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LETTER TO THE EDITOR

Bound electronic states of charged kink solitons in a linear MX chain

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Abstract. We have studied bound electronic states trapped by a charged kink soliton in a linear MX chain (M = transition metal ion and X = halogen ion) based on the Baeriswyl–Bishop model. The results show that there exists a new shallow-bound state in the Peierls gap distinct from the well known midgap state. Possible relations to optical absorption are discussed.

Recently, more and more attention has been paid to the class of quasi-one-dimensional materials consisting of chains of transition metal ions (M) bridged by halogens (X) [1–4]. The theoretical model for the linear MX chain, accepted by most research workers, is the Baeriswyl–Bishop (BB) Hamiltonian [5]. Based on this model, there exists a charge-density-wave (CDW) or bond-order-wave (BOW) ground state with two-fold degeneracy. It can therefore support soliton, or kink, and other intrinsic defect states, as in trans-polyacetylene [6]. The BB Hamiltonian is based on a discrete model and it cannot be solved analytically. In the CDW limit and by using the continuum approximation, the Hamiltonian becomes equivalent to the Takayama–Lin-Liu–Maki (TLM) model [7] of trans-polyacetylene [8]. It has been rigorously proved that there is only one localised or bound electronic state around a soliton, of which the level sits at the midpoint of the Peierls gap. In view of this, researchers have got the impression that a kink soliton in a MX chain has only one bound state.

We should mention that the real MX chain consists of atoms; they have a discrete structure. Our experiences tell us that the continuum approximation may lose some bound states. In the case of trans-polyacetylene, the TLM model lost four shallow-bound states [9]. So the conclusion that a kink soliton has only one bound state is based on the TLM model; it is not appropriate to impose this conclusion on the realistic MX chain structure. In this letter, we investigate what will happen to the bound electronic states around a charged kink soliton when the discrete structure of a linear MX chain is considered.

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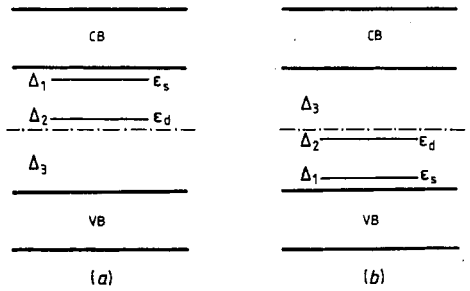

Figure 1. Levels of bound states trapped by the kink: (*a*) for a positively charged kink K^+; (b) for a negatively charged kink K^-. A chain curve represents the centre of the gap.

We consider the CDW limit of the BB model [5], i.e., set $u = 0$ in the model Hamiltonian, where u is the displacement of the M-ions. The Hamiltonian can be expressed as

$$H/t_0 = \sum_{n,\sigma} (-1)^n(\varphi_n + \varphi_{n+1})C^\dagger_{n,\sigma}C_{n,\sigma} - \sum_{n,\sigma}(C^\dagger_{n,\sigma}C_{n+1,\sigma} + C^\dagger_{n+1,\sigma}C_{n,\sigma}) + \frac{1}{\lambda\pi}\sum_n(\varphi_n^2 + \varphi_{n+1}^2) \tag{1}$$

where $C^\dagger_{n,\sigma}$ and $C_{n,\sigma}$ are the creation and annihilation operators of an electron on the nth M-ion with spin σ. φ_n is the dimensionless displacement of the nth X-ion, λ the electron–lattice coupling constant ($\lambda = \beta^2/\pi K t_0$), and t_0 is the electron hopping constant between two adjacent M-ions. The energy spectrum ε_μ and the wavefunction $\psi_\mu(n)$ is determined by the eigen equation of the Hamiltonian (1)

$$\varepsilon_\mu\psi_\mu(n) = (-1)^n(\varphi_n + \varphi_{n+1})\psi_\mu(n) - (\psi_\mu(n+1) + \psi_\mu(n-1)). \tag{2}$$

The equilibrium configuration φ_n of the lattice distortion can be determined by using the variational principle

$$\varphi_n = \tfrac{1}{2}\lambda\pi(-1)^n \sum_{\mu(\mathrm{occ}),\sigma}(\psi_\mu(n-1)\psi_\mu(n-1) - \psi_\mu(n)\psi_\mu(n)). \tag{3}$$

In (2) and (3), μ is the index of the electron state and '(occ)' means that the summation is over all occupied states. Solving these combined equations, all the bound states and the extended states can be obtained. We have taken a ring of 101 MX groups and 100 (for a positively charged kink, K^+) or 102 (for a negatively charged kink, K^-) electrons to make the numerical iterations. The initial value of the configuration $\{\varphi_n\}$ is assumed arbitrarily. Our accuracy is better than 10^{-5}. In such calculations, two bound states, $\psi_d(n)$ and $\psi_s(n)$, are found in the Peierls gap. Their levels are shown in figure 1. ε_d is a deep level; it is referred to the well known midgap state in the TLM model. ε_s comprises the new findings; it is a shallow level near the edge of the band. For K^+, it is close to the conduction band (CB); for K^-, it is close to the valence band (VB). The energy spectrum of K^- is the mirror image of the spectrum of K^+. We give the dependence of the spectrum on the electron–lattice coupling, λ, in table 1, and the eigenfunctions $\psi_s(n)$ and $\psi_d(n)$ in figures 2 and 3. The configuration of the lattice distortion is shown in figure 4.

The behaviour of $\psi_s(n)$ is interesting. With decreasing λ, $\psi_s(n)$ becomes more and more extensive (see figure 2) and its level ε_s gets closer to the band (see table 1). From the envelope of $\psi_s(n)$, we infer that 0.2 is the critical value of the coupling λ. When

Table 1. The electron–lattice coupling dependence of the energy spectrum. The values are in units of t_0.

λ	0.2	0.4	0.6
Δ_1	0.002	0.072	0.656
Δ_2	0.631	1.719	1.920
Δ_3	0.635	2.478	4.443
E_g	1.268	4.268	7.020
$\varepsilon_d(K^+)$	0.003	0.344	0.933
$\varepsilon_d(K^-)$	−0.003	−0.344	−0.933

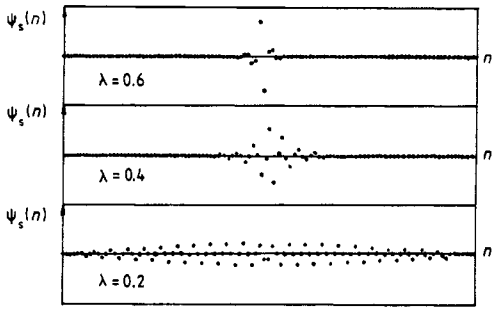

Figure 2. The eigenfunction of the new bound state $\psi_s(n)$.

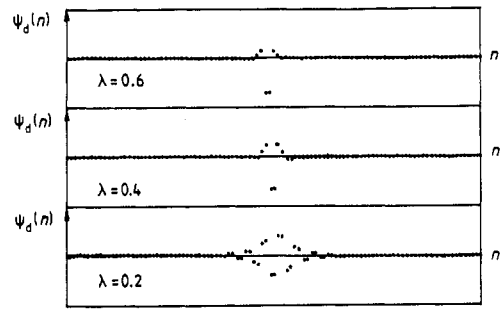

Figure 3. The eigenfunction of the deep-bound state $\psi_d(n)$.

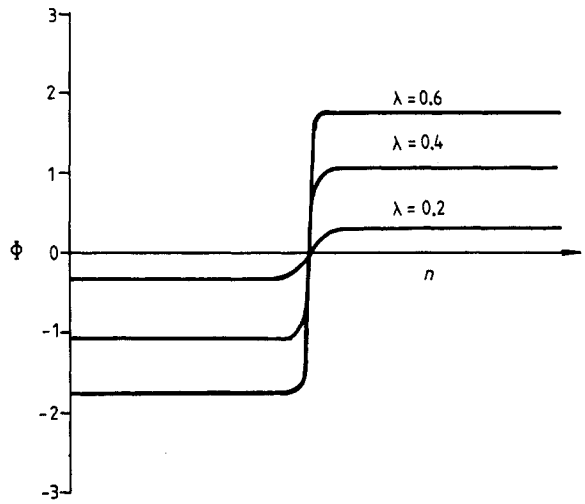

Figure 4. The configuration of the lattice distortion.

$\lambda \geqslant 0.2$, $\psi_s(n)$ is localised around the kink; when $\lambda < 0.2$, $\psi_s(n)$ is an extended state, and its eigenenergy ε_s enters into the band.

From these results, we conclude the following:

(i) When the electron–lattice coupling is strong or of medium strength, $0.2 \leqslant \lambda \leqslant 0.6$, there are two bound states around a charged kink soliton in the Peierls gap. One is a

deep-bound state which is referred to the midgap state in the TLM model. The other is the shallow level near the edge of the band. The two bound states are trapped more tightly by the kink soliton for increasing coupling, λ.

(ii) When the coupling is very weak, $\lambda < 0.2$, the deep-bound state survives but the shallow one becomes an extended state. The situation is described quite well in the TLM model.

(iii) With increasing λ, the deep level ε_d shifts towards the CB (for K^+) or the VB (for K^-) and it is farther and farther separated from the midpoint of the gap.

As discussion, we should mention the possible relationship between the theoretical results and some experimental data. The optical absorption in a linear PtCl chain exhibits three peaks (called A, B and C in the literature) at 1.68, 2.0 and 0.41 eV [2, 9]. Peaks A and B have been ascribed to the deep-level-to-band transition at the Z- and Γ-points of the zone edge. The origin of the C peak is debatable. From the results in the present work, it seems to be the shallow-level-to-band transition. Since a PtCl chain is a system with very strong electron–lattice coupling [10, 11], we take $\lambda = 0.6$ as a rough estimate. The electron hopping $t_0 = 0.5$–0.7 eV [2, 3]. Then the shallow-level-to-band transition is estimated to be $\Delta_1 = 0.33$–0.46 eV. It is consistent with the observed value of the C peak. Further calculations should consider the Coulomb interaction contribution. We will present the work in another paper.

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