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Fractionally charged kinks in one-third-filled band CDW systems with the step-potential model

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Abstract. The topological excitations (kinks) in a one-dimensional, one-third-filled band charge density wave system (i.e. a π electron system) and their electronic spectra are studied. The geometry is obtained by finding the self-consistency between bond lengths and π electron densities in the middle of each bond. The π electron density distributions are evaluated with the step potential model. It is shown that the ground state of the perfectly trimerized system has a long–short–long bond sequence as expected from the anti-integrable limit and in contrast to the Su–Schrieffer approach. Nevertheless the kinks obtained are fractionally charged. Type I kinks have the (spin, charge) relation $(\frac{1}{2}, -e/3)$ and $(0, +2e/3)$, type II kinks $(\frac{1}{2}, +e/3)$ and $(0, -2e/3)$.

1. Introduction

Nonlinear topological excitations (solitons) in a one-dimensional coupled electron–phonon charge density wave (CDW) system and their electronic structure based on Hückel-type, tight-binding approximations are well studied: for the half-filled band case [1, 2] and for the one-third-filled band case [3, 4] (for reviews see [5–7]). We have recently shown that the statics [8] and the dynamics [9] of solitonic excitations in polyacetylene (one electron per site, thus a half-filled band case) can be treated by a simple step potential model of a nearly free π electron (NFE) coupled to the elastic lattice of σ-bonded hydrocarbon ions. Solving the one-dimensional (along s) one-particle Schrödinger equation (m_e is the mass of the electron)

$$[-(\hbar^2/2m_e)\mathrm{d}^2/\mathrm{d}s^2 + V(s)]\varphi_k(s) = E_k\varphi_k(s) \tag{1}$$

with piecewise constant bond potentials $V(s) = V_i$ for $(i-1)a \leqslant s \leqslant ia$, each of width a and with the potential being lower for the shorter bond, the eigenstates E_k and the corresponding wave-functions $\varphi_k(s)$ are obtained. The π electron density distribution $\rho(s) = \sum_k^{occ} \varphi_k^2(s)$ is evaluated by summing the contribution of the occupied states (Pauli principle). The geometry of a system is obtained by finding the self-consistency between bond potential V_i and π electron density $\rho_i = \rho((i - \frac{1}{2})a)$ in the middle of each bond i [8]

$$V_i = \alpha a(\overline{\rho} - \rho_i)\frac{\hbar^2}{2m_e a^2}. \tag{2}$$

In the case of hydrocarbons (one electron per site) $\overline{\rho} = 1$, $a = 1.40$ Å, and the value of the electron–phonon coupling constant α scaled to butadiene and benzene is $\alpha = 1.95$.

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The physical background of equation (2) is the following: the π electron charge in a bond attracts the adjacent σ-bonded CH^+ ions by Coulomb forces and thus reduces the bond length and the corresponding bond potential V. The step potential model leads essentially to the same results as the SSH model, but it has no free parameters [10] and it is not restricted to electron–hole symmetry. The model can easily be refined by solving the Schrödinger equation for the given potential $V(s)$ which has troughs at each site in the chain, but this does not change the wave-functions essentially [8]. The troughs can easily be taken into account to check this statement. Using the step potential model [8] we confirmed an early result [11] that the polyene lattice (a chain with even number of sites) of assumed equal bond lengths is unstable and undergoes dimerization, thereby opening a gap in the electronic spectrum between filled and empty states. There are two degenerate phase patterns of the dimerization termed A phase and B phase, where the B phase pattern is a translation of the A phase pattern by one lattice spacing. As shown in [8] a topological soliton excitation or kink is formed by a domain wall separating regions of A phase and B phase material (i.e. in a large ring with an odd number of sites). This domain wall has a certain extent (~ 15 sites) and there is one intergap state with the wave-function localized at the domain wall. Depending on the occupation of this intergap state the soliton is neutral (singly occupied intergap state, thus with spin) or charged $\pm e$ (empty/doubly occupied intergap state, thus no spin), where e is the elementary charge.

It is of interest to apply the step potential model to the one-third-filled band case with possible application to tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) [12], which under 19 kbar pressure has commensurability three in the b direction and where *fractional* charged kinks are expected [3, 4, 13]. In the following we show that for the ground state of the one-third-filled band system (two π electrons per three sites; each site has charge $+2e/3$ on average) the lattice of assumed equal bond lengths is unstable and undergoes *trimerization*.

We use the step potential model [8] which is conceptually the simplest approach. To avoid boundary effects at the ends of a chain system we take a ring system consisting of $N = 3m$ sites and $M = 2m$ π electrons, m being either even ($m = 2n$) or odd ($m = 2n + 1$). In the case of assumed equal bond lengths we can solve the 'free particle in a ring' problem analytically by (note that the states $k > 0$ are doubly degenerate)

$$E_0 = 0 \qquad \varphi_0(s) = \sqrt{1/Na}$$

$$E_k = [h^2/2m_e(Na)^2]k^2 \qquad \begin{cases} \varphi_k(s) = \sqrt{2/Na}\sin((2k\pi/Na)(s - \phi a)) \\ \varphi_k(s) = \sqrt{2/Na}\cos((2k\pi/Na)(s - \phi a)) \end{cases} \tag{3}$$

$$k = 1, 2, 3, \ldots .$$

The CDW is then given analytically by equations (4)–(8) below for specific cases and the electron density $\rho_i = \rho((i - \frac{1}{2})a)$ in the middle of each bond can be evaluated for arbitrary phase ϕ. Relaxing the lattice from the configuration of assumed equal bond lengths by electron–phonon coupling we have to follow the numerical procedure applying equation (2) and solving the Schrödinger equation until convergence to self-consistency (i.e. with $\overline{\rho} = \frac{2}{3}$, $a = 1.40$ Å and $\alpha = 1.95$). *The most stable configuration is then found for a specific value of the phase* ϕ.

2. The perfectly trimerized system

For the ground state (GS) of a ring of assumed equal bond lengths m is set even. Thus a '$M = 4n$' ring is considered in order to create a CDW: the two uppermost electrons are both in the same highest occupied molecular orbital (HOMO; without losing generalization we take the sin function). Thus summing the contribution of the occupied states given in equation (3) the electron density distribution of the unrelaxed system in the (GS) becomes

$$\rho^{GS}(s) = \sum_{k}^{m/2} \varphi_k^2(s) = \frac{2}{3ma}\left((m-1) + 2\sin^2\left(\frac{m\pi}{3ma}(s - \phi a)\right)\right). \tag{4}$$

In this specific case of the free electron in a ring all electrons occupying states of lower energy ($k < m/2$) contribute to the charge density (first term in equation (4)), but do not contribute to the CDW, only the HOMO ($k = m/2$) contributes to the CDW amplitude (the second term in equation (4)), which goes to zero for $m \to \infty$. This is in contrast to the relaxed system after obtaining convergence to self-consistency by equation (2): there all the occupied wave-functions contribute to the CDW amplitude, which goes to a finite value depending on α for $m \to \infty$. The following three sequences of densities in the middle of bonds evaluated from equation (4) are distinguished:

(i) density sequence 'low–high–middle' (phase $\phi = \frac{1}{4}$) is unstable: it relaxes to bond sequences 'long–short–long';

(ii) density sequence 'low–high–high' (phase $\phi = \frac{1}{2}$) is metastable: it relaxes to bond sequences 'long–short–short';

(iii) density sequence 'low–high–low' (phase $\phi = 0$) has the energy minimum: it relaxes to bond sequences 'long–short–long'.

(See figure 1; the 'free particle' and the anti-integrable limit [14] defined by $\alpha = \infty$.) The ground state (GS) of the relaxed system has the bond sequences 'long–short–long' as expected from the anti-integrable limit (figure 1) and in contrast to the Su–Schrieffer approach [3]. The discrepancy of this result is due to the overproportional increase of the Coulomb attraction towards adjacent nuclei [10] neglected in the SSH Hamiltonian by restricting to the electron–hole symmetry [1]. There are three degenerate patterns of the bond sequence 'long–short–long' called A phase, B phase and C phase, where the B phase pattern is the A phase pattern shifted by one lattice constant to the right while the C phase pattern is the A phase pattern shifted by two. The domain walls between two different phase patterns are called topological solitonic excitations or kinks.

3. Kinks of fractional charge

Kinks are domain walls from a C phase pattern to an A phase pattern (type I), or domain walls from an A phase pattern to a C phase pattern (type II) (A/B phase pattern and B/C phase pattern domain walls correspondingly). The accumulated excess charge density along the arc is

$$\eta(s) = \int_0^s (\bar{\rho} - \rho(s'))\,\mathrm{d}s'. \tag{5}$$

In the anti-integrable limit the excess charge density of a kink is simply (number of sites) $\times(+\frac{2}{3})$ − (number of electrons). In the following kinks are created by the singly and doubly excited states of a ring of assumed equal bonds (free particle) with m being odd (thus an '$M = 4n + 2$' ring in order to create a CDW in the excited state). The asymmetric case gives a kink pair of type (I–II), while the symmetric case gives a kink triplet of type (I–I–I).

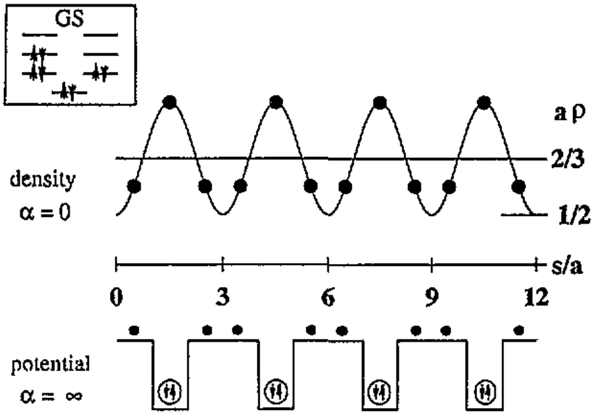

Figure 1. The perfectly trimerized ground state (GS) of a ring ($m = 4$, $N = 3m = 12$ sites, $M = 2m = 8$ π-electrons, thus a '$4n$' ring). Top, 'free particle'. Boxed, occupation of levels. Electron density distribution by equation (4), phase $\phi = 0$, sequence 'low–high–low' of densities in middle of bonds (points). Bottom, the step potential shows a 'long–short–long' bond sequence (short bond, lower bond potential). In the anti-integrable limit (electron–phonon coupling constant $\alpha = \infty$) the bond potential of each short bond is of infinite depth; two electrons with opposite spins (circles with two arrows) occupy the lowest state in each 'box' and are thus completely localized (bipolarons). Black points represent empty bonds (long bond).

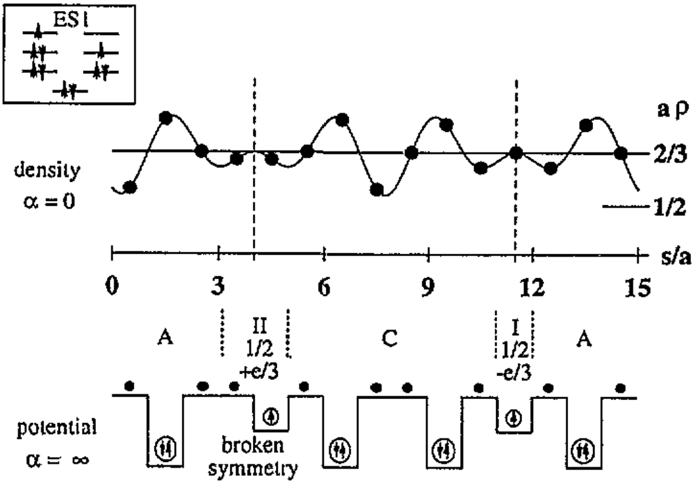

Figure 2. The kink pair (II–I) configuration of the singly excited state (ES1) of a ring ($m = 5$, $N = 3m = 15$ sites, $M = 2m = 10$ π-electrons). Top, 'free particle'. Boxed, occupation of levels. Electron density distribution by equation (6), $\phi = \frac{1}{4}$ (asymmetric case), sequence of densities in the middle of bonds (points). Bottom, the step potential in the anti-integrable limit. Circles with one arrow represent bonds occupied by one electron with spin up: the bond potential is less deep, but the unpaired electrons are still completely localized in their box (polarons). The C phase pattern is the A phase pattern shifted by two lattice constants to the right. The kink (spin, charge) of type II ($\frac{1}{2}, +e/3$) (left) is an A/C phase pattern domain wall; the kink of type I ($\frac{1}{2}, -e/3$) (right) is a C/A phase pattern domain wall.

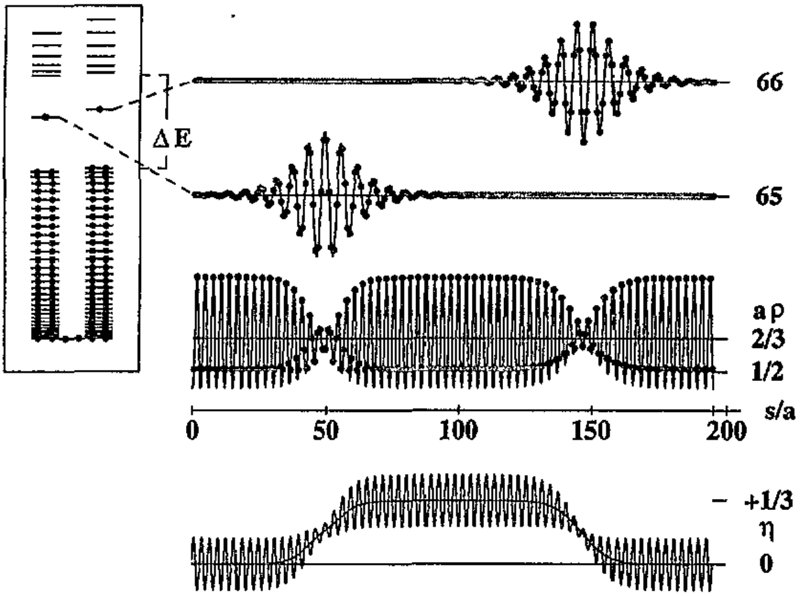

Figure 3. Electron density distribution and sequence of densities in the middle of bonds (points) of the singly excited state (ES1) of a ring ($m = 65$, $N = 3m = 195$ sites, $M = 2m = 130$ π-electrons) by self-consistent step potential starting with equation (6), $\phi = \frac{1}{4}$, asymmetric case. Left, type II kink ($\frac{1}{2}$, $+e/3$); right, type I kink ($\frac{1}{2}$, $-e/3$). Spectrum $\Delta E = 1.0$ eV and localized wave-functions of intergap states. The accumulated excess charge density is $\eta(s)$.

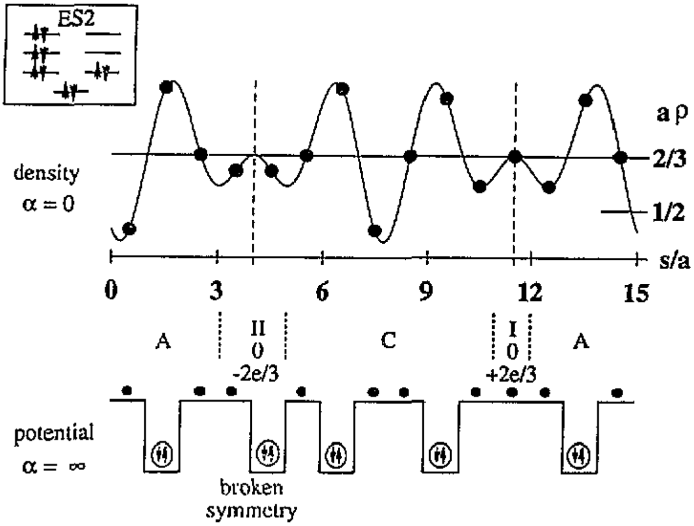

Figure 4. The kink-pair (II–I) configuration of the doubly excited state (ES2) of a ring ($m = 5$, $N = 3m = 15$ sites, $M = 2m = 10$ π-electrons). Top, 'free particle'. Boxed, occupation of levels. Electron density distribution by equation (7), $\phi = \frac{1}{4}$ (asymmetric case), sequence of densities in the middle of bonds (points). Bottom, the step potential in the anti-integrable limit. The kink (spin, charge) of type II (0, $-2e/3$) (left) is an A/C phase pattern domain wall; the kink of type I (0, $+2e/3$) (right) is a C/A phase pattern domain wall.

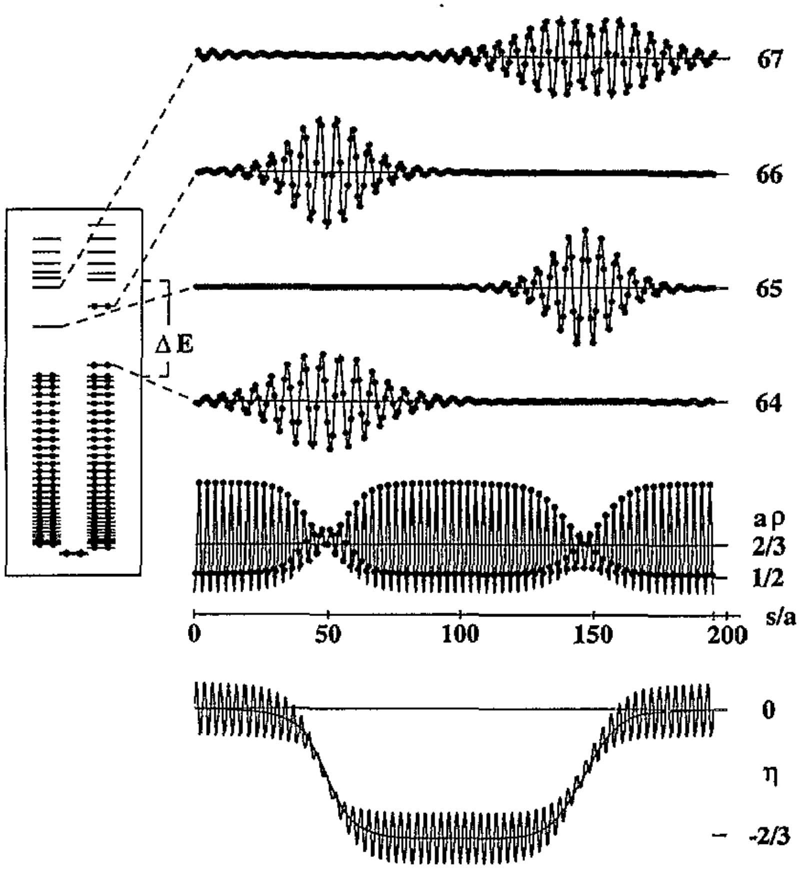

Figure 5. The electron density distribution and sequence of densities in the middle of bonds (points) of the doubly excited state (ES2) of a ring ($m = 65$, $N = 3m = 195$ sites, $M = 2m = 130$ π-electrons) by self-consistent step potential starting with equation (7), $\phi = \frac{1}{4}$, asymmetric case. Left, type II kink, $(0, -2e/3)$; right, type I kink $(0, +2e/3)$. Spectrum $\Delta E = 1.0$ eV and localized wave-functions of intergap states. The accumulated excess charge density is $\eta(s)$.

3.1. The kink pairs of type (I–II)

A pair of kinks each carrying a spin is created by the singly excited state (ES1), where the two uppermost electrons are in the HOMO, $2k = m - 1$, and HOMO + 1, $2k = m + 1$ respectively.

$$\rho^{ES1}(s) = (2/3ma)(m - 1 + \sin^2([(m-1)\pi/3ma](s - \phi a)) + \sin^2([(m+1)\pi/3ma](s - \phi a))) \tag{6}$$

with $\phi = \frac{1}{4}$ (asymmetric case; for $m = 5$ see figure 2) corresponds to density sequence 'low–high–middle'; domain wall of two bonds; density sequence 'middle–high–low, middle–high–low'; domain wall of one bond; density sequence 'low–high–middle'. Relaxing the lattice the bond sequences 'long–short–long' are established and the asymmetry is reinforced: charges in the region of the domain walls are separated. A kink of type II with charge $(2 \times (+\frac{2}{3}) - 1)e = +e/3$ and a kink of type I with charge $((+\frac{2}{3}) - 1)e = -e/3$

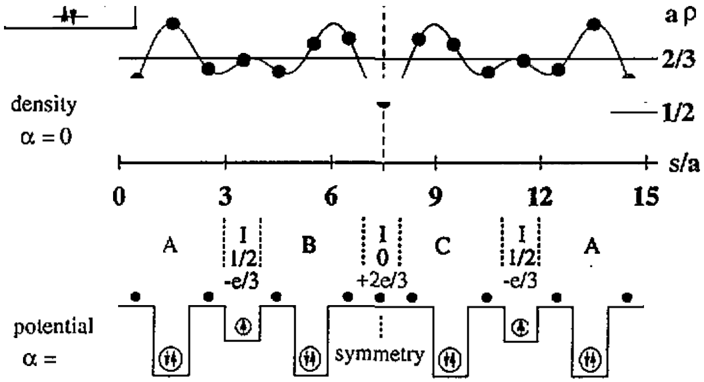

Figure 6. The kink triplet (I–I–I) configuration of the singly excited state (ES1) of a ring ($m = 5$, $N = 3m = 15$ sites, $M = 2m = 10$ π-electrons). Top, 'free particle'. Boxed, occupation of levels. Electron density distribution by equation (6) and $\phi = 0$ (symmetric case), sequence of densities in middle of bonds (points). Bottom, the step potential in the anti-integrable limit.

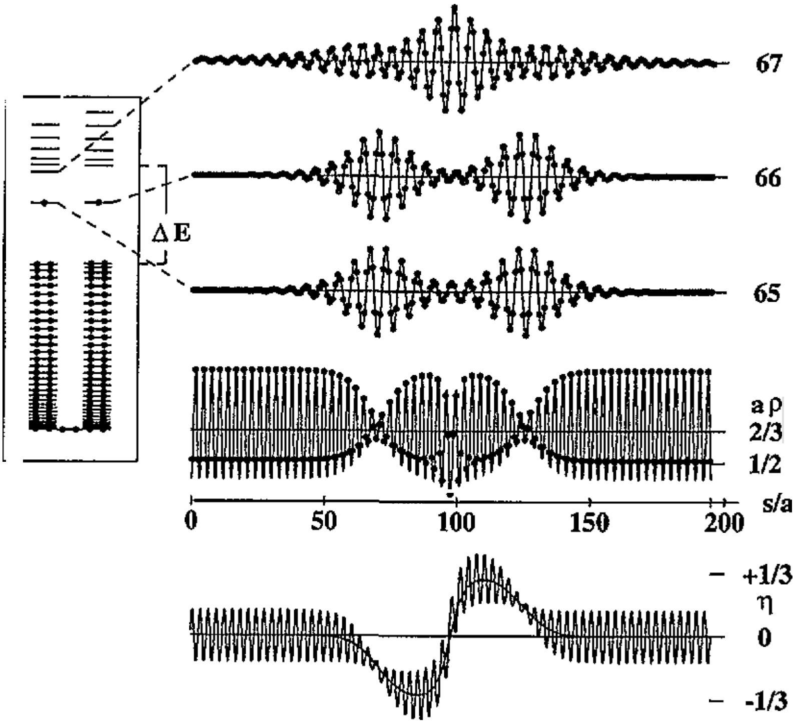

Figure 7. The electron density distribution and sequence of densities in middle of bonds (points) of the singly state (ES1) of a ring ($m = 65$, $N = 3m = 195$ sites, $M = 2m = 130$ π-electrons) by self-consistent step potential starting with equation (6), $\phi = 0$, symmetric case. Left and right, type I kinks ($\frac{1}{2}, -e/3$); middle, $(0, +2e/3)$. Spectrum $\Delta E = 1.0$ eV and localized wave-functions of intergap states. The accumulated excess charge density is $\eta(s)$.

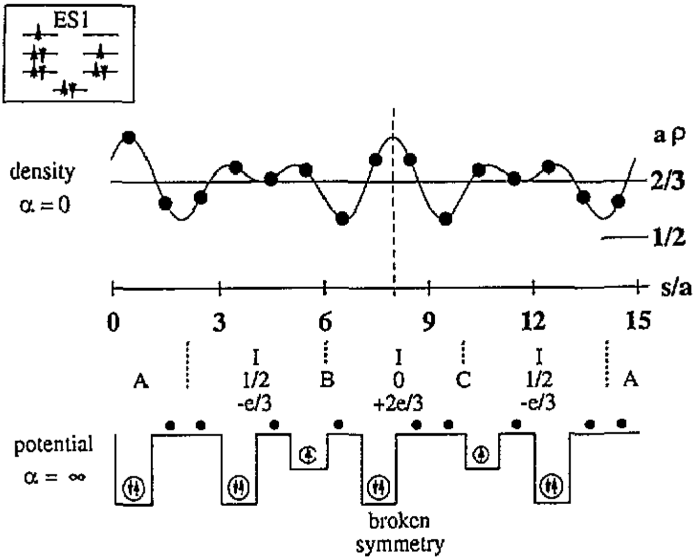

Figure 8. The kink triplet (I–I–I) configuration of the singly excited state (ES1) of a ring ($m = 5$, $N = 3m = 15$ sites, $M = 2m = 10$ π-electrons). Top, 'free particle'. Boxed, occupation of levels. Electron density distribution by equation (8) and $\phi = \frac{1}{2}$ (symmetric case), sequence of densities in middle of bonds (points). Bottom, the step potential in the anti-integrable limit.

emerge (figure 3). Similarly the spinless kink pair is created by the doubly excited state (ES2), where the two uppermost electrons are both in HOMO+1. The density sequence is given by

$$\rho^{ES2}(s) = (2/3ma)(m - 2 + 2\sin^2([(m-1)\pi/3ma](s - \phi a)) \\ + 2\sin^2([(m+1)\pi/3ma](s - \phi a))) \qquad (7)$$

with phase $\phi = \frac{1}{4}$ (asymmetric case; for $m = 5$ see figure 4). Relaxing the lattice the bond sequences 'long–short–long' are established and the asymmetry is reinforced: charges in the region of the domain walls are separated. A kink of type II with charge $(2 \times (+\frac{2}{3}) - 2)e = -2e/3$ and a kink of type I with charge $((+\frac{2}{3}) - 0)e = +2e/3$ emerge (figure 5).

3.2. The kink triplets of type (I–I–I)

The kink triplets of type (I–I–I) differ in the position of the symmetry axes: equation (6) with $\phi = 0$ (symmetric case) (figures 6 and 7) corresponds to density sequence 'low–high–low'; domain wall of one bond; density sequence 'low–high–high'; domain wall of one bond; density sequence 'high–high–low'; domain wall of one bond; density sequence 'low–high–low'.

$$\rho^{ES1}(s) = (2/3ma)(m - 1 + \cos^2([(m-1)\pi/3ma](s - \phi a) + \cos^2([(m+1)\pi/3ma](s - \phi a))) \qquad (8)$$

with $\phi = \frac{1}{2}$ (symmetric case) (figures 8 and 9) corresponds to density sequence '(low)–high–low'; domain wall of two bonds; density sequence 'high–high–low'; domain wall of

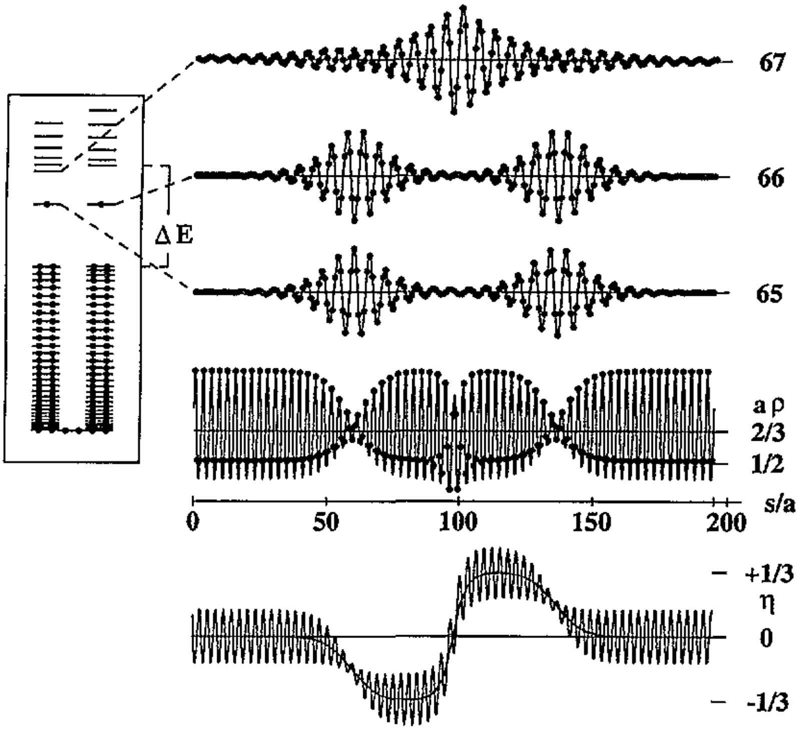

Figure 9. Electron density distribution and sequence of densities in middle of bonds (points) of the singly excited state (ES1) of a ring ($m = 65$, $N = 3m = 195$ sites, $M = 2m = 130$ π-electrons) by self-consistent step potential starting with equation (9), $\phi = \frac{1}{2}$, symmetric case. Left and right, type II kinks ($\frac{1}{2}, +e/3$); middle, ($0, -2e/3$). Spectrum $\Delta E = 1.0$ eV and localized wave-functions of intergap states. The accumulated excess charge density is $\eta(s)$.

two bonds; density sequence 'low–high–high'; domain wall of two bonds; density sequence 'low–(high–low)'. Relaxing the lattice while maintaining the symmetry in both cases the two sequences compete; first the fragment of the bond sequence 'long–short–long' becomes larger by its greater stability. Then the sequence 'low–high–high' changes to 'low–high–low' accompanied with the development of a third domain wall: the type I kink ($0, +2e/3$) in addition to two type I kinks ($\frac{1}{2}, -e/3$) (figures 6 and 7). The kink triplets of type (II–II–II) converge to the kink triplets of type (I–I–I) (figures 8 and 9).

4. Discussion and conclusion

X-ray diffraction studies [15] and x-ray photoelectron spectroscopies [16] of TTF–TCNQ show that at normal pressure $\rho = 0.59$ electrons are transferred from TTF (donor) to TCNQ (acceptor) to form TTF$^{+\rho}$–TCNQ$^{-\rho}$ [17]. Increasing pressure (decreasing the intermolecular distance b [18]) the wavenumber $2k_f$ is increased up to a lock in of $2k_f$ at $b^*/3$ at about 14.5 kbar [19]. The band gap below the Peierls transition is estimated to be 400 K = 0.35 eV [20], which is smaller than the value of 1.0 eV obtained by setting $\alpha = 1.95$, the parameter value for the electron–phonon coupling in polyacetylene, $a = 1.40$ Å, and solving for the one-third-filled band case.

The step potential model is the conceptually simplest approach to treat the electron–phonon coupling in π electron systems. Its only parameter is the strength of electron–phonon coupling. In the one-third-filled band case the ground state of the perfectly trimerized system shows a 'long–short–long' bond sequence as expected from the anti-integrable limit. The kinks obtained are fractionally charged.

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