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LETTER TO THE EDITOR

Amplitude breathers in diatomic Peierls systems

S R Phillpot†, A R Bishop‡ and B Horovitz‡§

† Xerox Webster Research Center, Webster, New York 14580, USA

‡ Center for Nonlinear Studies and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

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Abstract. Persistent non-linear oscillations—breathers—are studied in a dimerised one-dimensional electron–phonon system as a function of an alternating on-site potential $\pm\alpha$. Dimerisation is present if $\alpha < \Delta_0$, where $2\Delta_0$ is the electronic gap in the ground state. We show the existence of breathers in the adiabatic limit by both analytic expansions and numerical dynamics. For $\alpha \geqslant 0.3\Delta_0$ however, the breathers become progressively unstable towards pattern doubling. Semi-classical quantisation also shows an instability at $\alpha \geqslant 0.75\Delta_0$. Electron–hole excitations form a kink–anti-kink pair for all $\alpha < \Delta_0$, and are accompanied by a breather when $\alpha \leqslant 0.2\Delta_0$.

A variety of conjugated polymers have shown a photo-induced absorption peak somewhat below the band edge. These include *trans*- and *cis*-polyacetylene (Orenstein and Baker 1982, Orenstein *et al* 1983), polydiacetylene (Orenstein *et al* 1983) and poly-(1,6 heptadiyne) (Zemach *et al* 1985). In polyacetylene, this so-called 'high-energy peak' (HEP) has been interpreted as the absorption of a bound state of neutral solitons, the binding being due either to Coulomb correlations (Orenstein and Baker 1982) or to non-linear dynamics (Bishop *et al* 1984a, b). The bound state of the non-linear dynamics model is called a breather; after an electron–hole photo-excitation it can form either in addition to a kink–anti-kink pair (Bishop *et al* 1984a, b) or indirectly from the kink–anti-kink pair (Kivelson and Wu 1986, Bishop and Phillpot 1987). The breather bound state is a result of the non-harmonic shape of the energy as a function of dimerisation and should therefore apply to a large variety of systems.

In the present work we extend the study of breathers in monatomic Peierls systems (Bishop *et al* 1984a, b) to the case of a diatomic system where the sites have an alternating potential $\pm\alpha$ (Rice and Mele 1982). This corresponds to the poly-(1,6 heptadiyne) system which has shown a HEP feature (Zemach *et al* 1985); organic mixed stack compounds also belong to this class (Horovitz and Schaub 1983).

We consider first the continuum adiabatic electron–phonon model and derive a low-amplitude expansion. We find that breathers are solutions for all $\alpha < \Delta_0$, where $2\Delta_0$ is the electronic gap. We then test the analytic solution numerically using an adiabatic dynamics scheme (Su and Schrieffer 1980, Phillpot 1985, Phillpot *et al* 1986). We find

§Present address: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853-2501, USA; on leave from the Ben Gurion University, Beer-Sheva, Israel.

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that for $\alpha \geqslant 0.3\Delta_0$ the continuum model breathers become progressively unstable by doubling their pattern and spreading their shape. We also study electron–hole dynamics, for example following photo-excitation, and find that a kink–anti-kink pair is formed for all $\alpha < \Delta_0$; an additional independent breather is only formed, however, for $\alpha \leqslant 0.2\Delta_0$. Finally we quantise the breather in a semi-classical scheme and find that it is unstable towards decaying into phonons if $\alpha > 0.75\Delta_0$.

The analytic expansion for breathers proceeds in the following four steps. First, we define a tight-binding Hamiltonian on a lattice with $c^{\dagger}_{n,s}$ creating an electron with spin s at site n and u_n the nth ion displacement

$$\mathcal{H} = -\sum_{n,s}[t_0 + \beta(u_{n+i} - u_n)](C^{\dagger}_{n+1,s}C_{n,s} + \text{HC}) + \sum_{n,s}(-)^n \alpha C^{\dagger}_{n,s}C_{n,s} + \tfrac{1}{2}K\sum_n (u_{n+1} - u_n)^2 + \tfrac{1}{2}M\sum_n \dot{u}_n^2. \tag{1}$$

Here t_0 is the transfer integral, β the electron–phonon coupling, K the ion spring constant, M the ion mass and $M\dot{u}_n$ the conjugate momentum to u_n. The Hamiltonian (1) will be directly used in our numerical study. (The use of different masses for the two sites has no qualitative effect on the numerical results.) The second step is to obtain a continuum Hamiltonian for the dimerisation field $\Delta_d(x) = (-)^n 2\beta u_n$ where $x = na$, a being the lattice constant. The result is well known (Rice and Mele 1982, Horovitz and Schaub 1983) and has the adiabatic ground state at $\Delta_d = \Delta_d^0$ which satisfies

$$(\Delta_d^{02} + \alpha^2)^{1/2} = \Delta_0 \equiv 2E_c \exp(-1/2\lambda). \tag{2}$$

Here $E_c \simeq 2t_0$ is an energy cut-off and $\lambda = 2\alpha^2/(\pi t_0 K)$ is dimensionless. For $\alpha < \Delta_0$ the electronic gap is $2\Delta_0$ and the system is dimerised, i.e. $\Delta_d^0 \neq 0$; for $\alpha \geqslant \Delta_0$ the gap is 2α and $\Delta_d^0 = 0$.

The third step is to eliminate the electronic degrees of freedom and find an effective Lagrangian $\mathcal{L}$ for the slowly varying field $\Delta_d(x, t)$. This is obtained by the method of derivative expansions (Horovitz and Krumhansl 1984) which yields for our case, with a constrained constant α,

$$\mathcal{L} = N(0)\left[\frac{1}{2}\Delta^2\left(\ln\frac{2E_c}{\Delta} + \frac{1}{2}\right) - \frac{\Delta_d^2}{4\lambda} + \frac{\dot{\Delta}_d^2}{4\lambda\omega_0^2} - \frac{2\alpha^2 + \Delta^2}{24\Delta^4}(v_F^2\Delta_d'^2 - \dot{\Delta}_d^2)\right] \tag{3}$$

where $v_F = 2t_0 a$ is the Fermi velocity, $N(0) = 2/\pi v_F$ and $\Delta^2(x, t) = \Delta_d^2(x, t) + \alpha^2$, dot is $\partial/\partial t$ and prime is $\partial/\partial x$.

The fourth and final step is to solve for non-linear oscillations around the ground state. Define a slowly varying and low-amplitude field $\delta(x, t) = (\Delta_d(x, t)/\Delta_d^0) - 1$. Consider $\delta = O(\varepsilon)$, $\delta' = O(\varepsilon^2)$, $\omega_0/\Delta_0 = O(\varepsilon)$ and expand (3) to order ε^4 (the consistency of this expansion has been checked):

$$\mathcal{L} = -\tfrac{1}{2}N(0)\Delta_0^2\gamma^2\left[\delta^2 + \tfrac{1}{3}(3 - 2\gamma)\delta^3 - \tfrac{1}{12}(12\gamma - 3 - 8\gamma^2)\delta^4 + \frac{v_F^2}{\Delta_0^2}\frac{3 - 2\gamma}{12\gamma}\left(\frac{\partial\delta}{\partial x}\right)^2 - \frac{1}{\omega_R^2}\left(\frac{\partial\delta}{\partial t}\right)^2\right]. \tag{4}$$

The harmonic terms of (4) are solved by $\delta \sim \exp(i\omega t - iqx)$; for $q = 0$ the renormalised phonon frequency ω_R is

$$\omega_R = \omega_0(2\lambda\gamma)^{1/2}[1 + \lambda\omega_0^2(3 - 2\gamma)/6\Delta_0^2]^{-1/2} \tag{5}$$

and $\gamma = (\Delta_d^0/\Delta_0)^2 = 1 - (\alpha/\Delta_0)^2$.

We next look for localised solutions where the wave-vector q becomes imaginary and $\omega < \omega_R$. This suggests an *ansatz* of the form (Bishop *et al* 1984a, b)

$$\delta(x, t) = \varepsilon(A(X, T)\exp(i\omega_R t) + \text{cc}) + \varepsilon^2\delta_1(x, t) + \varepsilon^3\delta_2(x, t) \tag{6}$$

with a slowly varying envelope function $A(X, T)$ and $x = \varepsilon\bar{x}$, $\bar{x} = (x\Delta_0/v_F)[12\gamma/(3 - 2\gamma)]^{1/2}$, $T = \varepsilon^2\omega_R t$. Substituting (6) in the equation of motion for (4) yields a non-linear (cubic) Schrödinger equation for A:

$$2i\frac{\partial A}{\partial T} - \frac{\partial^2 A}{\partial X^2} - \frac{2(9 - 6\gamma - \gamma^2)}{3(3 - 2\gamma)^2}|A|^2 A = 0. \tag{7}$$

Equation (7) has a well known envelope soliton (Scott *et al* 1973) which yields to order ε^2 a breather-type solution

$$\delta(x, t) = \bar{\varepsilon}[12/(9 - 6\gamma - \gamma^2)]^{1/2}\,\text{sech}\,\bar{\varepsilon}\bar{x}\cos[(1 - \tfrac{1}{2}\bar{\varepsilon}^2)\omega_R t]$$

$$+ \bar{\varepsilon}^2[3(3 - 2\gamma)/(9 - 6\gamma - \gamma^2)]\,\text{sech}^2\,\bar{\varepsilon}\bar{x}\{\tfrac{1}{3}\cos[2(1 - \tfrac{1}{2}\bar{\varepsilon}^2)\omega_R t] - 1\}. \tag{8}$$

Here $\bar{\varepsilon} \sim \varepsilon$ is a continuous parameter which controls both the breather amplitude and its frequency, $\omega_B = (1 - \frac{1}{2}\bar{\varepsilon}^2)\omega_R$. When $\bar{\varepsilon}$ exceeds a threshold value the breather becomes unstable towards break-up into a kink–anti-kink pair (this was confirmed by the numerical scheme below).

We note that breathers may not be exact solutions due to terms which lie beyond all orders in the $\bar{\varepsilon}$ expansion. This has been shown for the φ^4 theory (Segur and Kruskal 1986) and yields a slow decay rate for breathers with a non-perturbative form $\sim\exp(-c/\bar{\varepsilon})$ where $c = O(1)$. For small $\bar{\varepsilon}$, breathers are still well defined excitations with a long lifetime.

We next present numerical data using the adiabatic dynamics scheme (Su and Schrieffer 1980, Phillpot 1985, Phillpot *et al* 1986) for the Hamiltonian (1); the electron states are solved for a frozen lattice at each time step, while the dynamics is governed by $M\ddot{u}_n = \delta\langle\mathcal{H}_u\rangle/\delta u_n$, where $\langle\mathcal{H}_u\rangle$ is the expectation value of (1) excluding the kinetic term. We use equation (8) as an initial condition with $\bar{\varepsilon} = 0.5$ and show in figure 1 its time evolution for the original Hamiltonian equation (1) with $\alpha = 0.3$ eV and $\Delta_0 = 1.92$ eV. We find that the localised large amplitude oscillation is persistent; some acoustic deformation is however generated and it interferes with the breather as it propagates through the periodic boundary back to the origin. Thus we cannot claim strict dynamic stability in the present finite discrete system. We have however run the $\alpha = 0$ case to about 100 oscillations in time where localised oscillations persisted although intermittent interferences and refocusing events were observed.

Figure 2 shows the time evolution for $\alpha = 0.9$ eV. In addition to generating an acoustic deformation, in this case there seems to be an inherent instability by which the number of maxima doubles, i.e. $1 \rightarrow 2 \rightarrow 4$, and the overall shape spreads with time. In the $\alpha = 0.3$ eV case there is a tendency to form a double maximum (figure 1), but no further splitting or spreading is observed up to about 25 periods.

The breather has two levels which strongly oscillate within the ground state gap. The lower level (top of valence band in ground state) is fully occupied by two electrons while the upper level (bottom of conduction band) is empty. We suggest that the

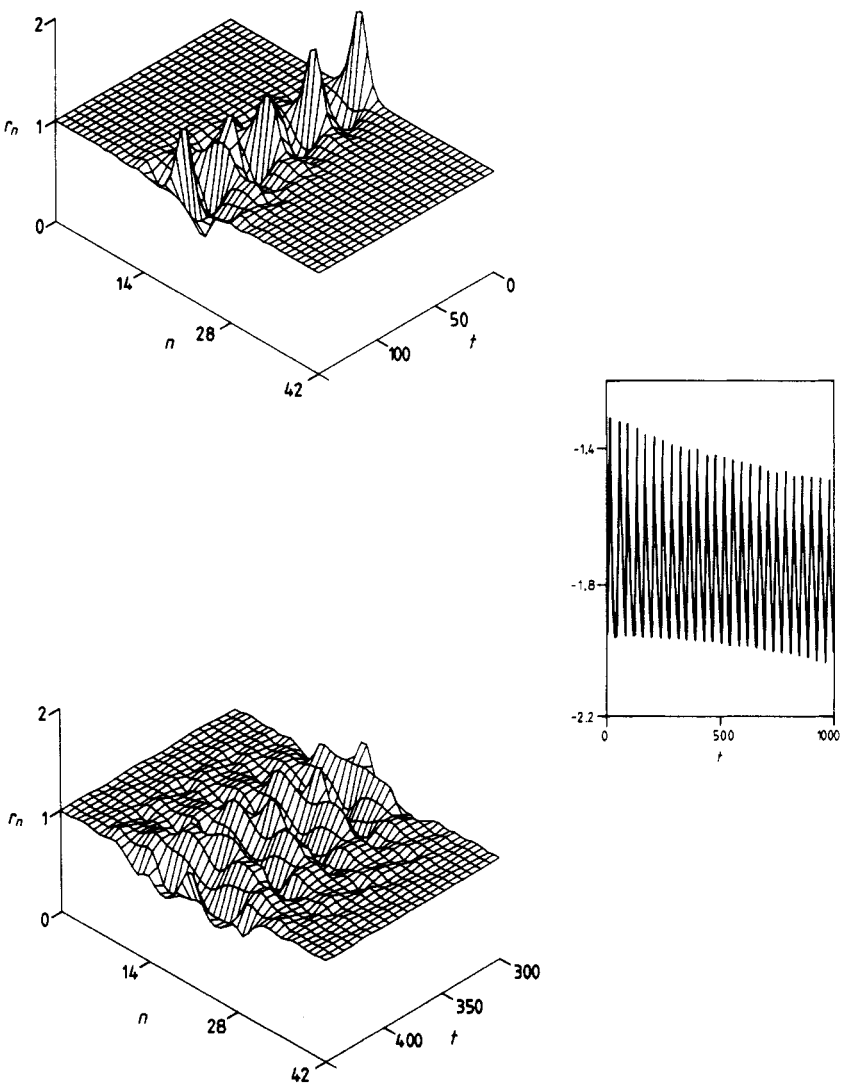

Figure 1. Dimerisation pattern $r_n = (-)^n(2u_n - u_{n+1} - u_{n-1})/4$ for times $0 < t < 150$ and $300 < t < 450$ for a 42 atom ring with 42 electrons occupying the lowest 21 states. The initial condition is a breather (equation (9)) with $\tilde{\varepsilon} = 0.5$. The Hamiltonian (1) has parameters $t_0 = 2.5$ eV, $\alpha = 0.3$ eV, $\beta = 4.8$ eV Å^{-1}, $K = 17.3$ eV Å^{-2}, $M = 13$ au (with these parameters $\Delta_0 = 1.92$ eV, $\omega_0 = 2.25 \times 10^{14}$ s^{-1}). The time unit is 10^{-15} s and r_n is in units of the ground state dimerisation $u_0 = 0.1$ Å. The inset shows the time dependence of the 21st electronic level.

optical transition between these two levels is the HEP that is observed experimentally. Figure 1 (inset) displays the time evolution of the lower level for $\alpha = 0.3$ eV which shows a periodic form whose amplitude decays slowly with time. Figure 2 (inset) shows the same for $\alpha = 0.9$; the amplitude decays faster and beating of two periods is apparent. Thus a distinct behaviour of $\alpha = 0.3$ eV and $\alpha = 0.9$ eV is also seen in the time dependence of the electronic levels.

We conclude so far that the breathers decay either by discreteness effects (e.g.

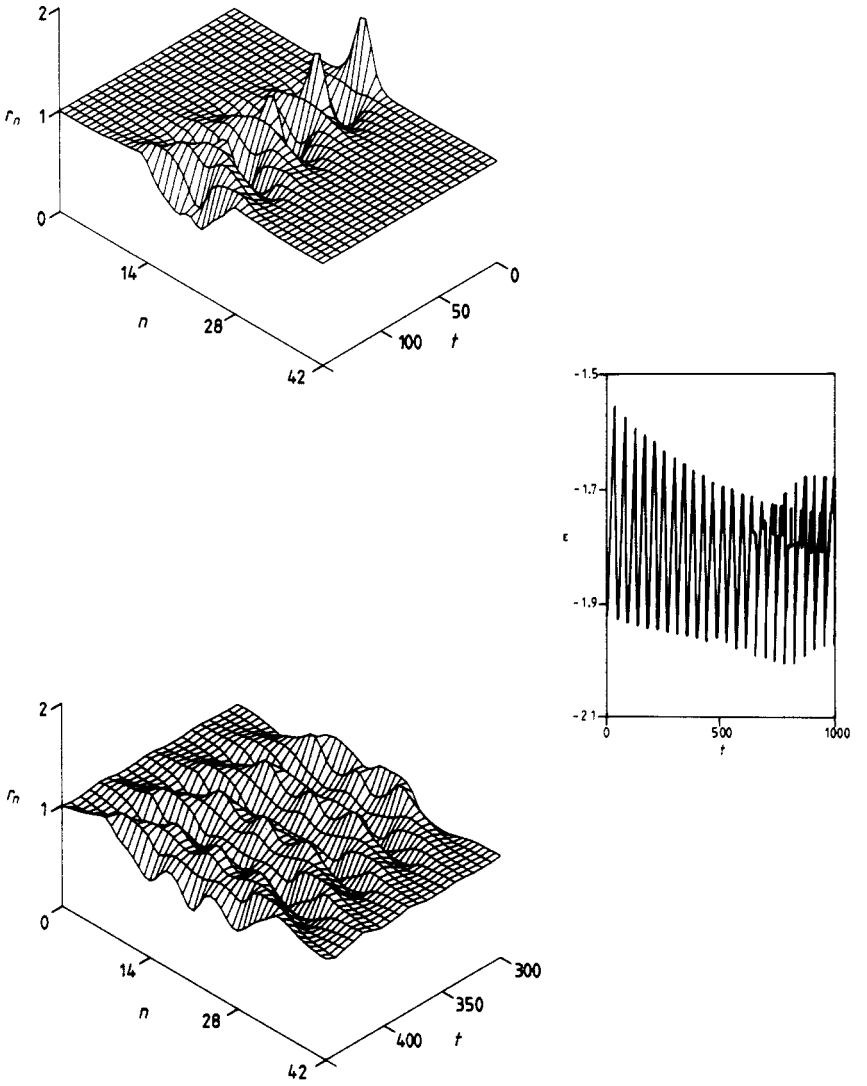

Figure 2. The same as figure 1, but for $\alpha = 0.9$ eV.

generation of acoustic deformations) or by a non-perturbative correction to breathers that is present even in the continuum model (Segur and Kruskal 1986). The decay rate increases with α and for $\alpha \gtrsim 0.6$ eV there seems to be a qualitatively additional decay mode.

Adiabatic dynamics is also an efficient tool for studying the evolution of the system after photo-excitation. We start from an electron–hole pair with the ions in the uniform ground state, and follow numerically the evolution of non-linear excitations. Figure 3 shows a case with $\alpha = 0.3$ eV, $\Delta_0 = 1.92$ eV where a kink and an anti-kink are formed and move in opposite directions. Since the initial excitation energy $2\Delta_0$ is much higher than the two kink rest masses (Rice and Mele 1982)

$$(4\Delta_0/\pi)[(1 - \alpha^2/\Delta_0^2)^{1/2} + (\alpha/\Delta_0)\sin^{-1}(\alpha/\Delta_0)]$$

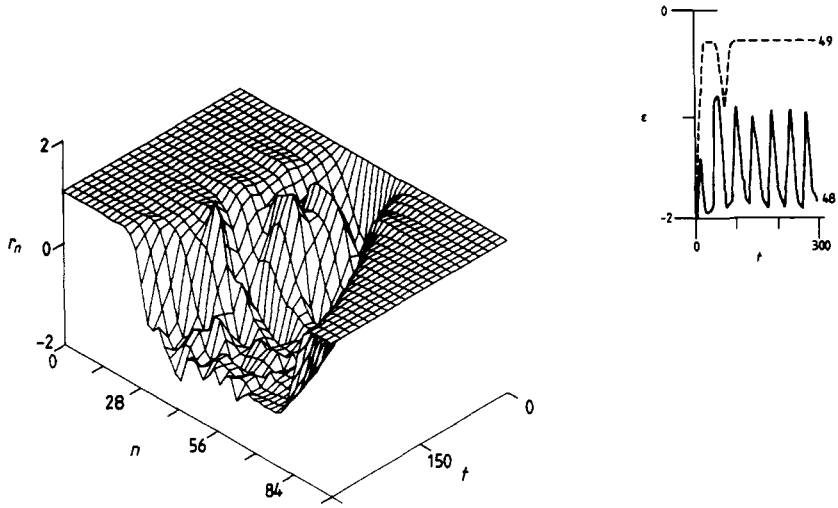

Figure 3. Time evolution of an excited electron–hole pair. The figure shows the dimerisation pattern for a 98 atom ring with 98 electrons occupying the lowest 48th states by pairs and singly occupying the 49th and 50th states. The initial dimerisation pattern is that of the ground state. Parameters as in figure 1 with $\alpha = 0.3$ eV. The inset shows the time evolution of the energy levels corresponding to the 49th and 48th states, as indicated.

there is in addition sufficient energy to generate a localised breather as seen in figure 3. The electronic levels show the rapid generation of the kink states at $\pm\alpha$ and the persistent oscillations of the next states which are associated with the breather. For larger α the kinetic energy gain from forming the kink–anti-kink pair is smaller and we find that for $\alpha/\Delta_0 \geqslant 0.2$ one of the generated kinks remains near the centre, bound to a localised oscillation. The electronic levels show the rapid formation of the kink states at $\pm\alpha$; however, the next excited states do not show a coherent, persistent oscillation. Thus an independent breather is not formed for $\alpha/\Delta_0 \geqslant 0.2$.

Finally we consider semi-classical quantisation. The amplitude $\bar{\varepsilon}$ of the breather in equation (8) is now discretised by an integer n such that

$$2\pi n = \int ax \int_0^{2\pi/\omega_R} dt \frac{\delta \mathcal{L}}{\delta(\dot{\Delta}_d)} \dot{\Delta}_d . \tag{9}$$

To leading order $n \sim \bar{\varepsilon}\Delta_0/\omega_0$ which shows that $\bar{\varepsilon}$ in fact measures the non-adiabatic corrections, $\bar{\varepsilon} \sim \omega_0/\Delta_0$.

The quantised breather energy is obtained by substituting (8) with $\bar{\varepsilon}$ determined by (9) into the Hamiltonian corresponding to (4). The result is

$$E_B(n) = n\omega_R\left[1 - \frac{30\gamma - 9 - 19\gamma^2}{2(3-2\gamma)\gamma^3}\left(\frac{\pi n}{12}\frac{\omega_R}{\Delta_0}\right)^2\right]. \tag{10}$$

The remarkable feature of this result is that the coefficient of the n^3 term changes sign at $\gamma = 0.40$, i.e. $\alpha/\Delta_0 = 0.75$. Thus for $\alpha/\Delta_0 > 0.75$, $E_B(n) > nE_B(1)$ and an $n > 1$ breather is unstable against breaking up into n phonons, the $n = 1$ breather being just a quantised phonon (cf Dashen *et al* 1975). The classical analogue of such an instability could be a *dynamical* instability, as seems to be the case in the numerical data for $\alpha \geqslant 0.3\Delta_0$.

To summarise, we have found that the presence of an alternating on-site potential limits the existence of breathers. The analytic expansion allows breathers for all $\alpha < \Delta_0$, but this does not prove dynamic stability. The numerical dynamics shows persistent breathers for $\alpha \leqslant 0.3\Delta_0$, but becoming dynamically unstable at higher α. We cannot exclude, however, the possibility that the continuum solution is not a good initial condition for higher α, and a different form might be a more persistent breather. Our quantised solution (equation (10)) is more definitive in showing an instability at $\alpha > 0.75\Delta_0$; this then correlates with a dynamic instability on a classical level.

A different type of limitation appears for breather generation in photo-induced data. Here our numerical data and energy balance arguments show that a breather can be generated in addition to a kink–anti-kink pair only if $\alpha \leqslant 0.2\Delta_0$. If the HEP observed in poly-(1,6 heptadiyne) at 1.0 eV is a breather transition then the on-site potential α should be $\alpha \leqslant 0.2$ eV since the gap is $2\Delta_0 \simeq 1.8$ eV (Zemach *et al* 1985). By controlling the side rings of poly-(1,6 heptadiyne) it should be possible to vary α and test the breather interpretation of the HEP.

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