Non-linear excitations of a diatomic polymer

V A Osipov, J Malek and V K Fedyanin

Joint Institute for Nuclear Research, Laboratory of Theoretical Physics, PO Box 79, Head Post Office, Moscow, USSR

Abstract. The continuum and self-consistent discrete analysis of the ground state, the soliton pair and the polaron static states of long-chain diatomic polymers is presented. The role of electron transfers between second-neighbour sites is discussed and shown to be considerably enhanced in comparison with the polyacetylene case. The Peierls gap $2\Delta_0$, the dimerisation coordinate u_0, the soliton charges Q_A and Q_B, and the creation and formation energies of AB soliton pairs and polarons are calculated. It is verified numerically that the finite-band version of the continuum theory accurately describes all the characteristics of non-linear states under study, even when very short characteristic lengths of the inhomogeneities are considered.

1. Introduction

In our previous paper (Fedyanin and Osipov 1988), we examined the ground-state properties and soliton excitations of AB polymers within the framework of the finite-band continuum scheme, first proposed by Gammel (1986) for polyacetylene chains. In the present paper, we study the physical characteristics of AB soliton pairs and polarons, both numerically and analytically. The aim of our paper is twofold. First, we extend the Hamiltonian of Rice and Mele (1982) by adding electron transfers between second-neighbour sites since their role in some AB polymers could be considerably enhanced in comparison with the polyacetylene case. Secondly, we investigate numerically π-electron spectra of finite AB chains to estimate effects caused by discreteness of the lattice.

Let us consider the model Hamiltonian

$$H = -\sum_{n,\sigma} \sum_{l=1}^{2} t_{n,n+l}(c_{n+l,\sigma}^{+}c_{n,\sigma} + \text{HC}) + \alpha \sum_{n,\sigma}(-1)^{n+1}c_{n,\sigma}^{+}c_{n,\sigma} + \frac{K}{2}\sum_{n}(u_{n+1} - u_{n})^{2}$$

(1)

for the linearly conjugated AB polymer, where $t_{n,n+l}$ ($n = 1, 2, \ldots, N$) denotes electron transfers between first and second neighbours, $c_{n,\sigma}^{+}$ and $c_{n,\sigma}$ are the creation and annihilation operators of π-electrons with spin σ at a site n, α is a one-site potential, K is a harmonic spring constant and u_n are lattice displacements. We note that elastic interactions are restricted to the nearest-neighbour atomic cores. Also, the kinetic energy term is omitted in (1) because we are interested here in static lattice configurations only. It is assumed that there is one π-electron per site.

As usual, we adopt the linear forms for hopping matrix elements:

$$t_{n,n+1} = t_0 - \gamma(u_{n+1} - u_n) \qquad t_{n,n+2} = t_{2A(2B)} - \gamma_{2A(2B)}(u_{n+2} - u_n)$$

(2)

where t_0 and $t_{2A(2B)}$ are the electron transfer integrals between first and second neighbours in a regular chain. The corresponding derivatives of $t_{n,n+1}$ and $t_{n,n+2}$ with respect to intersite separation a in the regular chain are denoted by $-\gamma$ and $-\gamma_{2A(2B)}$ for odd and even sites, respectively.

It is convenient to rewrite the Hamiltonian (1) in terms of the dimensionless bond-length changes $v_n = \gamma(u_{n+1} - u_n)/t_0$:

$$H = t_0 \Big(\alpha_0 \sum_{n,\sigma} (-1)^{n+1} c^+_{n,\sigma} c_{n,\sigma} + \sum_{n,\sigma} (v_n - 1)(c^+_{n+1,\sigma} c_{n,\sigma} + \mathrm{HC})$$

$$+ \sum_{n,\sigma} [\hat{\gamma}_n(v_{n+1} + v_n) - \tau_n](c^+_{n+2,\sigma} c_{n,\sigma} + \mathrm{HC}) + \frac{1}{2\beta} \sum_n v_n^2 \Big) \tag{3}$$

where the dimensionless interaction parameters are defined as

$$\alpha_0 = \alpha/t_0 \qquad \hat{\gamma}_n = \gamma_{2A}/\gamma \quad \text{or} \quad \gamma_{2B}/\gamma$$

$$\tau_n = \tau_A = t_{2A}/t_0 \quad \text{or} \quad \tau_n = \tau_B = t_{2B}/t_0 \tag{4}$$

for odd and even sites, respectively; $\beta = \gamma^2/Kt_0$.

It is well known that the ground state of (3) is the Peierls insulator possessing a spontaneous dimerisation with a displacement field $u_n = \pm u_0$. The ground-state electronic spectrum of (3) is

$$E_k = t_0 \Big[-(\tau_A + \tau_B) \cos(2ka) \pm 2\{ \tfrac{1}{4}[\alpha_0 + \Delta\tau \cos(2ka)]^2$$

$$+ \cos^2(ka) + z^2 \sin^2(ka) \}^{1/2} \Big]. \tag{5}$$

where $\Delta\tau = \tau_B - \tau_A$, $z = \Delta/2t_0 = 2\gamma u_0/t_0$ and $-\pi/2a \leqslant k < \pi/2a$. The spectrum (5) exhibits the Peierls gap

$$E_g = 2\Delta_0 = 2t_0[(\alpha_0 - \Delta\tau)^2 + (\Delta/t_0)^2]^{1/2} \tag{6}$$

at the Fermi wavevector $k_F = \pi/2a$. The parameter z or, equivalently, the dimerisation coordinate u_0 minimises the ground-state energy of the chain, i.e. it is determined as the solution of

$$\frac{1}{\lambda_{\text{eff}}} = \int_0^{\pi/2} \frac{\sin^2 t \, dt}{\{\tfrac{1}{4}[\alpha_0 + \Delta\tau \cos(2t)]^2 + \cos^2 t + z^2 \sin^2 t\}^{1/2}} \tag{7}$$

where $\lambda_{\text{eff}} = 4\gamma^2/\pi Kt_0$ is the dimensionless electron–phonon coupling constant. As follows from (6), dimerisation exists for $\Delta_0 > t_0(\alpha_0 - \Delta\tau)$ only. Hence, for some AB materials with α close to Δ_0 and $t_{2A} \neq t_{2B}$, the second-neighbour interactions can easily suppress the dimerised structure of the ground state. In a general case ($\tau_A \neq \tau_B$) equation (7) has to be solved numerically. For $\tau_A = \tau_B$, we find that

$$1/\lambda_{\text{eff}} = [(1 + y^2)^{1/2}/(1 - z^2)][K(m) - E(m)] \tag{8}$$

where $K(m)$ and $E(m)$ are the complete elliptic integrals of the first kind and second kind, respectively, $m^2 = (1 - z^2)/(1 + y^2)$ and $y = \alpha_0/2$. Finally, for $\Delta\tau \ll 1$ and $y \ll 1$, $z \ll 1$, equation (7) can be solved analytically even for $\tau_A \neq \tau_B$ and we find that

$$\Delta_0 = 2t_0[\tfrac{1}{4}(\alpha_0 - \Delta\tau)^2 + z^2]^{1/2} = 8t_0 \exp(-1/\lambda_{\text{eff}} - 1). \tag{9}$$

The charge transfer $2e^*$ between the A and B atoms becomes

$$\frac{e^*}{e} = \frac{1}{N} \sum_{k,\sigma}^{\text{occ}} \frac{\alpha_0 + \Delta\tau \cos(2ka)}{E_k}, \tag{10}$$

where E_k is given by (5), the sum runs over occupied states and $|e|$ denotes the magnitude of the charge e on the electron.

The soliton excitations or polaron states of (3) can be found exactly for finite AB chains by direct numerical calculation or analytically taking the continuum limit of (3) which, however, provides an accurate description for $z \ll 1$ only. We shall consider here both methods.

2. The continuum model

Let us discuss first the analytical approach. The continuum description of an AB polymer was first reported by Rice and Mele (1982). Recently, their linearised scheme has been extended by Fedyanin and Osipov (1988) to include the electronic dispersion. Since the finite-band scheme involves the Rice–Mele approach as a special case, we start with finite-band field equations (for details see Fedyanin and Osipov (1988)) for eigenvalues E_k, eigenstate amplitudes $A_k(x)$, $B_k(x)$ and the local dimerisation gap $\Delta(x)$ ($\hbar = 1$):

$$(E_k - \alpha - t_{2k}^A)A_k(x) = -iv_F(k)\, \partial B_k(x)/\partial x - [\varepsilon(k) - i\Delta_k(x)]B_k(x)$$
$$(E_k + \alpha - t_{2k}^B)B_k(x) = -iv_F(k)\, \partial A_k(x)/\partial x - [\varepsilon(k) + i\Delta_k(x)]A_k(x) \tag{11}$$

and

$$\Delta(x) = -\frac{i4\gamma^2 a}{K} \sum_{k,\sigma}^{\text{occ}} [A_k^*(x)B_k(x) - \text{cc}] \cos(ka) \tag{12}$$

where $x = na$; the eigenvector corresponding to the eigenvalue E_k is the spinor $\psi_k(x) = (\psi_k^A(x), \psi_k^B(x)) \equiv (A_k(x)\exp(-ikx), B_k(x)\exp(-ikx))$ normalised according to $\int_{-L/2}^{L/2} dx\, (|\psi_k^A(x)|^2 + |\psi_k^B(x)|^2) = 1$; $\Delta_k(x) = \Delta(x)\cos(ka)$; $v_F(k) = v_F\cos(ka)$, where v_F denotes the Fermi velocity $v_F = 2t_0 a$; $\varepsilon(k) = 2t_0\sin(ka)$; $t_{2k}^A = 2t_{2A}\cos(2ka)$, $t_{2k}^B = 2t_{2B}\cos(2ka)$ and, finally, the length of the chain $L = Na \to \infty$. Only linear terms in a/ξ_0 ($\xi_0 = v_F/\Delta$) are retained in (11) and (12) and, therefore, the derivatives $\gamma_{2A(2B)}$ (which appear in terms of the order of $(a/\xi_0)^2$) are absent in (11) and (12). We should note that here and hereafter the wavevector k is measured relative to $k_F = \pi/2a$.

For the ground state $\Delta(x) = $ constant, the solutions of (11) and (12) are plane waves with constant amplitudes and yield the eigenvalues given by (5) with $k \to \pi/2a - k$. In periodic chains the topologic constraints imply that the solitons can be created from the ground state only in the form of AB soliton pairs.

Let us consider first the case $t_{2k} \equiv t_{2k}^A = t_{2k}^B$. Since now the effect of the second-neighbour hoppings results in a shift of the chemical potential only, it is convenient to introduce a new energy variable $\hat{E}_k = E_k - t_{2k}$. For $\alpha < \Delta_0$, we have

$$\Delta(x) = \pm\Delta\tanh(x/\xi_0) \tag{13}$$

where the plus refers to an A soliton with energy $\hat{E}_A = +\alpha$ whereas the minus refers to a B soliton with energy $\hat{E}_B = -\alpha$. The continuum states have similar energies $\hat{E}_k$ to those of the dimerised chain but they are phase shifted by $\delta(k) = -\tan^{-1}(\Delta_k/\varepsilon_k)$.

The wavefunctions of a single A soliton ($k = 0$) are

$$\psi_0^A(x) = A_0(x) = N_A\,\text{sech}(x/\xi_0) \qquad \psi_0^B(x) = B_0(x) = 0 \tag{14}$$

where $N_A = [(1/2\xi_0)\coth(L/2\xi_0)]^{1/2}$. The amplitudes of continuum states ($k \neq 0$) become

$$A_k(x) = [B_k(x)/(\hat{E}_k - \alpha)][-\varepsilon(k) + i\Delta_k\tanh(x/\xi_0)] \qquad B_k(x) = (N_k L)^{-1/2} \tag{15}$$

where $N_k = 2[\hat{E}_k - \Delta_k^2\xi_0/L(\hat{E}_k - \alpha)]/(\hat{E}_k - \alpha)$. The amplitudes of a single B soliton and corresponding continuum states are obtained from (14) and (15) by changing A → B and $\alpha \rightarrow -\alpha$.

The change in the local electronic density of the dimerised chain induced by the presence of the AB soliton pair is

$$\Delta\rho(x) = (\nu_+ - 2I_+)\rho_0^A(x) + (\nu_- - 2I_-)\rho_0^B(x) \tag{16}$$

where ν_+ and ν_- are occupation numbers of A and B soliton energy levels, respectively. The local deficiency in the continuum states $I_\pm$ is given by

$$I_\pm = 1/2(1 \pm z) \mp [1/\pi(1 - z^2)][\pi/2 - K(m)E(\beta, m') \\ - E(m)F(\beta, m') + K(m)F(\beta, m')] \tag{17}$$

where $F(\beta, m')$ and $E(\beta, m')$ are the incomplete elliptic integrals of the first kind and second kind, respectively, $m' = (1 - m^2)^{1/2}$ and $\tan\beta = \Delta(1 + y^2)^{1/2}/\alpha(1 - z^2)^{1/2}$. The charge densities $\rho_0^A(x)$ and $\rho_0^B(x)$ are

$$\rho_0^A(x) = (1/2\xi_0)\,\text{sech}^2[(x - L/4)/\xi_0]$$
$$\rho_0^B(x) = (1/2\xi_0)\,\text{sech}^2[(x + L/4)/\xi_0]. \tag{18}$$

As follows from (16) the soliton charges of the AB pair are

$$Q_{A(B)} = -(\nu_\pm - 2I_\pm)|e|. \tag{19}$$

Finally, the creation energy of the AB soliton pair becomes

$$2E_{exc}(\nu_+, \nu_-) = \alpha(\nu_+ - \nu_-) + (4\Delta/\pi)\{(1/m^2)[E(m) - (1 - m^2)K(m)] \\ + [y^2/(1 + y^2)^{1/2}]\Pi(\pi/2, n, m)\} \tag{20}$$

where $\Pi(\pi/2, n, m)$ is the complete elliptic integral of the third kind and $n = -(1 - z^2)$.

Let us now discuss briefly the case $t_{2A} \neq t_{2B}$. As relevant derivations within the finite-band scheme are lengthy and do not result in closed analytical formulae, we restrict our analysis in this paper to only the linearised version of equations (11) and (12). Approximating in (11) $\sin x \propto x$ and $\cos x \propto 1$ and introducing a new energy variable $\hat{E}_k = E_k - (t_{2A} + t_{2B})$, we arrive at the modified equations of Rice and Mele (1982):

$$[\hat{E}_k - (\alpha - \Delta t)]\psi_A(x) = [-iv_F\nabla_x + i\Delta(x)]\psi_B(x)$$
$$[\hat{E}_k + (\alpha - \Delta t)]\psi_B(x) = [-iv_F\nabla_x - i\Delta(x)]\psi_A(x) \tag{21}$$

where $\Delta t = t_{2B} - t_{2A}$. Hence, changing simply $\alpha \rightarrow \alpha - \Delta t$, one can readily apply all the formulae in the paper by Rice and Mele (1982). For example, the creation energy of a neutral AB soliton pair is

$$2E_{exc}(\nu_+, \nu_-) = (\alpha - \Delta t)(2 + \nu_+ - \nu_-) \\ + (4/\pi)\{\Delta - (\alpha - \Delta t)\tan^{-1}[\Delta/(\alpha - \Delta t)]\}. \tag{22}$$

From (22) it follows that the second-neighbour interactions can significantly modify an energy required to excite an AB soliton pair. Similarly, changing $\alpha \rightarrow \alpha - \Delta t$ in polaron solutions of (21) (Campbell 1983), we find that the polaron becomes unstable at $(\alpha - \Delta t) > \Delta_0/\sqrt{2}$ and decays into an AB soliton pair. Thus the second-neighbour interactions also affect the stability of the polaron states.

3. The discrete model

To investigate effects caused by discreteness of the lattice, we carried out numerical calculations on periodic chains (i.e. rings with fixed lengths) using the self-consistent

discrete method proposed by Shastry (1983) and applied by several workers to poly-acetylene and polyyne chains and rings (Stafström and Chao 1984, Drechsler *et al* 1987, Malek *et al* 1988). The modification of the discrete method to a diatomic polymer case is straightforward. The eigenvalue problem for a periodic chain described by the Hamiltonian (3) is

$$H|k\rangle = E_k|k\rangle \qquad |k\rangle = \sum_{n=1}^{N} \psi_k(n) c_{n,\sigma}^+ |0\rangle \qquad (23)$$

where the eigenvalues E_k and the eigenvectors $|k\rangle$ (the index k now includes the spin index) depend, of course, on the bond length changes $\{v_n\}$. Minimising the total energy of the periodic chain

$$E_{\text{tot}} = \sum_{k=1}^{\text{occ}} E_k + \frac{1}{2\beta} \sum_{n=1}^{N} v_n^2 \qquad (24)$$

under the constraint condition expressing periodic boundary conditions

$$\sum_{n=1}^{N} v_n = 0 \qquad (25)$$

with respect to v_n, we arrive at the self-consistent equations

$$v_n = \beta \Big(\lambda - \sum_{k=1}^{\text{occ}} [\psi_k^*(n+1)\psi_k(n) + \hat{\gamma}_n \psi_k^*(n+2)\psi_k(n)$$

$$ + \hat{\gamma}_{n-1} \psi_k^*(n+1)\psi_k(n-1) + \text{cc}] \Big) \qquad (26)$$

where the Lagrange multiplier λ is

$$\lambda = \frac{1}{N} \sum_{n=1}^{N} \sum_{k=1}^{\text{occ}} [\psi_k^*(n+1)\psi_k(n) + \hat{\gamma}_n \psi_k^*(n+2)\psi_k(n)$$

$$ + \hat{\gamma}_{n-1} \psi_k^*(n+1)\psi_k(n-1) + \text{cc}] \qquad (27)$$

and the index k runs over all occupied spin orbitals.

Equations (23)–(27) may be solved by an iteration procedure for the ground-state, AB soliton pair and polaron states, respectively, utilising continuum theory expressions for displacements u_n as starting *ansatz*. The creation energy $2E_{\text{exc}}$ of an AB soliton pair and the formation energy $E_{\text{for}}^{\text{P}}$ of a polaron state are $2E_{\text{exc}} = E_{\text{tot}}^{\text{AB}} - E_{\text{tot}}^{\text{DIM}}$ and $E_{\text{for}}^{\text{P}} = E_{\text{tot}}^{\text{P}} - E_{\text{tot}}^{\text{DIM}}$, where $E_{\text{tot}}^{\text{AB}}$, $E_{\text{tot}}^{\text{P}}$ and $E_{\text{tot}}^{\text{DIM}}$ are the relevant total energies given by (24). The ground-state charge structure along the periodic chain (in the zero differential overlap (ZDO) approximation) is

$$q^{\text{DIM}}(n) = \Big(-\sum_{k=1}^{\text{occ}} |\psi_k^{\text{DIM}}(n)|^2 + 1 \Big)|e| \qquad (28)$$

where the second term in (28) describes the charge of atomic cores. The change $\Delta\rho^{\text{AB}}(n)$ in the charge distribution of the dimerised ring induced by the AB soliton pair or the change $\Delta\rho^{\text{P}}(n)$ induced by the polaron becomes

$$\Delta\rho^{\text{AB(P)}}(n) = -\sum_{k=1}^{\text{occ}} [|\psi_k^{\text{AB(P)}}(n)|^2 - |\psi_k^{\text{DIM}}(n)|^2]|e| \qquad (29)$$
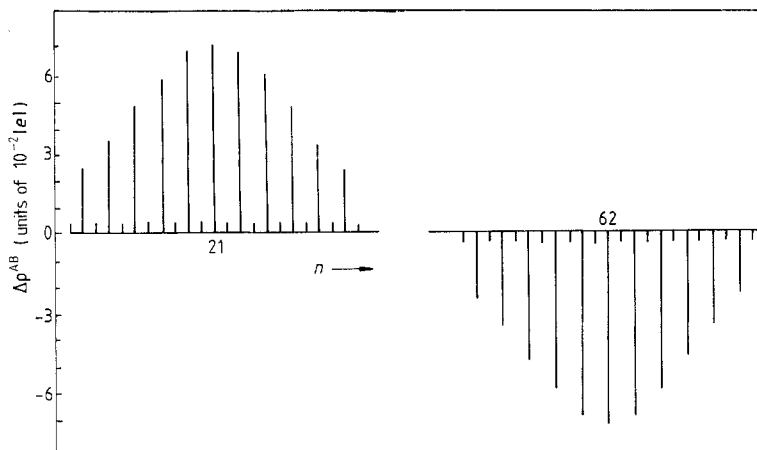
Figure 1. The charge distribution $\Delta\rho^{AB}(n)$ of an AB soliton pair along a ring with $N = 82$ sites. For the parameter set used, see table 1.

where $\{\psi_k^{AB}(n)\}$, $\{\psi_k^P(n)\}$ and $\{\psi_k^{DIM}(n)\}$ are the relevant eigenvectors of (3). A typical shape of the charge distribution $\Delta\rho^{AB}(n)$ is shown in figure 1.

The stable arrangement of a single AB soliton pair on the ring is such that ring regions with positive and negative values of the order parameter $(-1)^{n+1}v_n$, respectively, have the same number of sites. Thus, excited periodic chains of $N = 4M + 2$ sites can be divided into two 'open' chains of $2M + 1$ sites with soliton centres on their middle sites. For even values of M, the A soliton with energy $+\alpha$ is centred on the A atom and B soliton with energy $-\alpha$ on the B atom. The soliton charges Q_A and Q_B result from summing the charge distribution $\Delta\rho^{AB}(n)$ over the corresponding regions (i.e. over A or B 'open' chains) of the ring.

4. Results and discussion

We have performed numerical calculations on rings with $N = 82$, 162 and 202 atoms. Using the representative values $t_0 = 3$ eV, $K = 68.6$ eV Å^{-2}, $\gamma = 8$ eV Å^{-1} and $\alpha = 0.3$ eV, which yield the characteristic length $\xi_0 \propto 9.1a$, we calculated the Peierls gap $2\Delta_0$, the dimerisation coordinate u_0, the soliton charges Q_A and Q_B, and the creation and formation energies of AB soliton pairs and polarons. Neglecting second-neighbour transfers, we obtained the results given in tables 1 and 2. One can immediately observe the perfect agreement between the results of the finite-band version of the continuum theory and the discrete model. From tables 1 and 2 it follows also that for $a/\xi_0 \ll 1$ the Rice–Mele scheme is sufficiently accurate to describe well all the characteristics of the ground and excited or polaron states of AB polymers. We note that there is almost no difference between the numerical results derived from the rings with 162 and 202 sites.

To verify limits of the continuum theory, we changed the spring constant to $K = 34.3$ eV Å^{-2} which yields $\xi_0 \propto 2.0a$. The results can be found in table 3. In this case, of course, the linearised scheme does not work so well but the finite-band scheme still conforms well to the results of the discrete-model calculation. This is an important fact because, in AB analogues of the polyyne chains, one can expect solitons and polarons with very short characteristic lengths.

The decay process of the negatively charged polaron state into the charged pair of A

Table 1. The dimerisation gap parameter Δ_0 (see equations (8) and (9) for the finite-band and linearised version of the continuum theory, respectively), the dimerisation coordinate u_0 (determined as $u_0 = \Delta/4\gamma$ in the continuum model and as $u_0 = -t_0 v_1/2\gamma$ in the discrete mode), the soliton charges Q_A and Q_B, and the creation energy $2E_{exc}$ of the neutral AB soliton pair for $t_0 = 3$ eV, $K = 68.6$ eV Å^{-2}, $\gamma = 8$ eV Å^{-1}, $\alpha = 0.3$ eV, and $t_{2A} = t_{2B} = \gamma_{2A} = \gamma_{2B} = 0$.

Model	N (sites)	Δ_0 (eV)	u_0 (Å)	$Q_{A(B)}$ ($|e|$)	$2E_{exc}$ (eV)
Discrete	82	0.718	0.0193	± 0.685	0.390
	162	0.722	0.0204	± 0.722	0.391
	202	0.722	0.0204	± 0.722	0.391
Finite band	—	0.724	0.0206	± 0.722	0.394
Linearised	—	0.706	0.0200	± 0.721	0.382

Table 2. The characteristics of the negatively charged polaron. For notations and the parameter set used see table 1.

Model	N (sites)	Δ_0 (eV)	u_0 (Å)	$Q_{A(B)}$ ($|e|$)	E_{for}^P (eV)
Discrete	82	0.726	0.0203	-1	0.647
	162	0.722	0.0204	-1	0.645
	202	0.722	0.0204	-1	0.645
Linearised	—	0.706	0.0200	-1	0.636

Table 3. The characteristics of the neutral AB soliton pairs calculated with use of $t_0 = 3$ eV, $\gamma = 8$ eV Å^{-1}, $K = 34.3$ eV Å^{-2}, $\alpha = 0.3$ eV and $t_{2A} = t_{2B} = \gamma_{2A} = \gamma_{2B} = 0$ ($\xi_0 \propto 2.0a$).

Model	N (sites)	Δ_0 (eV)	u_0 (Å)	$Q_{A(B)}$ ($|e|$)	$2E_{exc}$ (eV)
Discrete	82	2.978	0.0920	± 0.923	2.877
	162	2.978	0.0927	± 0.923	2.875
	202	2.978	0.0927	± 0.923	2.875
Finite band	—	2.991	0.0930	± 0.923	2.844
Linearised	—	2.497	0.0775	± 0.923	2.603

and B solitons is shown in figure 2. The calculation was carried out on the ring with 162 atoms using the above-mentioned parameter set with $\alpha = 0.6$ eV and $t_{2A} = t_{2B} = 0$. The polaron decays into the B soliton with the charge $Q_B = -0.367|e|$ and the A soliton with $Q_A = -0.633|e|$. The linearised theory (see table 1) gives $\Delta_0 = 0.706$ eV and $\Delta = (\Delta_0^2 - \alpha^2)^{1/2} = 0.372$ eV which, in accord with discrete calculation, yields $Q_B = -(2/\pi)\tan^{-1}(\Delta/\alpha)|e| = -0.353|e|$ and $Q_A = -(1 + Q_A) = -0.647|e|$.

Finally, in figure 3, we show the effect of the second-neighbour transfers on the creation energy of a neutral AB soliton pair. The calculations were performed on the ring with 162 sites by using the parameter set with $\alpha = 0.3$ eV and Δt varied from -0.3 to 0.3 eV. The values $t_{2A} = t_{2B} = 0.05t_0$ were set as the centre of Δt interval. We assumed
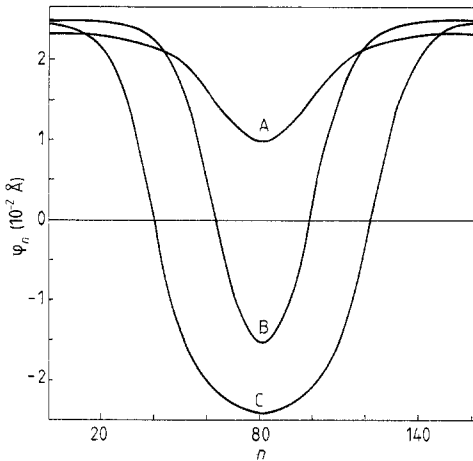
Figure 2. The decay process of a negatively charged polaron into a singly charged AB soliton pair in which the order parameter $\varphi_n = (-1)^{n+1} v_n t_0 / \gamma$ is shown: curve A, starting *ansatz*: curve B, φ_n after 100 iterations; curve C, self-consistent solution.
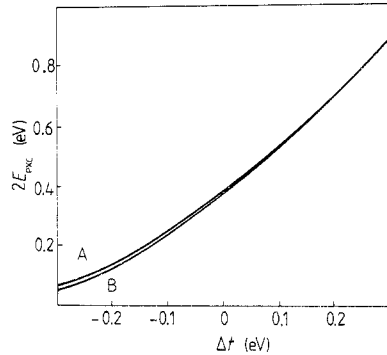
Figure 3. The creation energy of a neutral AB soliton pair as a function of $\Delta t \equiv t_{2B} - t_A$ and $\Delta \gamma \equiv \gamma_{2B} - \gamma_{2A}$: curve A, analytic continuum form with $\Delta \gamma = 0$; curve B, self-consistent discrete forms with $\Delta t / t_0 = \Delta \gamma / \gamma$.

exponential dependence of the hopping integrals t_{2A} and t_{2B} on the inter-atomic separation which yields $\tau_A = \hat{\gamma}_A$ and $\tau_B = \hat{\gamma}_B$, i.e. $\Delta \tau = \Delta \gamma \equiv \hat{\gamma}_B - \hat{\gamma}_A$ (see also (4)). In accord with analytical predictions (see (22)) the calculated creation energy $2E_{\text{exc}}$ strongly depends on the value of Δt. Since $a/\xi_0 \ll 1$ the second derivatives $\hat{\gamma}_n$ do not play any essential role. We note that for $\Delta t \rightarrow \alpha_0$ the localised levels are shifted to the midgap and we arrive at the well known picture of the *trans*-polyacetylene case. For $\Delta t \rightarrow \alpha - \Delta_0$ the localised levels tend to the band edges and, therefore, in the polymers with α close to Δ_0, the second neighbour transfers can make the creation of AB soliton pairs impossible.

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