x\ \psi_k^\dagger(x,t)x\psi_k(x,t) + 4ex_0\Re\beta_-\beta_+ e^{-2i\omega_p t}.$$

Its last term shows oscillations with a frequency $2\omega_p$ corresponding to the energy difference of the two soliton-pair gap states since $\psi_k(x,t)$ is a mixed state of the two (i.e. $\beta_\pm$ are both different from 0). The first term vanishes because of the parity of the eigenfunctions.

Focusing our attention now on the bound soliton pair (figure 2) in the time interval between about 400 and 600 fs we observe a dipole frequency of $2\omega_p = 2\pi/(17\text{ fs})$ corresponding to a gap state $\hbar\omega_p = 0.12$ eV. In figure 3 we display the time evolution of the instantaneous eigenstates. The mean energy of the highest instantaneous valence band state shows good agreement with $\varepsilon_- = -0.12$ eV in the time range mentioned above. Since from figure 3 an effective shrinking of the band gap is observed we assume an effective gap parameter $\Delta_0 = 0.5$ eV and find in the continuum model the width of the soliton pair as $2x_0 = 22a$ which again agrees with that in figure 2. Furthermore we have calculated the time evolution of the occupation numbers $n_\pm$ of the instantaneous eigenstates. The calculated occupation difference $\nu = 0.13$ of the $k = 70$th and the $k = 71$st instantaneous eigenstates of the chain which is approximately constant in the time interval 400–600 fs is somewhat smaller than the value 0.15 from equation (7) in the continuum model. The numerical value of the corresponding dipole moment $1.9 \times 10^{-9} e$ m is the same as in the continuum model.

The considerations of the continuum model break down for separated solitons since the influence of the excitations of the remaining chain may easily be stronger than the forces which tend to form an isolated soliton pair.

5. Nucleation by small fluctuations

We have further used small chain fluctuations conserving total energy to create nucleation centres. In the global minimum of the total energy, which is realized in the ground state, any chain fluctuation gives rise to an increase of the total energy. Fluctuations without change of the total energy are only possible if the chain is excited with respect to the ground state. We, therefore, first excite the chain with fluctuations $\delta u_n(t)$ given by

$$\delta u_n(t) = w_n(t)\,\Delta u^0 \qquad -1 \leqslant w_n(t) \leqslant +1$$

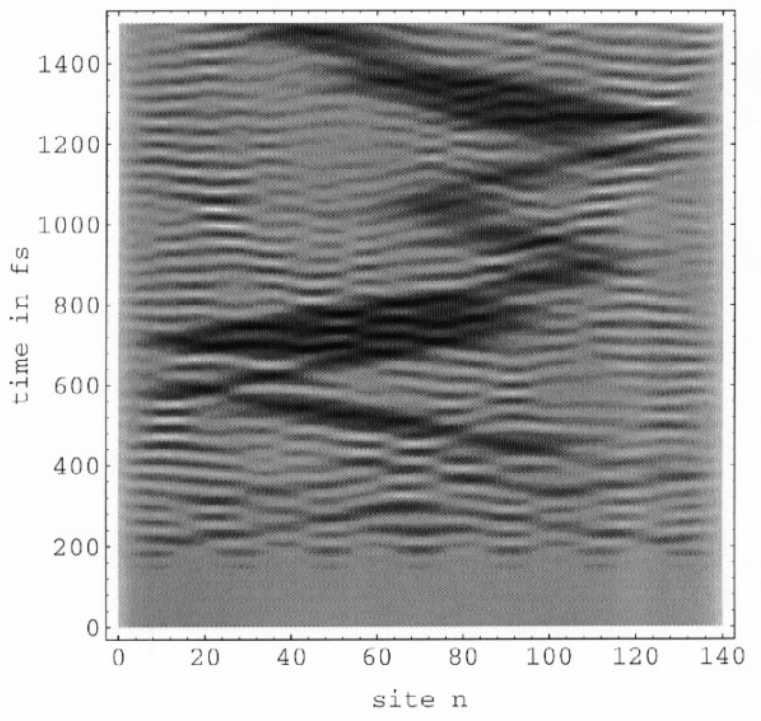

Figure 4. The time-dependent order parameter $r_n(t)$ for small chain fluctuations with parameters given in the text. The maximum value (white) and minimum value (black) are 8.3×10^{-10} m and -7.6×10^{-10} m, respectively.

where $w_n(t)$ is randomly distributed. Up to 1 fs at each time step the fluctuations $\delta u_n(t)$ give an additional contribution to the monomer motion and distortion of the ground-state order parameter.

After the chain has been excited, fluctuations $\delta u_n(t)$ with

$$\delta u_n(t) = w_n(t)\,\Delta u \qquad -1 \leqslant w_n(t) \leqslant +1$$

disturb the homogeneous dynamics of the chain at each time step, where now the total chain energy is conserved. This has been realized by selection of random sets $w_n(t)$, which lead to an alternating integrated energy error in the range from $-\epsilon$ to $+\epsilon$. Energy conservation is well satisfied, if this error is small compared with the numerical energy error due to the finite-time step size. This error is smaller than 10^{-5} eV within 1.5 ps at excitation energies of only a few eV and a step size of $\Delta t = 0.025$ fs. In contrast to in section 3, the positions of the nucleation centres are now randomly distributed along the chain depending on the start value of the random-number generator.

As an example of various calculations with different fluctuations and electric field strengths we discuss the results obtained with the following numerical values. The electric field of the laser pulse with frequency $\hbar\omega = 2.0$ eV achieves its maximum $E_0 = 2.5 \times 10^8$ V m^{-1} at 150 fs. The fluctuation parameters are given by

$$\Delta u^0 = 5 \times 10^{-20} \text{ m} \qquad \Delta u = 5 \times 10^{-17} \text{ m} \qquad \epsilon = 10^{-8} \text{ eV}.$$

The density plot of the order parameter $r_n(t)$ in figure 4 shows a bound soliton pair created at about 450 fs which moves to the left and is reflected from the chain edge at about

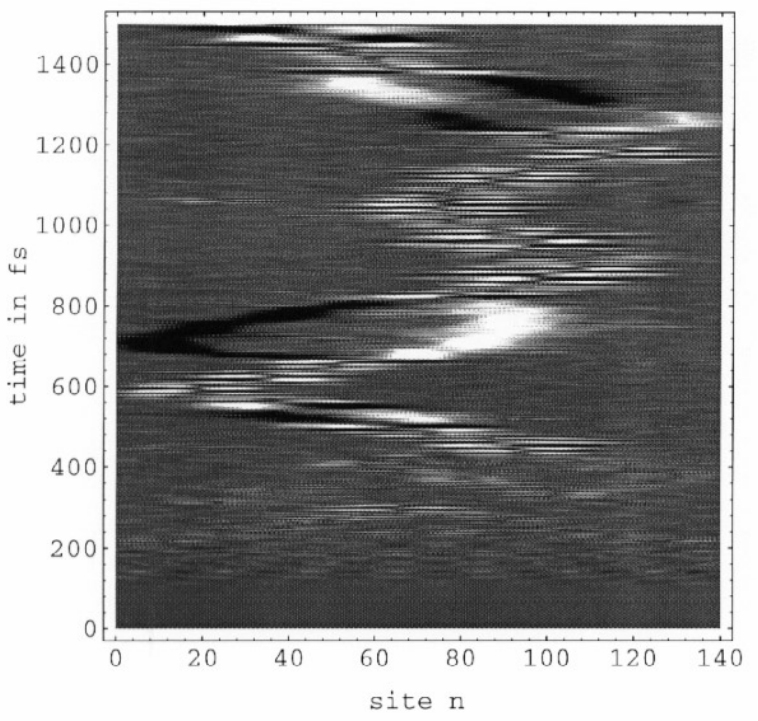

Figure 5. The charge density $\varrho_n(t)$ corresponding to figure 4. $\varrho_n(t)$ ranges from $-0.073e/a$ (black) to $0.085e/a$ (white).

600 fs. The formation of a free soliton pair at about 680 fs is apparently connected with the interaction of the bound soliton pair and one or two breathers. At about 800 fs again a bound soliton pair is formed which lasts up to 1200 fs. In this region apart from oscillations with the transition frequency between the two gap states as was discussed in section 4 the soliton pair shows charge pulsations with a lower frequency which is best shown in the charge density plot (figure 5) and the polarization (figure 6) of the chain. In figure 6 we depict the smoothed polarization where the high frequencies corresponding to more than 1 eV have been eliminated and compare it with the instantaneous eigenenergy of the gap state. Again there is good agreement with the parameters of the continuum model: the gap state pulsates between 0.14 eV and 0.3 eV which corresponds to $x_0 = 10a$ and $x_0 = 7a$ (again using an effective gap parameter of $\Delta_0 = 0.5$ eV), which agrees with the soliton pair width in figure 5. The oscillation frequency may be crudely deduced from the oscillations of the polarization (figure 6) and agrees with the pulsating frequency of transition between the gap states. An analytic description of these pulsations in the framework of the continuum model is, however, still lacking.

6. Conclusions

The numerical calculations of the dynamics during and after optical excitation in TPA presented in this paper show that for very small but finite disturbances of the chain homogeneity, extended excitations are able to decay into spatially localized and self-confined excitations like breathers and soliton pairs. Within some ps we observe the formation of

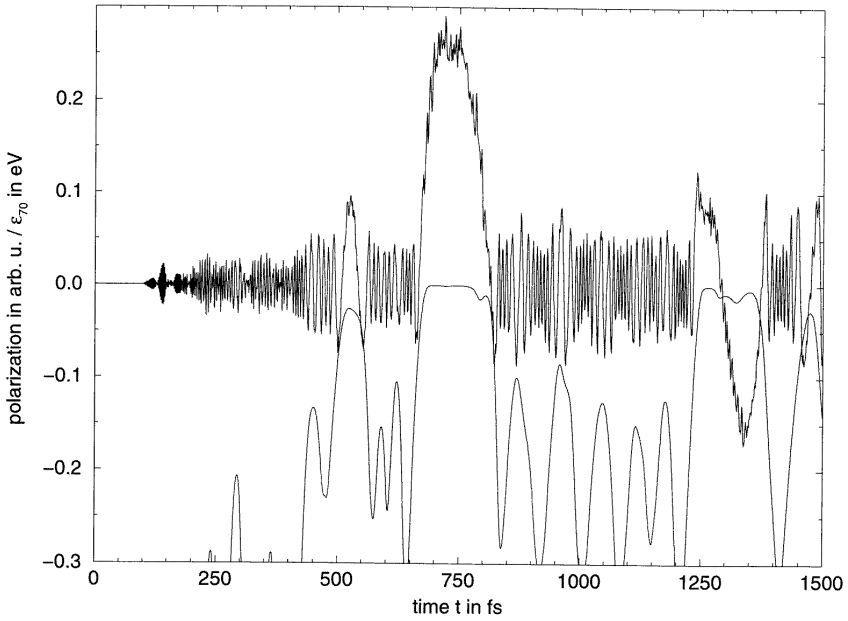

Figure 6. A comparison of the smoothed polarization with the instantaneous gap state energy (with parameters as in figure 4).

bound soliton pairs with higher occupation of the soliton bonding than of the anti-bonding level. This new species of self-localized excitations due to electron–phonon coupling is connected with a large chain polarization, whose frequency is determined by the energy separation of the soliton bonding and anti-bonding levels. Collisions of solitons with breathers lead to changes of the soliton and breather velocities along the chain and to transformations of bound into well separated soliton pairs and vice versa.

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